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FINAL REPORT

**MACROMOLECULAR STRUCTURE
ANALYSIS AND EFFECTIVE
LIQUEFACTION PRETREATMENT**

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Executive Summary

This project was concerned with characterizing the changes in coal macromolecular structure, that are of significance for liquefaction pretreatments of coal. The macromolecular structure of the insoluble portion of coal is difficult to characterize. Techniques that do so indirectly (based upon, for example, NMR and FTIR characterizations of atomic linkages) are not particularly sensitive for this purpose. Techniques that characterize the elastic structure (such as solvent swelling) are much more sensitive to subtle changes in the network structure. It is for this reason that we focused upon these techniques. The overall objective involved identifying pretreatments that reduce the crosslinking (physical or chemical) of the network structure, and thus lead to materials that can be handled to a greater extent by traditional liquid-phase processing techniques. These techniques tend to be inherently more efficient at producing desirable products.

This report is divided into seven chapters. Each is a relatively "stand-alone" section, and can be read independently of all others. This approach has the small disadvantage of repeating some background material and experimental technique material in each chapter, but has the advantage that the very different topics that are addressed in different chapters may be smoothly presented in understandable pieces.

Chapter II summarizes the main experimental approaches used throughout the project, and summarizes the main findings on the Argonne Premium coal samples. Chapter III considers synergistic effects of solvent pairs. It is divided into two subsections. The first is concerned with mixtures of CS₂ with electron donor solvents. These have recently attracted much attention due to their efficacy in medium rank bituminous coal processing. The second subsection is concerned with aromatic hydrocarbon - alcohol or hydrocarbon - alcohol mixtures, as might be of interest for pre-liquefaction delivery of catalysts into bituminous coals. Chapter IV deals with questions of how oxidation might influence the results that are obtained. Chapter V briefly details what conclusions may be drawn concerning the elastic behavior of coals, and the effects of thermal treatments on this behavior. Chapter VI is concerned with theories to describe the action of solvents that are capable of dissociating non-covalent crosslinks. Finally, Chapter VII discusses the practical implications of the study.

The most dramatic pretreatment effects are to be found in the medium and high volatile bituminous coals. These coals can be dramatically "opened up", with respect to reagent access, by proper temperature pretreatment in a zone of temperatures just below those needed for pyrolysis. Whether these particular coals can be of significant liquefaction interest is debatable, in that their high rank makes the potential products that can be derived from them of less interest than products from other coals.

The low rank coals have again shown themselves to be quite prone towards undesirable processes upon thermal pretreatment. The propensity towards crosslinking (covalent as well as non-

covalent) appears to be the main feature of their pretreatment. Water appears to play a major role in keeping the structure of the low rank coals "open", and its removal is accompanied in some cases by these undesired crosslinking processes, and in no case is thermal pretreatment beneficial. This is not to deny that other pretreatments based upon chemical features of low rank coals can and do have beneficial effects, but simple thermal pretreatments do not.

In coals of high volatile bituminous rank, the effects of thermal pretreatments are intermediate between the two cases cited above. Beneficial effects can be seen in a few cases, and deleterious effects in others.

In addition to thermal pretreatments, various solvent pretreatments were examined. The possibility of using solvent pairs to accomplish what has not been possible with single solvents is again noted. The results suggest that by clever manipulation of solvent combinations, it should be possible to preswell coals, to facilitate introduction of reagents or catalysts.

Finally, the importance of oxidation in altering the macromolecular network structure of coals was briefly examined. It was concluded that oxidation can have several effects. In coals of high rank, which contain little oxygen to begin with, oxidation can enhance the action of polar solvents in the coal. This is because the increased polarity of the coal surface with oxidation is beneficial to developing strong interactions. In lower rank coals, the oxidation has little benefit and appears to do some crosslinking. It appears, however, that the nature of the surface of coal is significantly altered by heating above a temperature of about 470 K. It appears that at this temperature, some significant rearrangements of the oxygen groups might occur, and with the rearrangements, some change in coal's macromolecular network structure might also occur.

One last, significant product of this research program is a much improved understanding of the factors that govern the thermodynamics of swelling of coals in solvents. These swelling processes are considerably more complicated than had been heretofore believed. This report shows the considerations that must go into formal interpretation of solvent swelling.

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2. "Physical Transitions in Pittsburgh No. 8 Coal as Observed by Differential Scanning Calorimetry and Solvent Swelling" *Energy and Fuels*, 6, 328, 1992
3. "Structural Changes in High-Rank Bituminous Coals Caused by Solvent Swelling and

- Heat" *ACS Div. Fuel Chem. Prepr.*, 37(2), 856, 1992.
4. "Oxidation-Induced Structural Changes in Argonne Coals Studied by DSC and Solvent Swelling" *ACS Div. Fuel Chem. Prepr.*, 37(3), 1184, 1992.
 5. "New Applications of Differential Scanning Calorimetry and Solvent Swelling for Studies of Coal Structural Relaxation" *Fuel*, 72, 1245, 1993.
 6. "Effects of Thermal and Solvent Pretreatments on the Elastic Properties of Coal" *ACS Div. Fuel Chem. Prepr.*, 38(2), 489, 1993.

In addition, as of this writing, two other papers are under review for publication in *Energy and Fuels* and in *Fuel*. Two further papers are in preparation.

I. Background and Objectives

I.1. Background

There is increasing interest in the chemistry of coal pretreatment (or preconversion) processes that can be used for increasing the yield of certain liquid products from (or reducing the required severity in) liquefaction processes. These pretreatments may involve heating the coal in steam, mildly hydrogenating it, solvent swelling it, or temperature programming through the preheating phase. Common to all of these different strategies is an attempt to influence the chemistry of the coal that will occur at higher temperatures by modifying its structure through lower temperature processing. The temperature that defines the lower and higher regimes may be crudely taken as 350°C, since above this temperature pyrolytic processes begin to strongly manifest themselves. This is certainly an arbitrary choice of temperatures, since as Nishioka and Larsen (1988) have shown, some pyrolytic cleavage of bonds is possible even at 250°C.

Regardless of the specific nature of a coal liquefaction process, the principal goal is always to convert a material with a basically insoluble crosslinked macromolecular nature into soluble molecules of low enough molecular weight such that they are either liquids themselves, or at least soluble in appropriate solvents at ordinary temperatures. As a practical matter, heat is generally selected as the agent for effecting bond cleavage in proposed commercial processes. This choice has the disadvantage that heat is not a selective agent, and it causes an enormous number of chemical pathways to occur simultaneously - some of these are desirable, and others such as gas formation or "retrograde" reactions (to coke as a product) are highly undesirable.

This project deals with the nature of the bond cleavage and formation processes that occur during the heating of coals under liquefaction-type conditions. The choice is made to work mainly with the whole coals, since even with all the knowledge at hand concerning the structure of coals, it would not yet be clear how to prepare a satisfactory macromolecular network model for coals. The value of model compound studies with low molecular weight compounds in establishing certain reaction mechanisms is undeniable, but such work sheds little light on questions concerning the distribution of molecular weight as a function of processing conditions. It is the latter aspect that is of interest in this project.

It is believed nowadays that much of the important chemistry occurs very early in the liquefaction process, possibly even in a "preheating section" of a process. It is with this realization that so much attention has been recently focused on "preconversion reactions."

In order to study this early phase of liquefaction, it is necessary to study the solid coal before it is fully converted into soluble products and/or coke. This approach may be viewed as unusual, in the

sense that traditional liquefaction studies generally focus mainly on soluble products and rarely deal with the macromolecular structure of the coal in the early stages of conversion. It is with the improved understanding of the macromolecular structure of coals that has developed over recent years that we may now profitably step back and examine liquefaction from the earliest stages, and thus gain insight into what reasonable "preconversion" processes might be.

I.2. Objectives

This project is concerned with the chemistry of breakdown of the macromolecular structure of coal that occurs, in the presence or absence of other reagents, below 350°C, in order to guide the search for more effective pretreatment conditions. As opposed to normal liquefaction studies, in which the focus is mainly on liquid products, this project is employing techniques for characterizing the changes in the not-yet-liquefied coal network. This includes the characterization of changes in the density of crosslinking bonds in the coal (by solvent swelling), an attempt at identifying the weak linkages through their degradation products, and the measurement of the kinetics of the network disruption processes.

Ultimately, this project is concerned with DOE's search for preliquefaction schemes for obtaining higher liquid yields, with enhanced quality, under mild conditions. The search is guided by improved knowledge of the macromolecular structure of coal and its changes upon applying each preliquefaction treatment. Results obtained from this study can be subsequently applied to select and model the most efficient pretreatment strategy in coal liquefaction.

II. Thermally- and Solvent-Induced Changes in the Macromolecular Structure of Coals

II-1. INTRODUCTION

There is increasing interest in the chemistry of coal pretreatment (or preconversion) processes that can be used for increasing the yield of certain liquid products from (or reducing the required severity in) liquefaction processes, because it is nowadays believed that much of the important chemistry occurs very early in the liquefaction process, possibly even in a preheating section of a process. These pretreatments may involve heating the coal in steam, mildly hydrogenating it, solvent swelling it, or temperature programming through the preheating phase. Common to all of these different strategies is an attempt to influence the chemistry of the coal that will occur at higher temperatures by modifying its structure through lower temperature processing.

In this regard, there have been several reports of structural changes in coal at low temperature ($<400^{\circ}\text{C}$) indicated by increased mobility of the coal [1] or by crosslinking (associated with the evolution of water and carbon dioxide [2,3]). Since little significant weight loss is normally observed in this low temperature range, glass transition and/or physical melting have been suspected as responsible in the case of the increased mobility observed at these temperatures in coals. Some bituminous coals, e.g., Pittsburgh No. 8 coal, are known to contain a considerable amount of thermally extractable mobile phase at temperatures below 400°C [4-6] and thus the role of physical structural changes in releasing this material is strongly suspected. Recent results on preliquefaction treatment of coal by solvent swelling [7-9] and preheating [10] have proved that elevated temperatures (below those needed for thermal decomposition) help enhance the efficacy of the liquefaction, perhaps by promoting greater accessibility of the structure in coal. Likewise exposure to steam helps increase pyrolytic liquid yields [10-12]. Furthermore, ^1H NMR [1,13,14], pyrolysis-mass spectrometry [5,15], and field ionization mass spectrometry [4,6] have strongly suggested that fundamentally different processes, e.g., physical desorption, are occurring in the low temperature region in contrast to the ensuing pyrolytic processes involving chemical decomposition. All these observations indicate that the macromolecular structural changes at low temperature ($<400^{\circ}\text{C}$) deserve more detailed study.

The aim of this study was to examine the macromolecular structural changes, induced by heat and solvents, occurring below the temperature range of the major pyrolytic decomposition reactions. The study employs two analytical techniques: differential scanning calorimetry (DSC) and solvent swelling. DSC has earlier been used for measurements of the heats of pyrolysis and hydropyrolysis [16-19], as well as for the determination of glass transition temperatures of coal [20,21]. Because of

its sensitive nature, DSC is an ideal tool for investigating the thermal changes associated with softening as well as glass transition and thus for identifying the temperatures of significant structural changes. Therefore, DSC has been heavily applied in polymer science and many commercial devices are available. The application of DSC to coal has been hampered by problems caused by weight loss that accompanies most heat effects and also by tar condensation in the DSC cell. Although hermetic sealing of the coal sample is possible, the pressure build-up inside the cell can easily exceed the maximum allowable pressure of the normally sealed capsules (usually 4 atm).

In this study, we applied DSC in a way such that small heat effects could be identified by subtracting consecutive DSC scans. Several groups have already applied this type of methodology in helping identify problems with heat capacity measurement [22,23], but did not draw any conclusions concerning the role of structural changes in heat effects. In combination with solvent swelling, which has been also extensively used for characterizing the density of crosslinking in the macromolecular structure of coal, DSC appears to be a powerful tool for evaluating the extent of thermally induced structural changes.

II-2. EXPERIMENTAL

Eight coal samples were obtained from the Argonne National Laboratory - Premium Coal Sample Program. These samples included Pocahontas No.3 (-20 mesh), Upper Freeport (-100 mesh), Pittsburgh No. 8 (-20 mesh), Illinois No. 6 (-20 mesh), Blind Canyon (-100 mesh), Lewiston-Stockton (-100 mesh), Wyodak (-100 mesh), and Beulah-Zap (-100 mesh) coals. They were used as-received. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [24] and reported compositions are given in Table II-1.

In addition, results will be presented on two other samples in this chapter. The first is from the Blind Canyon seam, but is of different origin than the Argonne Premium sample. This sample is the DOE standard sample DECS-17, which has been heavily studied in the DOE liquefaction program. This sample is the same as the Penn State sample PSOC-1554. The other sample that was examined in this chapter is a Pocahontas No. 5 high volatile bituminous coal. The elemental compositions of these latter two samples are shown in Table II-2. Additionally, there are elemental compositions shown for several samples that will be discussed in other chapters.

Differential Scanning Calorimetry A TA Instruments 2910 DSC system with a liquid nitrogen cooling accessory (LNCA-II) was employed in this study. The sample cell was operated under a nitrogen flow rate of 90 ml/min in order to keep the cell free of oxygen during measurement. Aluminum sample pans were used in an unsealed mode. This was done by pushing down the top

sample pan cover gently onto the bottom pan containing the coal. On the other hand, the experiments for comparing the effects of heating rate were performed with aluminum sample pans, which were perforated by puncturing with a needle (ca. 30 holes per pan), and pressed in an encapsulating press with nonhermetic dies. Such open pans were used in order to minimize mass transfer limitations in the water evaporation process. Samples were initially kept isothermal at 30°C for five minutes and then heated at the specified rate. Unless stated otherwise the usual heating rate used in this study was 8 °C/min. Typically 6-12 mg of sample was used in an experiment.

Cooling of the cell between consecutive heating scans normally involved air convection in the heating assembly, but the sample itself was always kept under nitrogen flow. Initially, dried coals (prepared at 100°C for several hours under vacuum) were used. Remaining strongly adsorbed H₂O overshadowed any small DSC trends even up to 250°C. Therefore as-received coals were used for all DSC experiments, except the experiments requiring pretreated samples. All DSC thermograms were baseline corrected by subtraction of a blank run of empty sample and reference pans. This baseline experiment was performed just before each DSC run. Temperature was calibrated by using an indium standard, and the calibration was performed at each heating rate to ensure the accuracy of temperature measurement.

Solvent Swelling Coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm high) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. The choice of 7500 rpm was rather arbitrary and selected only to be as high as could be comfortably tolerated by the equipment. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again (7500 rpm for 3 min), the swollen coal height measured, and the solvent replaced with the clean solvent. This assured that the concentration of extractables was not so high as to interfere with the measurement. When the supernatant of the centrifuged sample was too dark to read the height, the height was measured after decanting the supernatant and replacing with fresh solvent.

Samples (22-28 mg) for solvent swelling were prepared in the DSC at a heating rate of 8 °C/min under a nitrogen flowrate of 90 ml/min. After reaching the desired temperature, each sample was cooled immediately by contacting the bottom of the sample pan with ice or cold water. Swelling solvents employed (tetrahydrofuran(THF), pyridine, carbon disulfide (CS₂)) were all reagent grade and were used without any further purification.

Sample Pretreatment In order to determine the main parameters governing the relaxation of coal structure, several treatments were performed before subjecting the samples to DSC or solvent swelling. These included preswelling by solvent, pyridine Soxhlet extraction, acetylation, and heat treatment. Solvent preswelling was performed in two ways. One method involved swelling coal samples in the constant diameter glass tubes, which were used in the normal swelling experiments described earlier. The swelling was performed in excess solvent at room temperature for about 3-4 days with frequent replacement of extract-laden solvent with fresh solvent. The samples were subsequently dried under vacuum (<30 inH_g) at room temperature for about two days. Another approach involved Soxhlet extraction of samples with pyridine for about two days, until the color of pyridine in the extraction tube indicated no further extraction. Then the sample was washed with deionized water, filtered using a water aspirator, and dried under vacuum (<30 inH_g) at room temperature for about two days. Thus in the first case the samples were swelled but not exhaustively extracted, whereas in the second case the samples were exhaustively extracted (as well as presumably being fully swelled). Acetylation of hydroxyls was accomplished by mixing coal with excess pyridine and excess acetic anhydride at room temperature for about three days, and then excess acetic anhydride was destroyed by reaction with water while excess pyridine was removed by washing the sample with water. The acetylated sample was subsequently dried under vacuum at room temperature for about two days.

II.3 RESULTS AND DISCUSSION

Standard DSC measurements

DSC is a very sensitive technique for determining the difference in heat flow between a sample and a reference material, either heated or cooled at a controlled rate. The main purpose in employing DSC here was to determine whether DSC can be used effectively as a tool for examining structural changes in coal, particularly those that occur before pyrolysis. The phenomena we were concerned with were pre-pyrolysis physical transitions, possibly involving the so-called glass transition, though we now believe that it would be inaccurate to term most of them as such. The formal glass transition temperature, T_g , is defined as the temperature at which amorphous polymers transform in structure from the glassy state to liquid/rubbery state. In coal, this transformation has been suggested to appear just before thermal degradation begins [20,37]. We are dubious about the interpretation of these high temperature transitions as glass transitions. The clearest evidence for true glass transitions has been obtained at much lower temperatures, below ambient temperature in one case [21] and another at around 385 K in another [50].

Due to the heterogeneity and complexity of constituents involved in coal, a clear-cut

determination of T_g in coal has thus been difficult. There should not be an expectation that there is a *single* transition in any coal. Because of the highly heterogeneous nature of coals, several transitions, involving relaxations in different macerals or even in different parts of the same maceral's network structure, would have to be expected. This suggests that when a DSC spectrum is considered, complexity should be expected. This is indeed what is observed. We further feel that to avoid confusion, what is reported as a glass transition should not be irreversible - i.e. visible only on first heating and not thereafter.

The original DSC results for four coals examined in this study are typical of what is found in the pre-pyrolytic range of temperatures. Figure II-1 shows DSC responses of two high volatile bituminous coals (lower panel) and two higher rank coals (upper panel), under a nitrogen atmosphere and at a heating rate of 8°C/min. There are some general features common to all the DSC spectra. The endothermic peaks at around 100°C are of course caused by water evaporation, and obscure any other relaxations that might occur in that temperature range. Predrying the coals has certain disadvantages, as will be noted later, so we did not use this procedure to eliminate the water evaporation endotherms. The fact that the endotherms associated with water loss extend to temperatures well above 100°C reflects the existence of transport limitations in the sample and pans. This is of no significance for the present study.

The sharp rises toward the exothermic direction at high temperatures (visible in three of the four samples) coincide with the onset of rapid pyrolytic mass loss, but do not necessarily reflect an exothermic pyrolysis process. Rather, a complicated series of processes occurs at the time that pyrolysis begins, which renders data that are difficult to interpret. The coal begins to rapidly lose mass, so the expression of results on the basis of *original* mass is no longer valid. The representation of the heat effects on the basis of original sample mass is however convenient, and will be used throughout this report. Additionally, the mass of coal often greatly expands as it pyrolytically softens, and gas bubbles form within the plastic mass. The effect is to markedly reduce the efficacy of heat transfer from the DSC cell to the sample interior. Thus the true heat flows are not particularly well measured when pyrolysis is actively occurring. In summary, the onset of vigorous pyrolysis is clearly visible from the results, and we generally disregarded any data from that point onwards. This was consistent with our interest in pre-pyrolytic treatments.

A typical DSC thermogram for high volatile bituminous coals can be seen in the case of Illinois No. 6 coal, in which the water evaporation process (endothermic) is followed by a more or less straight DSC response curve corresponding to the heat capacity of coal (and its temperature dependence). There is then a "peak" visible at a temperature above 350°C. The Pittsburgh No. 8 spectrum is similar, but displays greater richness in features. The difficulty in interpreting the various peaks - or even in concluding what are peaks - is evident. This again attests to the difficulty of

identifying transitions.

The most noticeable difference between the upper and lower panels of Figure II-1 is that Upper Freeport and Pocahontas No. 3 coals in the upper panel exhibit distinctly endothermic peaks around 350°C and 430°C, respectively. These peaks are relatively clear endotherms, but in the context of a search for glass transitions, they might be similar to the "hysteresis" peak normally occurring just after the glass transition temperature in stressed polymers [25]. The hysteresis peak is mainly caused by stress relief of the structure by heat, quite often observed in amorphous polymers such as epoxies, polycarbonate, polystyrene.

These high temperature endothermic peaks observed with the Upper Freeport and Pocahontas coals are not ordinary melting endotherms because these samples do not give an analogous "heat of fusion" peak upon cooling, as illustrated in Figure II-2. These peaks do not result from ordinary glass transition, because they are irreversible, as is apparent from their absence in a second scan after cooling (see Figure II-2). Endothermic reaction could also be possible for the peaks, but this possibility can be ruled out on the basis of other evidence to be presented later. Thus an explanation in terms of an enthalpy associated with an irreversible relaxation appears the most plausible.

Interpretation of the spectra has been greatly aided by the recognition that the relaxation processes that are observed are irreversible. Since heat capacity variation with temperature should not be irreversible, subtraction of two consecutive DSC scans' spectra should yield a spectrum in which any irreversible events are greatly enhanced. Such spectra will be henceforth termed "difference DSC spectra".

The results of the procedure are seen in Figure II-3, for Pittsburgh No. 8 coal. If all that were happening during heating was a series of reproducible, and thus reversible, processes, then the difference of two spectra would be a flat line at a value of zero. Clearly this is not the case, although that behavior begins to obtain when the second DSC scan's spectrum is subtracted from the third scan's spectrum. The fact that the second minus third curve is not yet perfectly flat implies that even during the second heating, the coal is irreversibly changing. Part of the reason for this is that it was difficult to stop the scans before any pyrolysis occurred. Thus, there was certainly mass loss during all three scans, and the problem of comparing results normalized by starting mass becomes visible. Clearly, there is more mass present in scan 2 than in scan 3, so that the endothermic events should be of greater total intensity in 2 than 3. Because of the difficulties inherent in trying to obtain sample masses between scans (e.g. oxidation) all heat effects are expressed on the basis of starting mass, rather than true mass. This is why many difference DSC spectra presented in this report will involve a horizontal line at a slightly negative value. It is whether the curve is or is not horizontal, as opposed to the fact that it has negative value, that is significant for most purposes of discussion.

The observations in Figure II-3 appear to confirm an earlier suggestion [26] that Pittsburgh No.

8 coal has an unusual irreversible heat effect associated with what is thought to be a physical transition around 275°C. Note the considerable enhancement of this feature, relative to what is discernible in Figure II-1. The interpretation of the feature is greatly enhanced by simultaneous examination of other data, as seen in Figure II-3. These additional data will be described in the next subsection.

Results of Difference DSC and Solvent Swelling Experiments

Pittsburgh No.8 Bituminous Coal

While the DSC thermograms for Upper Freeport and Pocahontas No. 3 coals in Figure II-1 exhibit distinct endothermic transition peaks as described above, subtle effects in the DSC thermogram for Pittsburgh No. 8 coals can be better scrutinized by difference DSC thermograms. It must be repeated that the endothermic transition observed at around 275°C is irreversible, otherwise it would not be visible in the subtractive technique. Pittsburgh No. 8 coal exhibited initial agglomeration behavior from ca. 340°C (at 8°C/min), as observed visually from the coal samples after cooling. Thus the softening of coal, leading to gross agglomeration, has not yet commenced at the observed temperature range of the physical transition that was revealed by DSC.

As we have reported [26,27,51], the interpretation of the transition revealed in the DSC is aided greatly by a knowledge of the solvent swelling behavior of the coal as a function of temperature. Figure II-3 shows a comparison of pyridine and THF swelling behavior of the Pittsburgh No. 8 coal obtained on the samples after only a single DSC scan. It is noted that there is an irreversible increase in THF swellability achieved in heating the coal to the range of temperatures 200-300°C. This is not accompanied by any significant weight loss. Nor is this change accompanied by any increase in pyridine swellability (in fact, a small decrease is seen, if anything).

Pyridine is a stronger solvent for this coal, and can be expected to disrupt all noncovalent interactions in the coal. Pyridine swelling helps reveal the extent to which the *covalent* network structure has been altered. The extent of swelling is a measure of the crosslink density in coal - the more crosslinked the structure, the less it can swell. Pyridine is believed to be an effective solvent for disrupting non-covalent interactions in this coal; it should be able to solvate most hydrogen bonding interactions. It is observed that no other solvent swells the coal more. Thus it is believed that the extent of swelling in pyridine measures the covalent crosslink density. The "weaker" solvent THF (a poorer electron donor) is not as effective in removing all noncovalent crosslinks, as is suggested by the fact that it does not swell the coal as much. Note that the molecular sizes are quite similar for pyridine and THF, so on the basis of molecular size accessibility should be quite comparable and this cannot explain the difference in swelling behavior in the two solvents.

For Pittsburgh No. 8 coal, heating the coal to the range of temperatures 200-300°C apparently results in an irreversible removal of *noncovalent* crosslinks (as suggested by the increase in THF swellability), but not much change in covalent crosslinks (as suggested by the constancy of pyridine swellability). This was hypothesized to occur because the coal structure undergoes a relaxation in this temperature range, and the structure achieves a new equilibrium configuration which is more easily swelled by THF. This effect is presumably related to the observation made by Larsen and coworkers [28] that the first cycle of a swelling in a good solvent such as pyridine normally involves an irreversible expansion of the network structure, due to structural relaxation. This transition is not evident in post-heating pyridine swelling of coals because pyridine itself is completely effective at relaxing the structure without the need for heating. This is consistent with the results of Sakurovs et al. [13,14], which showed pyridine to be as effective as heating with respect to creating "mobility" (at least in bituminous coals up to 86% C daf content).

The significance of the greater degree of relaxation of the thermally pretreated samples is also clearly seen from the dynamics of the swelling process. Figure II-3 shows that much more time is required to reach THF swelling equilibrium in samples not heated above 250°C than for those heated above this temperature. This indicates that the accessibility of the coal is irreversibly increased by heat treatment above 250°C. There is relatively little effect of heat treatment below about 250°C on either the rate or extent of swelling by solvent. The abruptness of relaxation onset in a narrow temperature range suggests a strongly thermally activated process, as is characteristic of relaxations in macromolecular systems.

The DSC results suggest an increase in the molecular degrees of freedom at around 250°C, indicated by the apparent increase in ability to absorb heat per unit temperature change. Consequently there can be little doubt about the conclusion that the structure is loosened above 250°C. Thus the DSC and THF swelling results are mutually supportive. Again, there is no evidence for the relaxation in the pyridine swelling results because pyridine is effective at relaxing the structure without thermal pretreatment.

There might be a practical consequence of the relaxation processes that have been observed. It has been noted that there is a low temperature evolution of tars from this Pittsburgh No. 8 coal, that is hypothesized to involve escape of "guest molecules." [4,29,30] This evolution is reported to occur between 250°C and 370°C for a heating rate of 3°C/min [30], and between 250°C and 400°C for a heating rate of 100°C/min [4]. The low temperature onset (at 250°C) and temperature range for both the guest molecule loss process and the relaxation processes correspond so closely that there appears to be strong suggestion that relaxation is accompanied by physical escape of entrapped molecules. As observed earlier, the process of release of guest molecules blends smoothly into that which involves release of tars, which is pyrolytically mediated. The distinction is made between the two

processes on the basis of the very different compositions of the "early" and "late" condensable products, suggesting different origins [4,29].

Based upon DSC evidence, the relaxation processes appear to extend to temperatures near 400°C. We hesitate to assign an upper limit to the temperature of the relaxation processes because, as noted above, they merge smoothly into what is obviously a pyrolytic process, accompanied by both mass loss and the commonly noted decrease in pyridine swellability [31]. Interestingly, the DSC-based suggestion of continuation of relaxation into the pyrolysis zone is at odds with the THF swelling behavior, which suggests that the relaxation is complete by 350°C. We have no explanation for this observation, but can plausibly speculate that it might reflect that when the coal's structure is thermally loosened to some extent, then the THF can "finish the job" of relaxing the structure.

Finally, it may be noted from Figure II-3 that the pyridine swelling ratio of the Pittsburgh No. 8 coal decreases slightly with *time of swelling*, in contrast to the behavior of the coal in THF. This is presumably due to weight loss from the solid coal by extraction into pyridine during the swelling tests (recall that extract was removed and replaced by fresh solvent during these tests). The decrease of pyridine swelling ratio with increase in *thermal pretreatment temperature* is, on the other hand, a common observation for all coals at high temperatures. The loss of pyridine swellability is seen to parallel a decrease in THF swellability.

The loss of swellability as the active pyrolysis zone is approached could reflect either two things. The most obvious possibility is that the structure crosslinks as pyrolysis begins, and becomes less swellable. The degree to which this occurs has been hypothesized to be the reason for the difference between the behavior of lignites and bituminous coals during pyrolysis. The softening behavior of bituminous coals during pyrolysis is not observed in lignites, because the latter crosslink much more heavily than do the former, at low temperatures [2,36]. The earlier studies were, however, generally concerned with higher temperatures than are of interest here, since they focused upon the active pyrolysis zone.

A second possibility for the temperature-increase-induced decrease in swellability of the coal receives little attention in the literature. This possibility has to do with removal of certain key functional groups from the coal. If the coal's surface changes, due to loss or rearrangement of functional groups, then the thermodynamic driving force for interaction with electron donors such as pyridine and THF can be decreased. The surface might prefer to more strongly interact with itself than with the solvents. The result might be decreased swellability. Consequently, hypotheses as to the causes of changes in swellability during periods of pyrolytic mass loss must be viewed with caution, unless verified by other corroborating evidence.

Illinois No. 6 Bituminous Coal

With the understanding that was derived from the analysis of the Pittsburgh No. 8 behavior, the thermal pretreatment behaviors of all other Argonne Premium coal samples could be likewise examined. Figure II- 4 shows changes of the swelling ratio in THF and pyridine against pyrolysis temperature for Illinois No. 6 coal, along with the weight loss profile and difference DSC thermograms. It should be noted from Figure II-4 that the weight loss in the 150-300°C range was 10.3-10.9 wt%, which is slightly higher than the recently reported ASTM moisture content of about 9.5 wt% of this coal [32]. This shows that an arbitrary drying procedure, such as the ASTM procedure, might not give the correct picture regarding moisture loss.

In Illinois No. 6 coal the water evaporation endotherm is the dominant feature of the DSC thermogram, as could be expected from the high moisture content of this coal. However, very subtle changes are visible above 300°C in the difference DSC thermograms. These subtle peaks in the DSC difference spectra are again believed to be associated with irreversible physical changes, since they were not accompanied by large amounts of mass loss (again there could be a hint of "guest molecule" release). The evidence in this case is, however, far weaker, since it is not corroborated by any significant changes in the solvent swelling behavior of the coal.

Illinois No. 6 coal exhibits a drastically different behavior with heat treatment temperature than does Pittsburgh No. 8 coal. In the DSC spectra, there are few features visible in the 250-300°C range that was so prominent in the case of the Pittsburgh No. 8 coal. In the THF swelling behavior, there are also large differences noted. Higher THF swelling ratios were always obtained with this coal than with the Pittsburgh coal. The fact that Illinois No. 6 coal can swell significantly in THF without any heat treatment reflects a much different starting structure than that of Pittsburgh No. 8 coal. Also, given the much faster THF swelling dynamics of the Illinois No. 6 coal, the structure was already much more loose prior to heating, than that of the Pittsburgh No. 8 coal. This is consistent with other results [33] showing that the diffusion of solvents into the unpretreated Illinois No. 6 coal is much faster than into unpretreated Pittsburgh No. 8 coal. This clearly demonstrates the importance of initial coal structure in determining swelling behavior.

The pyridine swelling behavior suggests the possibility of actual chemical reactions of some kind in the range of temperatures 300 to 375°C. Since the pyridine swellability of the coal begins to sharply decrease in this range, this suggests formation of new crosslinks in the structure. Again, pyridine swellability has been seen to drop during early pyrolysis [31]. It is difficult to say that the apparently "earlier" decrease in pyridine, as compared to THF, swellability is significant.

There is one additional problem of interpretation that arose in connection with these data. As noted in the case of the Pittsburgh sample, there is often an apparent decrease in pyridine swellability *in time* due to extraction of the coal by pyridine. In this case, the decrease of swelling ratio *with temperature* might not reflect crosslinking, but actually opening up of the structure to greater

extraction. In this case, there is practically no limitation to diffusion of species in the structure, so any extractables that are present are removed very quickly. It is thus unclear whether the decrease in swellability of the samples above 300°C is indicative of crosslinking, or merely an increase in extractability. Clearly further work could be done to resolve the issue, but this was not pursued here.

It is notable that where the DSC and pyridine swellability results do suggest some irreversible changes in the structure of the Illinois No. 6 coal (at temperatures between 300°C and 375°C), this coincides well with the range of temperatures (320°C to 360°C), at which steam pretreatment has been shown to be effective at increasing pyrolysis yields from this coal [12]. We conclude, therefore, that there could well be some chemical reaction processes involved in this range of temperatures.

Lewiston-Stockton High Volatile Bituminous Coal

The results for Lewiston-Stockton high volatile bituminous coal (Figure II-5) appear in some ways similar to those of the Illinois No. 6 coal and in other ways similar to those of the Pittsburgh No. 8 coal. As in Pittsburgh No. 8 coal, there is a tendency towards faster swelling in THF, following thermal treatment. Again, there is an increase in rates at near 250°C. There is, however, no major transition visible in the DSC results. Instead, there is a very gentle deviation from horizontal in the difference spectra. This means that relaxations can occur without clear thermal signatures. Note that the relaxation occurs without any significant mass loss, just as in the case of the Pittsburgh No. 8 coal.

In the temperature range above 350°C, there are the beginnings of a difference DSC peak that is similar to that observed in the Illinois No. 6 sample. Just as in the case of the Illinois No. 6 coal, this transition coincides with the beginning of a decline in pyridine swellability. Once more, pyridine swelling ratios decrease more dramatically with temperature than THF swelling ratios. And again, above 350°C, the weight loss starts to increase rapidly, as pyrolysis begins.

Pocahontas Low Volatile Bituminous Coal and Upper Freeport Medium Volatile Bituminous Coal

The two higher rank coals - Pocahontas and Upper Freeport- will be discussed together because of the similarities in their behaviors. Figures II-6 and II-7 illustrate the correlation between DSC thermograms obtained at 8 °C/min and solvent swelling profiles in these two coals. Swelling ratios for these two coals are virtually 1.0 at temperatures below 250°C and start to increase dramatically at temperatures corresponding to the structural relaxation process, as revealed by the endotherm in the

DSC results. In contrast to this behavior in the low and medium volatile bituminous coals, it should be recalled that high volatile bituminous coals showed relatively higher swelling ratios at temperatures below 250°C (for example, see Figures II-3, II-4, and II-5). Thus the higher rank coals start out with a much more tightly crosslinked structure, but can be thermally relaxed to a state not unlike that in lower rank bituminous coals.

In the case of Upper Freeport medium volatile bituminous coal, the main endothermic relaxation process starts from ca. 310°C (Figure II-6(a)) and the THF swelling ratio starts to increase at around the same temperature (Figure II-6(b)). The end of the endothermic peak appears to be at around 400°C, when it appears as though the pyrolysis rate becomes significant. Similarly, in Pocahontas No. 3 low volatile bituminous coal (see Figure II-7), the DSC difference thermogram exhibits a rather sharp endothermic profile from ca. 390°C, which also coincides with the onset of dramatic changes in pyridine and THF swelling profiles. Again, the endothermic peak is immediately followed by the onset of rapid pyrolysis. In this case, it is a bit harder to define a clear endpoint for the endothermic peak.

The Upper Freeport coal exhibited initial agglomeration behavior from about 350°C (at 8°C/min), as observed visually from the samples after cooling. The Pocahontas No. 3 coal never showed any sign of agglomeration up to 450°C at 8°C/min. Based upon the fact that the endotherms are irreversible, and the fact that the endotherms did not consistently correspond to any visible softening, it appears that the endotherms do not correspond to a simple fusion process.

Once again, we note the correspondence between the observed transition temperature for the Upper Freeport coal and the temperature at which the "guest molecules" are seen to emerge [29]. The range of temperatures for these to emerge from the Upper Freeport coal was the same as it was for the Pittsburgh No. 8 coal, meaning that the onset is at around 250°C, and the process continues up until active pyrolysis begins at around 400°C. Figure II-6 illustrates a gradual decline in the first minus second (and first minus third) DSC difference spectra from 250°C upward. It should be kept in mind that it is the deviation from horizontal in a difference spectrum that indicates that an irreversible process has occurred. The main endothermic peak is centered at 350°C, but the decline from 250°C suggests the irreversible relaxation process begins earlier. This again mirrors the shape of evolution peaks for guest molecules [29].

The Pocahontas No. 3 coal is also noted to give a small amount of low temperature tar, ascribed to guest molecule release [4,29]. It is also possible that the gradual decline in the difference DSC spectrum that begins as low as almost 150°C (see Figure II-7) reflects this process.

The data in Figures II-6 and II-7 reveal that significant *increases* in solvent swellability precede the period of rapid pyrolytic mass loss in both the Upper Freeport and Pocahontas coals. The period of rapid mass loss, however, always seems to coincide with swellability *decreases*. Note,

however, the low extents of mass loss up to 450°C. The points at which experiments were terminated were very early in the pyrolysis process. For reference, when fully pyrolyzed the Upper Freeport coal typically exhibits a mass loss of 25.2 wt% and the Pocahontas No. 3 coal, 20.6 wt% [34].

In the temperature range above 350°C, the pyridine swelling ratio of the Upper Freeport coal decreases with temperature, while THF swelling ratio stays virtually the same, showing perhaps only a slight decrease. The decreases are indicative of crosslinking, since the dynamics of extraction in this case are slow enough that the short-time swelling ratios give indication of the degree of crosslinking of the structure, and are not influenced by mass loss. The increasing extent of extractability with temperature (indicated by the divergence of the short and long time swelling curves) actually suggests that there is a simultaneous process of crosslinking and extractables formation, above 350°C. In fact, however, significant extractables formation is already observed to occur at the beginning of the relaxation process. The slowing of extractables removal above 350 °C might actually reflect the greater degree of crosslinking of the structure, and increased impediments to extractables removal. In any case, the processes of physical relaxation and pyrolysis smoothly merge above 350°C, and clean interpretation of phenomena becomes difficult. Nevertheless, as will be shown below, the basic relaxation process can be demonstrated to be of physical origin, rather than being associated with pyrolytic bond cleavage.

The fact that the observed relaxations seem to generally move to higher temperatures with increased rank argues that there is some rank-dependent characteristic responsible for keeping the coal in an unrelaxed state. Since higher rank coals contain progressively lesser quantities of functional groups (e.g., hydroxyl groups) and higher aromatic contents, it might be reasoned that it is some aromatic features that are responding to thermal treatment. Aromatic-aromatic stacking interactions would be expected to increase as aromatic content increases with rank and it might be these interactions that are thermally dissociated. This hypothesis would be consistent with a physical transition, such as a "melting", glass transition, or other relaxation of the structure, any of which could give rise to an endotherm. Once again, the argument in favor of the endotherms or transitions actually indicating an irreversible relaxation, rather than reversible melting or true glass transition, is that there is no corresponding crystallization peak during cooling.

There is still the question as to whether the observed transitions might not be a manifestation of covalent bond cleavage processes. The argument against this might be based on the fact that the transitions occur at progressively higher temperatures with increasing rank; it could be asked why pyrolysis reactions would start at different temperatures in different ranks. It has recently, however, been argued [30] that there is a shift of pyrolysis kinetics with rank, since the more mature coals have had an opportunity to "pyrolyze" under natural geological conditions for a very long timescales.

The main line of argument against the relaxations being a result of covalent bond breakage comes from experiments in which solvents can be used to induce the relaxation at room temperature. These experiments will be described below.

Rawhide Subbituminous Coal and Beulah-Zap Lignite

Compared with the above results, rather dramatically different responses to solvent and heat exposure are exhibited by the two lowest rank coals (see Figures II-8 and II-9). Both these coals have much higher moisture contents than do the higher rank coals, and this explains some of the most obvious differences. The very large endotherm associated with drying of the coals extends to much higher temperatures than in the higher rank coals. The endotherm would obscure any transitions that would occur below 150°C. These endotherms coincide with a rather steep increase in the pyridine swellability of the coals, and a more gentle increase in THF swellability. It has been noted that the increase in swellability in the range of temperatures associated with drying is only an apparent increase [52]. The apparent increase is attributable to the fact that another swelling solvent, water, is being removed by drying, so that the coal swells from a smaller base value. The pyridine is a larger swelling molecule, so the extent of swelling in pyridine is greater than the extent of swelling in water.

In the Wyodak subbituminous coal pretreated at any temperature above those needed for drying, the swelling in THF or pyridine increase with time of swelling, up through several days (Figure II-8). This suggests that solvent-caused relaxation is occurring on a timescale of several days, and implies that heat pretreatment alone is *not* effective as a relaxing agent in this coal. The same conclusion is drawn from the data on Beulah-Zap lignite (Figure II-9). In general, it even appears that gradual crosslinking is occurring with increasing temperature of pretreatment. This is consistent with other data in the literature, that suggest that any heating, even at low temperatures, tends to compact and crosslink lignite structure [52,53].

A large coal-to-coal variability is once more visible in the behavior of these two samples. The rate of solvent swelling in Beulah-Zap coal is considerably slower than in Wyodak coal. In the Beulah-Zap lignite sample, the influence of water to solvent swelling kinetics is clearly seen such that moist coal swells much faster in solvent than dried coal samples. It has earlier been reported that water can serve as a plasticizing agent for transport in coals [52].

Powhatan No. 5 Bituminous Coal

The results of the usual battery of experiments performed on Powhatan No. 5 coal are shown in Figure II-10. This coal, which is also of high volatile rank, exhibits several very unusual characteristics. The endotherm, normally ascribed to moisture loss, is of quite unusual shape. It is

quite a bit more skewed towards higher temperatures than in most other coals. In fact, the moisture loss process appears to have been largely completed before the end of the peak. This is based upon the 1.1% moisture content of the coal, which the weight loss curve shows is attained between 100 and 150°C. Thus we hypothesize that the water evaporation endotherm merges with that of a low temperature relaxation process that has nothing to do with the water removal process, but occurs at around the same temperature. This is confirmed by the fact that the THF swelling kinetics are greatly enhanced as temperatures approach 200°C, and the pyridine extractability is also slightly enhanced over the same range of temperatures. The continual loss of mass in the very low temperature range between 200 and 300°C might reflect the loss of guest molecules, but we have no definite proof that this is the case. It should be noted that relaxations of coal structure in the temperature range associated with water loss have been recently reported by others [50].

Another unusual feature of the DSC spectra for this coal is the event at 300°C. The usual downward sloping first minus second and first minus third scans are seen up to 300°C. Though quite often observed, this downward sloping behavior has not been clearly assignable to any particular relaxation or crosslinking events, but seems to be more associated with very small pre-pyrolytic loss of mass. We thus believe that it is reflective of the absorption of a latent heat of evaporation by small amounts of guest species that are evaporating in this temperature range. Here, there is a very minor apparent increase in pyridine swellability and significant mass loss associated with this period.

Once 300°C is attained, there is clear evidence of an event that alters the course of processes. There is a sharp upturn in the DSC spectrum and there is a very abrupt decrease in pyridine swellability. Mass loss continues to increase, however, and THF swellability is not much affected. This appears to suggest the occurrence of chemical reactions that have some significant affect on pyridine swellability. It cannot be clearly concluded that the decrease in pyridine swellability reflects a loss of some particular functional groups with which the pyridine strongly interacts, or more likely, a suddenly increased degree of crosslinking due to some retrograde reaction. The THF might not reflect a higher degree of crosslinking, because as far as this weaker solvent is concerned, the structure is already much more crosslinked anyway; swelling in THF would not be expected to be as sensitive to addition of extra crosslinks.

Blind Canyon Bituminous Coals

Two different Blind Canyon high volatile bituminous coals are discussed here, separately from the other high volatile bituminous coals because their complex behaviors comprise elements of behavior observed for the other high volatile bituminous coals, as well as for the low rank coals. The data for the Argonne Premium Blind Canyon coal are illustrated in Figure II-11.

Swelling ratios in pyridine and THF increase up to 150°C. This appears to be similar to the behavior in the low rank coals, in which the increase in swellability is apparent, and due to the fact that the coal shrinks as moisture is lost. As discussed below, however, the increase appears to be perhaps more than might be explained on this basis. There is a difference from the low rank behavior in that the rate of swelling is also *slowest* when water is present.

Above 250°C, the strongly sloping difference DSC difference spectrum appears comparable to what is seen with Pittsburgh, Upper Freeport and Pocahontas coals. There is a small amount of mass loss during this time, which might correspond to guest molecule release. There is also a tendency towards greater extractability of the coal, as it is heat treated above 250 °C. This is evident from the observation that swelling ratio generally decreases with swelling time, as is typical in such cases. The general downward trend in pyridine and THF swelling ratios with pretreatment temperatures indicates that gradual crosslinking is occurring. Consequently, it appears as though heat treatment is both crosslinking the structure, but at the same time it is serving to make it more extractable.

In addition to the Argonne Premium Blind Canyon seam coal, the DOE standard sample DECS-17 was also examined. The results are shown in Figure II-12. The behavior is, not surprisingly, quite similar in both the Blind Canyon samples. The DECS-17 gives a simpler picture, in that there is less scatter in the pyridine solvent swelling results. The coal is clearly more swellable in pyridine once the moisture is removed. It appears that the increase is more than could be explained based upon the shrinkage of the coal upon drying. The coal loses only about 4% by mass moisture during drying up to 150°C. Based upon our earlier correlation [52], this would suggest that the coal would have shrunk by about 4%. Clearly the pyridine swelling increased far more than would be expected from a decrease of 4% in the base relative to which swelling is measured. Since a similarly significant increase was seen with the other sample of Blind Canyon coal, this is not an artifact of a particular sample, but a general characteristic of this coal seam.

Also the rate of THF swelling in this case is again enhanced by the loss of water. The pyridine swelling rate is not significantly affected, as it was in the other case. It appears that the coal structure is effectively more crosslinked before heat treatment to 150°C. Therefore in this case, the behavior is more akin to that observed with Powhatan No. 5 than like that in the lower rank coals. The fact that the relaxation of the structure coincides with the loss of water does not mean that there is causality. Again, it appears that in these coals there are certain non-covalent interactions that might involve polar interactions, dissociable at these low temperatures. Note that just as in the case of the Powhatan coal, the DSC endotherm extends well beyond the period during which moisture loss appears to occur, based upon mass loss. These noncovalent interactions initially make the coal more rigid. These would no doubt be relaxed during any ordinary drying procedure, and thus may give little evidence of themselves during actual coal processing.

Above 150°C, the pyridine and THF swelling ratios of the DECS-17 Blind Canyon sample both decline significantly. As in the other sample of Blind Canyon coal, it appears that there is a gradual relaxation of the structure, resulting in greater extractability, with increased temperature. It is unclear based upon the work performed to date whether the decline in apparent swellability reflects more the effects of extraction or crosslinking. The fact that the results for THF and pyridine parallel one another so closely suggests that it is actually crosslinking (retrograde) reactions that are the key. The weaker extraction solvent THF shows the same decline in swellability as the pyridine. It would not be expected that the curves could parallel each other so closely if the decline were due to extraction of materials from the coal; pyridine would be pulling out much more. Thus the likely reason for the decline in swellability is retrograde crosslinking processes.

Where liquefaction is concerned, it is already abundantly clear that the structure is clearly more relaxed by preheating to this range of temperatures. The speed of swelling establishes this clearly. What therefore remains to be established more quantitatively is the extent to which retrograde reactions are occurring as well.

Effects of heating rate on DSC difference spectra

The distinction between a true phase change and a relaxation or transition process in DSC can be confirmed by examining the effect of heating rate on the temperature of transition. An ordinary phase transition, such as melting, occurs at a well-defined temperature, regardless of heating rate (in the absence of any transport limitations, of course). Other types of relaxation processes typically involve crossing some sort of activation energy barrier, and will show themselves at different temperatures, when heated at different rates. Thus measurements of glass transition temperatures are actually kinetic measurements, and the reported values depend upon the heating rate of the experiment used to obtain them. In the case of a transition with a high activation energy, over a limited range of heating rates, the transition may appear to occur at roughly constant temperature.

The effect of heating rate on the DSC thermograms of coals is illustrated in Figure II-13. The effect on the "transition temperatures" in Pittsburgh No. 8 and Upper Freeport coals are reported in Figure II-14. The endothermic peaks observed in the 70-120°C range in Figure II-13 were caused by water desorption. The shift of these peaks with heating rate reflects the possible role of a transport or kinetic limitation in water loss from coal, as is well known. It is the higher temperature peaks that are of interest in terms of relaxation phenomena.

The DSC difference spectrum for Pittsburgh No. 8 coal exhibits the characteristic sigmoid shape in an endothermic direction, in the 270-310°C range. This represents a physical transition that is activated, given the shift of the curve to higher temperatures at higher heating rates. Figure II-14

displays the midpoint of the transition range, as a function of heating rate. The irreversible transition in the 270-310°C range is more pronounced at higher heating rates, as is normal for activated processes studied by DSC.

The DSC thermograms for Upper Freeport coal show the distinct endotherm character at all heating rates. Again, there is a definite shift towards higher temperatures with heating rate, suggestive of an activated process. The temperature of the peak minimum as a function of heating rate are shown in Figure II-14.

These results are quite contrary to recently reported data [35] suggesting a lack of effect of heating rate on " T_g " in coals. In that study, there was no effect of heating rate upon T_g in the range of heating rates from 5 to 40°C/min. In our work, for a change of heating rate from 10 to 80°C/min, the transition temperatures shift by 30°C (from 280°C to 310°C) in Pittsburgh No. 8 coal and by 25°C (from 350°C to 375°C) in the Upper Freeport coal (see Figure II-14). We have no explanation for the discrepancy between the studies. As noted above, a true glass transition is, on theoretical grounds, expected to be a function of heating rate. The development of significant segmental mobility in the network, which is what glass transition reflects, depends upon how long the chains are given to relax at temperatures near the event. This is in contrast to an ordinary first order phase transition such as melting or evaporation, in which all the molecular interactions that define the existence of the phase, become unstable at a well-defined temperature. In polymer characterization, shifts of 5 to 10°C with heating rate variations of 10°C/min to 40°C/min are not uncommon (e.g. polystyrene[36]). The shifts in transition temperatures exhibited by coals are somewhat larger, possibly reflecting stronger initial interactions.

It should of course be remembered that *any* activated process will give a DSC signature that shifts with heating rate. There is, thus, again no proof that the shifts of the kind exhibited in Figures II-13 and II-14 are not due to covalent bond breakage process, except again it would be difficult to reconcile the shape of the curves in Figure II-13, and the other observations above, with purely reaction processes. Thus, we believe that the transitions of interest involve physical relaxation-type transitions of high activation energy.

Integration of the peaks in Figure II-14 for the Upper Freeport transition at the four different heating rates gives 11.3 J/g for 10°C/min, 11.2 J/g for 20°C/min, 10.1 J/g for 40°C/min, and 9.7 J/g for 80°C/min (integration was to an arbitrary 400°C endpoint). While clearly the peaks at the higher heating rates are not quite complete, the comparability of these values (particularly those at the lower rates, for which integration is better) suggests an endothermic process whose basic nature does not change with heating rate. To put the magnitude of these values in perspective, it is worth noting that the heat of fusion of pure naphthalene is 146.7 J/g, that for pure anthracene is 161.9 J/g, that for cyclohexane is 31.3 J/g, and that for anthraquinone is 156.8 J/g [39]. Thus the magnitude of the

observed endotherms is too small to reflect a generalized "melting" of the coal, but it is large enough to suggest that a significant part of the coal structure is effectively "melting". In fact, in polymers, a fractional crystallinity can be defined from the enthalpy of fusion relative to the enthalpy of fusion of a hypothetical "purely crystalline" polymer. There is probably an analogous situation in the coal, though of course the coal is not a true polymer with well-defined repeat units.

Since there are effects of heating rate on the transition temperatures, Kissinger's method [40] may be applied to estimation of the activation energy from such thermal analysis data. The activation energy so calculated from these data is as follows: ca. 10 kcal/mol for water evaporation steps both in Pittsburgh No. 8 and Upper Freeport coal, ca. 50 kcal/mol for the transition in Pittsburgh No. 8 coal, ca. 80 kcal/mol for the transition in Upper Freeport coal. The latter two values might again evoke concerns about the interpretation in terms of physical relaxation processes as opposed to chemical reaction processes. In this regard, it should however be noted that various analyses of the kinetic parameters associated with the glass transition in polymers have provided values that are comparable. For example, the activation energy of transition in polystyrene has been reported to be between 95 and 102 kcal/mol in one study [41] and about 90 kcal/mol in another [42]. Polymethylmethacrylate gave 77 kcal/mol and polyvinyl chloride 81 kcal/mol in the same study [42]. Thus we stand by our conclusion that physical processes are responsible, even in Upper Freeport coal. Further support for the conclusion is provided below.

Effects of solvent exposure prior to DSC

The DSC spectra described above were monitored in cases in which solvents were used to pre-relax the coals. If strong solvents, such as pyridine, are in fact able to relax the coal structure at room temperature, then there should be no residual thermal signature of relaxation in the DSC spectra. The approach involved relaxing the coals in either pyridine or CS₂/pyridine mixtures.

The coals could easily be treated by soaking or extracting in pyridine, as described above. The more challenging aspect of the experiments was the removal of pyridine without subjecting the samples to thermal treatment that would potentially cause the very effect of interest. The difficulties encountered in this respect are illustrated in Figure II-15. These results showed that pyridine cannot be successfully removed by simple vacuum drying at room temperature. Even the exhaustive extraction method employed by Joseph [7] was unsuccessful in removing this peak. The difference DSC thermogram for dried coal, presented for comparison in Figure II-15, was obtained after heating the coal sample at 8°C/min up to 200°C and keeping isothermal for five minutes inside the DSC cell under constant nitrogen purge. Enormous peaks associated with pyridine removal from the pyridine-treated coals are centered at around 190-200°C and extend into the range of temperatures of interest for examining the transitions (marked as a shaded area). The identity of the peak around

190-200°C, as due to pyridine, was confirmed by an additional experiment in which more pyridine was added to the pyridine Soxhlet extracted sample before subjecting it to DSC.

The result of drying samples inside the DSC cell, even up to 200°C, strongly suggests that the remaining pyridine cannot be removed in full by heating or drying under vacuum. Thus it is impossible to say anything about the effect of pyridine pretreatment on the transitions in the Pittsburgh No. 8 coal, based on these results. We would have expected the transitions to be absent, because we believe in this case that the pyridine itself is quite effective at relaxing the structure.

The issue of pyridine removal is less troublesome in the case of the Upper Freeport medium volatile bituminous and Pocahontas No.3 low volatile bituminous coals (see Figure II-16). In these cases, the incomplete removal of pyridine does not obscure the main transition peaks around 350°C and 430°C. The relaxation processes in these coals are not affected by prior pyridine exposure.

Vertical dotted lines in Figure II-16 indicate the transition temperatures observed in as-received Upper Freeport and Pocahontas No. 3 coals at the same heating rate as used in examining pyridine Soxhlet extracted coals. The fact that the same temperatures were obtained regardless of pyridine exposure reveals the ineffectiveness of pyridine for relaxing the structures of high rank coals (>86 %C daf). This is not a proof that solvent relaxation can have no effect on transitions in coal, however. The swelling of Upper Freeport and Pocahontas No. 3 coals in pyridine at room temperature is negligible; the pyridine is just an ineffective solvent for relaxing the structure. The present observations agree with the results of Sakurovs et al. [13,14] in that heat is more effective than pyridine in destabilizing molecular structures in coals of >86 %C daf.

Recent work with CS₂/pyridine mixtures [44-46] has suggested that this combination of solvents might be more effective in the higher range of ranks that is of interest here. Figure II-16 shows that room temperature solvent relaxation of the structure of the Upper Freeport coal is indeed possible; the peak at 350°C is totally absent after such treatment. This strongly supports the present contention that the transition in this coal involves purely physical processes [43]. The peak centered at around 240°C in the CS₂/pyridine swelled Upper Freeport coal involves evaporation of pyridine, and does not reflect a transition in the coal structure.

Pretreatment of the Pocahontas No. 3 coal in CS₂/pyridine produced no swelling of the coal and was, therefore, ineffective also in removing the thermally induced transition (see Figure II-17).

Effects of CS₂ containing solvent mixtures

The Upper Freeport coal shows a large degree of *room temperature* swellability in a mixture of pyridine and CS₂. The compositional dependence of the swelling in the mixed solvent is shown in Figure II-18. The fact that maximum swelling occurs at roughly equimolar composition suggests that the power of the mixed solvent system derives from some coupling of the solvent partners.

Since there is no need to heat treat the coal to achieve significant swellability in the mixed solvent, this strongly suggests that a physical relaxation of the structure is all that is involved. There is, of course, the possibility that CS_2 undergoes chemical reaction with the coal, cleaving similar types of bonds as are cleaved during heat treatment. Xanthate formation is an apparent possibility in the presence of CS_2 [47-49]. There is no strong reason to believe that this should be so in this case, since it would be difficult to understand why, if CS_2 is a chemically reacting agent, a 1:1 stoichiometry would be needed, when both solvents are in large excess relative to the coal. We thus are led to the conclusion that the CS_2 /pyridine mixtures are effective mainly because of specific solvent properties.

The fact that the CS_2 /pyridine mixture is unique in relaxing the coal structure in a manner similar to heat, is shown in Figure II-17. Treating the coal with CS_2 alone, pyridine alone, or chloroform/pyridine mixtures leaves intact the relaxation DSC peak. Again, the Upper Freeport coal treated in CS_2 /pyridine no longer shows such a relaxation event at 350°C . Thus it is not merely exposure to CS_2 or to a mixed solvent of pyridine and something with a solubility parameter close to that of CS_2 that is responsible for the observed behavior.

The CS_2 /pyridine mixture is not nearly as effective a swelling agent for Pocahontas No. 3 coal as for Upper Freeport coal. This, too, is confirmed by the DSC spectra. There is still a significant relaxation event for the previously pyridine/ CS_2 treated Pocahontas No. 3 coal (see lower panel of Figure II-17). Apparently this specific solvent combination is only effective for a certain range of ranks. This is consistent with the observations of Iino et al.[45].

There is nothing particularly unique about the choice of pyridine in mixture with CS_2 . As Iino et al. earlier showed [44,45], N-methylpyrrolidone/ CS_2 mixtures are also effective for swelling coals of the same general rank as the Upper Freeport coal. We have established, as Iino et al. noted, that CS_2 /dimethylsulfoxide(DMSO) and CS_2 /dimethylformamide are also effective mixtures. Thus the solvent pair need not even include a nitrogen base, since DMSO is not. Further discussion of the synergistic nature of the solvent interactions will be taken up in the next chapter.

As can be expected from DSC responses for CS_2 /pyridine-swollen Pocahontas No. 3 coal (see Figure II-17), even CS_2 /pyridine mixture was not as effective in swelling as for Upper Freeport coal. However, heat treatment up to 450°C can relax the coal structure enough to induce swelling of more than 60% by THF and pyridine. At present, only heat appears to be an effective agent for loosening the structure of low volatile bituminous coal significantly.

II.4 CONCLUSIONS

- The experiments reported here demonstrate that combined applications of DSC and solvent swelling

techniques provide additional insights into heat- and solvent-induced macromolecular structural changes in coals. DSC confirms what was suspected from THF solvent swelling of the Pittsburgh No. 8 bituminous coal - that there is a structural transition in the range of temperature from about 250 to 400°C. In general, there are thermally induced (prepyrolysis) structural relaxations in bituminous coals at ca. 270-430°C (540-700 K) temperature range that make them more easily penetrable, swellable and extractable in solvents. However, these relaxations are not observed in subbituminous and lignite samples. In these low-rank coal samples, gradual crosslinking with temperature was dominant.

- In coals of medium and low volatile bituminous rank, the structural relaxation apparently occurred at temperatures lower than those for pyrolytic bond breakage. Endothermic transitions always accompanied an increase in solvent swellability of coals. They occurred in temperature ranges earlier noted to involve release of "guest molecules", and seemingly preceded the onset of major pyrolytic reaction events.
- DSC thermograms appear to correlate with THF swelling ratio profiles, with regard to the information they convey on structural relaxation.
- As in amorphous polymers, the relaxation transitions observed in coals exhibit a strong dependence on heating rate. Responding to heating rate changes of 10 to 80°C/min, the Pittsburgh No. 8 and Upper Freeport coals show about 30°C shifts in the transition temperatures.
- No relaxation of structure was caused by pyridine preswelling of coals of rank higher than high volatile bituminous (> 86 %C daf). Heat appears to disrupt the macromolecular structure more effectively than can pyridine at > 86 %C daf, as previously suggested by Sakurovs et al.[7,8] CS₂/pyridine is, however, effective in relaxing the structure of the Upper Freeport coal.
- Even strong solvents cannot swell the structure of high-rank coals more than ten percent at low temperatures (<250°C) whereas heat treatment above 300°C and solvent swelling by mixtures of solvents (e.g., with CS₂) enhance the swelling of coal structure significantly.
- The origin of efficacy in swelling of a medium volatile rank coal by mixed solvents of CS₂ and certain solvents (e.g., pyridine, dimethylsulfoxide, dimethylformamide) appears to be physical.

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Table II-1. Ultimate and Proximate Analysis Data on PCSP Ampoule Samples Used in This Study

<u>Coal</u>	<u>Pocahontas No.3</u>	<u>Upper Freeport</u>	<u>Pittsburgh No.8</u>	<u>Lewiston-Stockton</u>	<u>Blind Canyon</u>	<u>Illinois No.6</u>	<u>Wyodak</u>	<u>Beulah-Zap</u>
<u>Proximate Analysis (as-received basis)</u>								
H ₂ O	0.65	1.13	1.65	2.42	4.63	7.97	28.09	32.24
Ash	4.74	13.03	9.10	19.36	4.49	14.25	6.31	6.59
VM	18.48	27.14	37.20	29.44	43.72	36.86	32.17	30.45
FC	76.13	58.70	52.05	48.78	47.16	40.92	33.43	30.72
S	0.66	2.29	2.15	0.69	0.59	4.45	0.45	0.54
Btu	14926	13315	13404	11524	13280	10999	8426	7454
<u>Ultimate Analysis (dry-ash-free basis)</u>								
C	91.05	85.50	83.20	82.58	80.69	77.67	75.01	72.94
H	4.44	4.70	5.32	5.25	5.76	5.00	5.35	4.83
N	1.33	1.55	1.64	1.56	1.57	1.37	1.12	1.15
O*	2.47	7.51	8.83	9.83	11.58	13.51	18.02	20.34
Org S	0.50	0.74	0.89	0.65	0.37	2.38	0.47	0.70
Cl	0.20	0.00	0.12	0.12	0.03	0.06	0.03	0.04
<u>Major Ash Elements (% Mass in Whole Coal, by Atomic Emission Spectroscopy)</u>								
Si	0.88	3.3	2.3	5.2**	0.86**	3.3	0.77	0.60**
Al	0.85	2.0	1.3	0.4**	3.9**	2.0	0.48	0.23**
Fe	0.69	2.3	1.3	0.4**	0.24**	2.3	0.29	0.37**
Mg	0.08	0.10	0.05	0.1**	0.04**	0.10	0.20	0.51**
Ca	0.80	0.58	0.29	0.08**	0.29**	1.7	1.0	1.3**
Na	0.13**	0.05**	0.04**	0.04**	0.07**	0.15**	0.13**	0.25**
K	0.04**	0.3**	0.13**	0.36**	0.02**	0.26**	0.03**	0.04**

*by difference, ** based upon ash analysis

Abbreviations: VM = volatile matter; FC = fixed carbon

Ref.: Vorres, K.S., 1989 & 1993 Users Handbook for the Argonne Premium Coal Sample Program, Argonne National Laboratory, Argonne, IL.

Table II-2 -Ultimate Analyses of Non-Argonne Coals Studied

<u>SAMPLE</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>ASH</u>	<u>O</u>	<u>Moisture@</u>	<u>Moisture*</u>
Beulah lignite	65.6	3.6	1.1	0.8	11.0	17.9	29.4	29.4
Freedom lignite	63.5	3.8	0.9	1.4	6.1	24.3	27.9	18.7
Glenn Harold lignite	61.1	4.4	0.8	0.4	7.4	25.9	34.5	34.5
Gascoyne lignite	60.9	4.2	0.6	1.4	8.2	24.7	30.7	28.9
Powhatan No. 5 HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1	2.0
Blind Canyon (DECS-17)	76.3	5.8	1.3	0.4	6.6	9.7	3.7	-

•All results on a dry weight percent basis, except moisture@ which is reported ASTM value on an as-received, bed moist basis. Moisture* represents the actual moisture content of the samples as they were used in the present tests (note that some had dried upon storage or handling).

•Oxygen by difference.

Figure II-1. Comparison of DSC thermograms obtained at 8°C/min from different rank coals. Carbon contents designated in the figure are on dry-ash-free basis.

Figure II-2. First and second DSC thermograms obtained at 8°C/min for Upper Freeport and Pocahontas No.3 coals. Each thermogram illustrates heating and cooling cycles.

Figure II-3. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Pittsburgh No. 8 high volatile bituminous coal (-20 mesh).

Figure II-4. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Illinois No. 6 coal (swelling time: ○, 5 hr; ●, 7 days).

Lewiston-Stockton HVB coal (82.6 %C, daf)

Figure II-5. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Lewiston-Stockton high volatile bituminous coal.

Figure II-6. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Upper Freeport coal (swelling time: ○, 5 hr; ●, 7 days).

Figure II-7. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Pocahontas No. 3 coal (swelling time: ○, 5 hr; ●, 7 days).

Figure II-8. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Wyodak subbituminous coal.

Figure II-9. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Beulah-Zap lignite coal.

Figure II-10. Difference DSC thermogram as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Powhatan No.5 bituminous coal. Solvent swelling times are indicated beside the swelling profiles.

Figure II-11. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from Blind Canyon high volatile bituminous coal.

Figure II-12. Difference DSC thermogram as well as profiles of solvent swelling ratio and weight loss obtained at 8°C/min from DECS-17 (PSOC-1554) Blind Canyon seam coal. Solvent swelling times are indicated beside the swelling profiles.

Figure II-13. Difference DSC thermograms (1st-2nd) illustrating the shift of transition temperatures with heating rate.

Figure II-14. Effect of heating rate on the transition temperature.

Figure II-15. Comparison of difference DSC thermograms obtained at 8°C/min between dried and pyridine-swelled Pittsburgh No. 8 coals.

Figure II-16. DSC thermograms obtained at 10°C/min for two pyridine Soxhlet extracted high-rank bituminous coals. Dotted lines indicate transition temperatures observed in as-received coals at 10°C/min.

Figure II-17. DSC thermograms obtained at 10°C/min for differently pretreated samples, illustrating the relaxed coal structure already at room temperature in CS₂/pyridine (1:1 v/v) swelled Upper Freeport Coal.

Figure II-18. Changes of volumetric swelling ratio by mixed solvents of CS₂ and pyridine for Upper Freeport coal.

III. Synergistic Effects of Solvents on Structural Changes in Coal

III.1. The Basis of the Unusual Efficacy of CS₂ containing Solvent Mixtures

III.1.1. Introduction

High-rank coals (>86 %C daf) have been known to exhibit fundamentally different response characteristics to heat and solvent treatments than lower-rank coals (< 86 %C daf). Sakurovs et al.[1] reported that heat is more effective than pyridine for creating mobility in coal structure, for coals of 86-90 %C daf. Also Iino et al.[2] showed that extraction yields using solvent mixtures of CS₂/N-methyl-2-pyrrolidinone(NMP) (1:1 v/v) increase with carbon content up to 86 %C daf and then falls rapidly with further increase in carbon content.

High-rank coals do not significantly swell in pyridine, while most lower-rank coals show a substantial amount of swelling in that solvent. However, some combinations of solvents, especially with CS₂, yield for the higher-rank coals similar swelling ratios as can be obtained in lower-rank coals. The work of Iino et al.[2-4] is especially noteworthy, since they first reported the benefit of mixing CS₂ (which is a known good solvent for fats, resins, and rubbers) to several solvents (i.e., pyridine, dimethylsulfoxide, dimethylformamide, dimethylacetoamide, NMP) in enhancing extraction yield and volumetric swelling of coal, particularly for coals of around 86 %C daf.

It has also been demonstrated that the structure of high-rank bituminous coals can be thermally loosened, to yield high volumetric swelling ratios in pyridine, when the coals are heated to above 350°C (see Chapter II) [5,6]. These swelling ratios are similar to those which can be obtained at room temperature in mixtures of CS₂/pyridine, CS₂/dimethylsulfoxide, or CS₂/dimethylformamide as will be shown in this paper.

In order to understand the underlying structural changes caused both by mixed solvents and heat, as well as to explore possible effective pre-liquefaction strategies for these high-rank bituminous coals, two coals, viz., Upper Freeport (mvb) and Pocahontas No. 3 (lvb), were studied using the differential scanning calorimetry (DSC) and solvent swelling techniques described in the previous chapter.

III.1.2. Experimental

Aliquots of the coal samples were obtained from the Argonne National Laboratory - Premium Coal Sample Program. For the purposes of this section, only two samples will be considered - Upper

Freeport (-100 mesh), and Pocahontas No. 3 (-20 mesh) coals. They were used as-received. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [7].

Differential Scanning Calorimetry

Just as in the previous chapter, a DuPont 2910 DSC system with a liquid nitrogen cooling accessory (LNCA-II) was employed in this study. The sample cell was operated under a nitrogen flow rate of 90 ml/min in order to keep the cell free of oxygen during measurement. Aluminum sample pans were used in an unsealed mode. This was done by just pushing down the top sample pan cover gently onto the bottom pan containing the coal. Samples were heated from 30°C at 8 °C/min or 10 °C/min. Typically 6-9 mg of sample was used in an experiment. Cooling of the cell between consecutive heating scans normally involved air convection.

Solvent Swelling

Coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm high) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again, the swollen coal height measured, and the solvent replaced with clean solvent. This assured that the concentration of extractable was not so high as to interfere with the measurement.

Samples (22-28 mg) for solvent swelling were prepared in the DSC at a heating rate of 8 °C/min under a nitrogen flowrate of 90 ml/min. After reaching the desired temperature, each sample was cooled immediately by contacting the bottom of the sample pan with ice or cold water. Swelling solvents employed were all reagent grade and were used without any further purification.

Sample Pretreatment

In order to determine the main parameters governing the relaxation of coal structure, several treatment were performed before subjecting the samples to DSC or solvent swelling. These include preswelling by solvent, pyridine Soxhlet extraction, acetylation, and heat treatment. Solvent preswelling was performed in two ways. One method involved swelling coal samples in the constant diameter glass tubes, which were used in the normal swelling experiments described earlier. The swelling was performed in excess solvent at room temperature for about 3-4 days with frequent replacement of extracts with fresh solvent. The samples were subsequently dried under vacuum (<

5×10^{-5} torr) at room temperature for about two days.

Another solvent pretreatment involved Soxhlet extraction of samples with pyridine for about two days, until the color of pyridine in the extraction tube indicated no further extraction. Then the sample was washed with deionized water, filtered using a water aspirator, and dried under vacuum ($< 5 \times 10^{-5}$ torr) at room temperature for about two days. Thus in the first case the samples were swelled but not exhaustively extracted, whereas in the second case the samples were exhaustively extracted (as well as presumably being fully swelled).

Acetylation of hydroxyls was accomplished by mixing coal with excess pyridine and excess acetic anhydride at room temperature for about three days. The excess acetic anhydride was then destroyed by reaction with water, while excess pyridine was removed by washing the sample with water. The acetylated sample was subsequently dried under vacuum at room temperature for about two days.

III.1.3. Result and Discussion

Figures II-6 and II-7 showed the difference DSC spectra, solvent swelling ratios in pyridine and tetrahydrofuran (THF), and pyrolytic mass loss for the Upper Freeport and Pocahontas No. 3 coals. The key aspects of these results will be resummarized here. The mass loss and DSC endotherms at around 100°C , in both coals, show the loss of moisture (around 1% in each). The significant features of the data are seen at temperatures above 100°C .

The solvent swellabilities of the raw Upper Freeport and Pocahontas No. 3 samples are seen to be very low, prior to heat treatment. Both exhibit a volumetric swelling ratio of roughly 1.1 in pyridine, prior to heat treatment. As discussed earlier [Chapter II and 5,6], heat treatment above a certain temperature appears to irreversibly "relax" the coal structure, such that both swellability in pyridine and THF is greatly enhanced, as is clearly visible in Figures II-6 and II-7. The temperature at which solvent swellability first increases is around 300°C in both the Upper Freeport coal and the Pocahontas No. 3 coal. From the DSC results, the peak of the endotherms associated with the relaxation occur at about 350°C in the Upper Freeport coal and at about 430°C in the Pocahontas coal.

The endotherms are clearly not ordinary fusion endotherms, since they are irreversible. Any interpretation in terms of an ordinary glass transition can therefore also be ruled out. The endothermic peaks for these coals are similar to "hysteresis" peaks normally occurring just above a glass transition temperature in stressed polymers [8]. Such hysteresis peaks are caused by stress relief of the structure by heat, and quite often observed in amorphous polymers, e.g., epoxies, polycarbonate, polystyrene.

What appears to support the view that the peaks are associated with a physical process is that the relaxation could be induced at room temperature, in one of the coals, by using the proper solvents. It has been noted [2-4] that higher rank bituminous coals show a remarkably high degree of extractability and swellability in mixtures of certain solvents with CS_2 . In testing with a pyridine/ CS_2 mixture, Upper Freeport coal shows a high degree of *room temperature* swellability, as illustrated in Figure II-18. Since there is no need to heat treat the coal to achieve significant swellability, this suggests that a physical relaxation of the structure is all that is involved. Since there is a maximum in swelling ratio for the 1:1 by volume mixture of pyridine and CS_2 the effect is unlikely to involve a chemical reaction, since both solvents are in large excess.

Finally, the fact that the CS_2 /pyridine mixture relaxes the coal structure in a manner similar to heat, is established in Figure II-17. Treating the coal with CS_2 alone, pyridine alone, or chloroform/pyridine mixtures leaves intact the DSC peak that corresponds to the relaxation of the structure. The Upper Freeport coal treated in CS_2 /pyridine, however, no longer shows a relaxation event at 350°C . The CS_2 /pyridine mixture is not nearly as effective a swelling agent for Pocahontas No. 3 coal as for Upper Freeport coal. This is confirmed by the DSC which still records a significant relaxation event for the previously pyridine/ CS_2 treated Pocahontas No. 3 coal (see Figure II-17). Apparently this specific solvent combination is only effective for a certain range of ranks. This is consistent with the observations of Iino et al.[3].

The Basis of CS_2 Mixture Efficacy

There is nothing particularly unique about the choice of pyridine in mixture with CS_2 . As Iino et al. earlier showed [2,3], NMP/ CS_2 mixtures are also effective. We have established, as Iino et al. noted, that CS_2 /dimethylsulfoxide(DMSO) and CS_2 /dimethylformamide are also effective mixtures (see Table III-1). Thus the solvent pair need not even include a nitrogen base, since DMSO is not.

All the effective solvents in CS_2 mixtures are, however, fairly good electron donors. The electron donor strength can be measured by the so-called Donor Number of Gutmann [12], and some typical values for the solvents of interest are given in Table III-2, which will be discussed below. An indication of the electron acceptor capability [12] and solubility parameters of some of the solvents is provided in Tables III-1 and III-2 as well.

Combinations of pyridine with solvents having similar solubility parameter as CS_2 are seen in Table III-1 to indicate that this widely used solvent characterization parameter does not explain the efficacy of the carbon disulfide. There is a more specific property of the CS_2 involved. It should also be recalled that Figure II-18 and Table III-2 show that the CS_2 without pyridine or another electron donor present, is ineffective. Table III-1 and Table III-2 suggest that the materials that are effective in mixtures with CS_2 are all not only good electron donors, but are also not strong electron acceptors.

This might imply that it is the CS₂ itself as an electron acceptor, acting together with a strong electron donor, that imparts unique properties to these solvent pairs.

It is, however, important to note from Table III-1 that not all mixtures of a strong electron donor with CS₂ are effective. Note that the mixture of CS₂ with the very strong base, n-butylamine, is ineffective as a swelling agent. The Donor Number of n-butylamine has not been reported, but would likely be greater than that of pyridine.

Another strategy involved examining solvents of various acceptor strengths together with pyridine. Of course, the other solvent pairs tested did not include particularly strong electron acceptors (strong acids) together with pyridine, since these combinations would have presented an experimental problem. Still, the methanol/pyridine mixture of Table III-1, showed that a high acceptor number solvent combined with a high donor number solvent does not assure high swelling either. Thus the characterization of solvents in terms of the very general electron donor and acceptor properties appears to be incapable of describing the efficacy of these very special solvent mixtures. As of this writing, there is no other hypothesis as to the origin of the efficacy of these solvent pairs.

Not surprisingly, pretreatment of the Upper Freeport coal by pyridine extraction has little effect on the ability of the CS₂/pyridine mixtures to swell the coal (see Table III-1). Since pyridine alone is ineffective as a swelling and extraction agent for this coal, it cannot be expected that the subsequent swelling in the more effective swelling mixture should be affected. The structure of the coal is unaltered by ordinary pyridine extraction-type treatment, but immediately opens up upon exposure to pyridine/CS₂/

Pretreatment of the coal by acetylation only modestly reduces its swelling in CS₂/pyridine mixtures (Table III-1). This means that the network structure is not significantly altered by the acetylation. The acetylation should act on the hydroxyl groups, among the most polar groups remaining in these higher rank coals, converting them to esters, which cannot as easily form strong hydrogen bonding linkages. As Table III-2 shows, however, acetylation does not significantly enhance swellability in either pure CS₂ or pyridine. This shows that the structure is itself not relaxed by acetylation, which in turn strongly suggests that the nature of the links holding the structure together is not simple polar-group hydrogen bonding interactions. It is not surprising that this is the result, since otherwise pyridine would, in all likelihood, be an effective swelling solvent by itself.

The above results also reduce concerns about the efficacy of the CS₂/pyridine mixtures being due to xanthate-forming reactions involving the hydroxyls and CS₂ [9-11]. Since the hydroxyls are removed by acetylation and the structure does not relax, this means that this mechanism of action is unlikely. Again, the results of Figure II-18 must also be interpreted as support for this view. Again, the CS₂/electron donor systems appear to work by some physical mechanism.

Further to the above conclusion, other experiments were performed in which there was

sequential, rather than simultaneous, exposure to the two solvents. The coal was pretreated in CS_2 , followed by removal of the CS_2 , by evaporation, and then subjected to pyridine swelling. The sequence resulted in pyridine swelling comparable to that of the raw untreated coal (see Table III-2). Reversing the order of sequential exposure was also not effective (again see Table III-2). These results further showed the importance of the *interaction* of pyridine and CS_2 .

After the coal is "relaxed" by exposure to CS_2 /pyridine mixtures, it is much more swellable by both pyridine and CS_2 (see Table III-2). The fact that the apparent swellability in these solvents is not as great as when relaxation is induced by thermal treatment to 350°C , is also seen in Table III-2. This is probably because once swollen in pyridine/ CS_2 mixture, it is difficult to fully remove all of the pyridine from the coal by vacuum drying. Thus the coal pretreated in pyridine/ CS_2 is already in a partially swollen state, due to the irreversibly bound pyridine. Heating a CS_2 /pyridine swollen coal to 350°C results in a higher subsequent pyridine swellability (relative to the vacuum dried CS_2 /pyridine swelled coal, see Table III-2), because the pyridine is fully lost upon heating.

All attempts to relax the Pocahontas No. 3 coal with solvents or solvent mixtures failed. The results are given in Table III-3. As was shown in Figure II-18, the relaxation endotherm was always present, even if the coal was pretreated with the same pyridine/ CS_2 mixture that was effective for relaxing the Upper Freeport coal. These results are consistent with the "window" of efficacy that has been identified for this class of mixed solvents [2-4]. The Pocahontas coal is of higher rank than what has been identified for efficacy. As is seen clearly from Table III-3, thermal relaxation is very effective.

III.1.4. Conclusions

- Two high-rank bituminous (Upper Freeport: mvb, Pocahontas No. 3: lvb) coals exhibit a distinct endothermic DSC peak corresponding to the irreversible relaxation of the structure. The relaxation appears to involve physical processes rather than chemical reaction processes.
- Even strong solvents cannot swell the structure of high-rank coals more than ten percent at low temperatures ($<250^\circ\text{C}$) whereas heat treatment, and in certain cases, solvent swelling by mixtures of solvents (e.g., pyridine with CS_2) can relax the structure, enhancing the swellability of coal in ordinary pure solvents significantly.
- The origin of the efficacy of mixed solvents consisting of CS_2 and certain electron donor solvents (e.g., pyridine, dimethylsulfoxide, dimethylformamide) appears to be physical as opposed to chemical. These mixtures appear to relax certain structures that do not involve hydrogen bonding by hydroxyls. It is therefore likely that the mixtures are effective on aromatic-aromatic interactions

of some kind.

-The particular characteristics that determine an "effective" solvent pair remain unestablished. The reasons why solvent pairs effective for some coals are not effective for others, is also unclear.

IV.1.5. References

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III.2. Swelling Behavior in Other Mixtures of Solvents

III.2.1. Introduction

Coal liquefaction schemes will become more economically attractive as less severe liquefaction conditions (in terms of temperature and pressure) can be employed. This may become more likely if enhanced accessibility of catalysts and/or donor solvents can be achieved by modifying the original macromolecular structure of coal. Recently, there have been reported beneficial effects of preliquefaction treatments by solvents [1,2], steam [3], preheating [4], mild hydrogenation [5], or mild alkylation [6]. The main objective of all of these pretreatments is to modify the starting coal structure in a way that leads to higher liquid yields and enhanced liquid quality in the subsequent

liquefaction processes. Although direct modifications of coal structure are possible (for example, by mild alkylation) the most economical ways of pretreating coal appear to involve appropriate thermal treatment and/or contact with inexpensive solvents. These generally seek to meet the main objective by modifying the accessibility of coal or by reducing initial crosslinking. Accessibility is important, since it is necessary that catalysts and/or hydrogenating agents can gain access into the bulk of the coal, so as to react more readily with the coal.

In this section, the ability of a previously little investigated class of solvents to swell coal was examined in connection with the issue of improved accessibility. It has been suggested that alkyl aromatics might be effective carriers for certain types of liquefaction catalysts. These catalysts can be prepared in highly dispersed form, and it was reasoned that if they are soluble in a solvent that also was effective at swelling the coal, good dispersion of the catalysts could be achieved in the coal. A candidate class of solvents is alkyl aromatics, and in particular, the Project Manager suggested the investigation of short-chain alkyl naphthalenes which are liquid at room temperature. A study was thus initiated on how effective these solvents are at swelling a coal representative of those considered candidates for liquefaction. Utah Blind Canyon bituminous coal was selected for this study.

Initially there were concerns about the possibility that these solvents might be effective for non-specific solvation of the coal, but ineffective for disrupting strong intra-coal hydrogen bonding. This led to work with mixtures of the alkyl naphthalenes with n-alkanols. The latter class of solvents should be more effective for solvation of hydrogen bonded groups.

III.2.2. Experimental

The Utah Blind Canyon coal (-20 mesh) obtained from the Argonne National Laboratory - Premium Coal Sample Program was used as-received. Detailed petrographic, chemical, and physical analysis data on the Blind Canyon coal can be found elsewhere [7].

Solvent Swelling

Coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm high) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again (7500 rpm for 3 min), the swollen coal height measured, and the solvent replaced with the clean solvent. This assured that the concentration of extractable was not so high as to interfere with the measurement. Swelling solvents

employed were all reagent grade and were used without any further purification.

III.2.3. Results and Discussion

Alkyl naphthalenes as swelling agents

The Blind Canyon coal is known to have a mainly aromatic carbon character, but it also has a significant aliphatic character, since it contains 11 wt% liptinite (mostly as resinite). Three alkyl naphthalenes, i.e., 1-methylnaphthalene, 1-ethylnaphthalene, and 2-ethylnaphthalene, were studied. Since alkyl naphthalenes do not contain any polar functional groups, involving nitrogen or oxygen, they can be classified as nonspecifically interacting solvents, implying that relatively moderate or negligible swelling by these solvents might be expected. On the other hand, creosote oil (typical creosote oil contains 10 wt% naphthalene, 3 wt% 1-methylnaphthalene, 8 wt% 2-methylnaphthalene, 17 wt% anthracene/phenanthrene) has been known as one of the more effective solvents for coal liquefaction [8]. During World War II, Germany used this type of heavy oil (boiling point above 350°C) for the Pott-Broche liquefaction process [9]. Accordingly, significant solubilization of some coals near the boiling temperature of alkyl naphthalenes can be expected.

The swelling results for Blind Canyon coal in alkyl naphthalenes, alkyl-naphthalene/alcohol mixtures and pure alcohols are given in Table III-4 and shown graphically in Figures III-1 and III-2. Pure alkyl-naphthalene solvents produce modest (3-12 vol%) swelling at room temperature. An increase in swelling was observed with increase in the swelling temperature (see Figure III-1). Note that the swelling behavior at 200°C was monitored only during the initial 30 min because vigorous bubbling behavior developed inside the swelling glass tube in 1-methylnaphthalene solvent at 200°C. At this temperature, the coal sample tends to overflow out of the tube. This temperature is below the boiling point of pure 1-methylnaphthalene (241.5°C), so the actual mechanism of bubble nucleation is unclear. It might involve highly non-ideal solution behavior, or the liberation of gases from the coal by any of a number of mechanisms.

Figure III-2 demonstrates the "synergistic" effect of adding alcohols to 1-methylnaphthalene. Pure alcohols swell the coal by 6-15 wt% at room temperature, with relatively minor effect of the carbon-chain length. Pure alkyl-naphthalenes also show a modest 3-12 vol% swelling at room temperature.

Substituting 50% of 1-methylnaphthalene by methanol dramatically enhances the swelling ratio. As Figure III-2 shows, there is a noticeable dependence of carbon chainlength in alkanols on the swelling ratio in 1-methylnaphthalene/alkanol mixtures. According to some recent results [10,11], carbon-chain length has various effects on swelling, depending on the solvent structure. For example, an increase of chain length in alkyl-amines [10,11] enhances swelling, while a decrease in

swelling ratio was observed for alkyl-aniline with increasing amounts of alkyl substitutes [11]. The variation in swelling ratio was observed to be small with chainlength in alcohols [10]. Consistent with earlier reported results, we observed little effect of alkanol chain length on swelling ratio in pure alcohols.

These results clearly demonstrate that an increase in temperature, as well as addition of alcohols to alkyl-naphthalenes, increases the swelling ratio of Blind Canyon coal significantly.

Mixtures of solvents as swelling agents

In the above section, a significant increase in swellability of Blind Canyon coal was noted upon addition of methanol to 1-methylnaphthalene. More tests with different solvents, similar in terms of functional groups, were performed on Blind Canyon coal. Figure III-3 illustrates the results of swelling ratio in toluene, methanol/toluene (1:1 v/v), and phenol/1-methylnaphthalene (1:1 w/w). Blind Canyon coal in toluene exhibited similar swelling ratio (1.12) to that in methanol (1.15). However, upon adding equal proportion of each solvent, a swelling ratio of 1.51 was obtained. Similarly, the equal weight solution of phenol and 1-methylnaphthalene resulted in a swelling ratio of 1.46 after 9 days, although the rate of swelling in this case was rather slower compared to the methanol/toluene mixture. In comparison, equal volume methanol/1-methylnaphthalene solution yielded a swelling ratio of 1.75 for the same coal.

Since the observed synergistic effects of solvent mixtures on swelling ratio were significant, we performed further experiments to probe the causes behind the effect. Figure III-4 shows the effect of adding methanol/1-methylnaphthalene alternately on the swelling ratio in Blind Canyon coal. Initially methanol yielded a slightly higher swelling ratio than in 1-methylnaphthalene (1.17 vs. 1.10), after which adding 1-methylnaphthalene exhibited a dramatic increase in swelling ratio and in swelling rate. Although both solvent alternation routes appear to reach the same final swelling ratio eventually, adding 1-methylnaphthalene after swelling coal by methanol is the faster way to reach the final swelling ratio in methanol/1-methylnaphthalene mixtures. This result indicates that methanol probably causes a relaxation in the coal structure and allows 1-methylnaphthalene to more easily enter the network afterwards.

A recent report by Miller et al.[12] suggested the addition of methanol / HCl (100:1 w/w) to coal causes a mild alkylation process (ca. 0.2 methyl groups added / 100 carbon atoms) on coal and they observed an enhanced liquid yields in subsequent liquefaction (350°C, under H₂, with 9,10 - dihydrophenanthrene as a hydrogen donor vehicle). They inferred from Photoacoustic FTIR results on these methanol / HCl treated coals that alcohols are preferentially alkylating coal at oxygen sites, rather than carbon sites, in the coal structure. Sharma et al.[13] have reported that alkylation with n-butanol and dry HCl gas enhanced the extractability of a bituminous coal in quinoline. Alkylation

has been known to be a beneficial pretreatment for gasification and for liquefaction [13-15]. The efficacy of methanol in promoting access of 1-methylnaphthalene to the coal structure might be then thought to be related to this kind of chemistry. It is, however, doubtful that this is the case, particularly in view of our sequential exposure results.

Methanol probably induces a loosening of coal structure by disrupting hydrogen bonds in a physical process. The possibility of producing an intermediate that can react with coal, even at room temperature, when solvents are added together cannot be ruled out. In this case, however, the 1-methylnaphthalene is probably not a strong enough acid to promote such esterification reactions. In any case, the sequential exposure experiments suggest that chemical reaction explanations, requiring both agents to be present simultaneously, are not valid. Instead the methanol merely substitutes for intracoal hydrogen bonding interactions, and thus effectively mobilizing the chains.

Mixtures of methanol and 1-methylnaphthalene when applied to Blind Canyon coal, produce immiscible two phase mixtures after few days at room temperature. Preliminary results indicate that the 1-methylnaphthalene phase contain most of the extracted oily coal liquids whereas methanol phase contains many unknown compounds which show rather vigorous mixing with water (probably polar compounds [16]).

III.2.4. Conclusions

An increase in temperature as well as addition of short-chain alcohols (e.g., methanol, ethanol) to alkyl-naphthalene appears to enhance the swelling ratio of Blind Canyon coal significantly. The reason behind this behavior appears that short-chain alcohols cause a relaxation in the coal structure by inducing the disruption of hydrogen bonds, even at room temperature, and subsequently allowing naphthalenes penetrate more easily to the coal network structure.

Moreover, solvent mixtures of methanol/toluene (1:1 v/v) and phenol/1-methylnaphthalene (1:1 v/v) yielded, in Blind Canyon coal, a comparable final swelling ratio of ca. 1.5 compared to the final swelling ratio of ca. 1.7 in the solvent mixture of methanol/1-methylnaphthalene.

There is a noticeable dependence of carbon chainlength in alkanols on the swelling ratio of Blind Canyon coal in 1-methylnaphthalene/alkanol mixtures, while pure alkanols exhibit little effect by carbon chainlength on swelling ratios of Blind Canyon coal .

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Table III-1. Volumetric Swelling Ratio by Mixed Solvents (1:1 v/v) for Upper Freeport Medium Volatile Bituminous Coal

Pretreatment	Solvent mixture (1:1 v/v)	Solvent characteristics			Q**
		Solvent	Acceptor Number	δ (H)*	
None	CS ₂ /pyridine	pyridine	14.2	10.4	1.95
	CS ₂ /dimethylsulfoxide	dimethylsulfoxide	19.3	12.8	1.75
	CS ₂ /dimethylformamide	dimethylformamide	16.0	11.5	1.92
	CS ₂ /n-butylamine	n-butylamine	-	-	1.21
	pyridine/water	water	-	9.4	1.08
	pyridine/methanol	methanol	41.3	12.9	1.09
	pyridine/chlorobenzene	chlorobenzene	-	9.5	1.12
	pyridine/chloroform	chloroform	-	9.3	1.13
	pyridine/methylene chloride	methylene chloride	-	9.7	1.14
	pyridine/nitroethane	nitroethane	-	11.1	1.09
Pyridine Soxhlet extracted	CS ₂ /pyridine	CS ₂	-	10.0	1.83
Acetylated	CS ₂ /pyridine	CS ₂	-	10.0	1.71

* δ : solubility parameter in Hildebrand which is equivalent to cal^{1/2}cm^{-3/2}

**Q: volumetric swelling ratio

Table III-2. Solvent Swelling Results for Upper Freeport Medium Volatile Bituminous Coal

Pretreatment	Solvent	Solvent Properties				Q*	Swelling number** ($\times 10^3$)
		Donor No.	Acceptor No.	$\delta(H)^\dagger$	Molar Vol.(cc/mol)		
None	pyridine	33.1	14.2	10.4	80.9	1.14	1.73
	CS ₂	-	-	10.0	60.3	1.08	1.33
	n-butylamine	-	-	-	99.8	1.12	1.20
	THF	20.0	8.0	9.1	81.1	1.08	0.99
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.09	1.27
	dimethylformamide	26.6	16.0	11.5	77.4	1.08	1.03
CS ₂ swelled	pyridine	33.1	14.2	10.4	80.9	1.12	1.48
Pyridine Soxhlet extracted	pyridine	33.1	14.2	10.4	80.9	1.19	2.35
	CS ₂	-	-	10.0	60.3	1.07	1.16
CS ₂ /pyridine (1:1 v/v) swelled	pyridine	33.1	14.2	10.4	80.9	1.40	4.94
	CS ₂	-	-	10.0	60.3	1.30	4.97
Heated under N ₂ up to 350°C	THF	20.0	8.0	9.1	81.1	1.82	10.11
	pyridine	33.1	14.2	10.4	80.9	2.17	14.46
	CS ₂	-	-	10.0	60.3	1.50	8.29
	dimethylsulfoxide	29.8	19.3	12.8	71.0	1.49	6.90
	chlorobenzene	-	-	9.5	101.7	1.40	3.93
CS ₂ /pyridine swelled and heated up to 350°C	pyridine	33.1	14.2	10.4	80.9	1.83	10.26
Acetylated	pyridine	33.1	14.2	10.4	80.9	1.10	1.24
	CS ₂	-	-	10.0	60.3	1.06	0.99

$^\dagger \delta$: solubility parameter in Hildebrand which is equivalent to $\text{cal}^{1/2}\text{cm}^{-3/2}$ *Q: volumetric swelling ratio ** $(Q-1)/\text{molar volume}$

Table III-3. Solvent Swelling Results for Pocahontas No. 3 Low Volatile Bituminous Coal

<u>Pretreatment</u>	<u>Solvent</u>	<u>O</u>	<u>Swelling number ($\times 10^3$)</u>
None	pyridine	1.12	1.48
	CS ₂	1.16	2.65
	THF	1.10	1.23
	CS ₂ /pyridine (1:1 v/v)	1.16	-
CS ₂ swelled	pyridine	1.13	1.61
Heated under N ₂ up to 450°C	THF	1.65	8.01
	pyridine	1.72	8.90

Table III-4. Swelling Ratios of Blind Canyon Coal in Several Solvents

Solvent	Temperature (°C)	Swelling Time (hr)	Swelling Ratio
<u>Naphthalenes</u>			
1-ethylnaphthalene	25	55	1.08
2-ethylnaphthalene	25	55	1.12
1-methylnaphthalene	25	40	1.10
1-methylnaphthalene	100	49	1.17
1-methylnaphthalene	200	0.5	1.24
<u>Naphthalenes/Alcohols</u> (1:1 v/v)			
1-ethylnaphthalene/methanol	25	46.5	1.37
2-ethylnaphthalene/methanol	25	46.5	1.41
1-methylnaphthalene/methanol	25	47.5	1.75
1-methylnaphthalene/ethanol	25	47.5	1.45
1-methylnaphthalene/1-propanol	25	47.5	1.29
1-methylnaphthalene/n-butyl alcohol	25	47.5	1.25
1-methylnaphthalene/hexyl alcohol	25	47.5	1.18
<u>Alcohols</u>			
methanol	25	41	1.15
ethanol	25	47.5	1.14
1-propanol	25	47.5	1.06
n-butyl alcohol	25	47.5	1.12
hexyl alcohol	25	47.5	1.12

Figure III-1. Effect of temperature on the swelling ratio of Blind Canyon coal in 1-methylnaphthalene. Note that swelling time at 200°C was 30 min whereas those at 25°C and 100°C were 40 hours and 49 hours, respectively.

Figure III-2. Change of the swelling ratio against carbon-chain length of alcohols in Blind Canyon coal.

Figure III-3. Change of swelling ratio with time for undried Blind Canyon coal (-20 mesh) at room temperature.

Figure III-4. Effect of changing solvents on swelling ratio for undried Blind Canyon coal (-20 mesh) at room temperature. MeOH and 1-mN denote methanol and 1-methylnaphthalene, respectively. Changes of solvent occur at the times indicated by the dashed vertical line. Change of solvent involves a simple decanting of the old solvent and a quick replacement with the new. No attempt was made to completely remove the old solvent; what is inside of the coal particles remains.

IV. Oxidation-Induced Structural Changes in Argonne Coals Studied by Differential Scanning Calorimetry and Solvent Swelling

IV.1. Introduction

It is widely known that oxidation/weathering has a profound effect on many important coal properties such as coking characteristics, slurry pH, flotability, tar yield, extractability, etc., as well as on coal utilization processes such as combustion, pyrolysis, gasification and liquefaction [1-5]. In addition, there have been many reports as to the high sensitivity of coal structure to aerial oxidation, especially in steam-pretreated coal. For example, Graff and Brandes [6] reported the decrease of liquid yield from 61% to 25% after exposing steam-treated Illinois No. 6 coal to air at room temperature for just two minutes. Because of these reports that have established the extreme vulnerability of coal structure to air, even at room temperature, major accommodations, to prevent air contact, have ensued in many studies on coal. The basic question here is how air causes change in coal structure, even at room temperature in such a short time (minutes). At higher temperatures, e.g., at temperatures which can cause the thermal degradation of coal structure, the sensitivity of the response of oxidized coal to heat or solvents has been well established, and can be easily understood, since even small amounts of oxidized functional groups might act as initiators of chain processes that can magnify the total response.

This chapter is concerned with the effect of aerial oxidation on the solvent swelling ratio of several pretreated coal samples (i.e., water-treated, heat-treated). Our studies [7,8] have clearly illustrated that heating under an inert environment renders coal structure relaxed in such a way that solvent and/or catalysts for liquefaction can be efficiently employed or incorporated into coal structure. The question that we pose here is whether the effects of oxidation make themselves known at low temperatures, in terms of changes in macromolecular structure, that might mitigate some pretreatment effects.

IV.2. Experimental

Aliquots of three coal samples, obtained from the Argonne National Laboratory - Premium Coal Sample Program, were analyzed by differential scanning calorimetry (DSC) and solvent swelling techniques. These samples included Upper Freeport (-100 mesh), Pittsburgh No. 8 (-100 mesh), and Illinois No. 6 (-20 mesh) coals. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [9]. Detailed experimental procedures for DSC and solvent swelling can be also found elsewhere [8,10]. One point should be carefully noted with respect to the latter measurements, the supernatant swelling solvent was replaced every day. This is important,

because the coal is effectively solvent extracted by this procedure.

Aerial oxidation was performed in two ways. One method involved oxidizing the coal sample in a tube furnace at 115°C or 120°C for one day under room air. Another method involved oxidizing the sample inside the DSC at 120°C for 15 hr with dry air flow of 100 ml/min over the aluminum pan containing the coal sample. Which method was used in any particular experiment will be cited below.

IV.3. Results and Discussion

Effects of Pre-Oxidation on Thermal Relaxation Behavior in a High Rank Coal

We examined the effect of aerial oxidation on solvent swellability by comparing as-received and oxidized coals. For this purpose, Upper Freeport medium volatile bituminous coal was oxidized at 120°C in the tube furnace for one day, under room air. The resulting oxidized coal, as well as as-received coal, were heat-treated inside the DSC under a continuous flow of nitrogen up to a specified temperature, followed by quench-cooling and pyridine swelling. In this way, the effects of pre-oxidation on thermally induced relaxation processes could be studied.

The results of the above experiments are illustrated in Figure IV-1, in which pyridine swellability is shown as a function of the post-oxidative heat-treatment temperature. It is noteworthy that the aerial oxidation led to generally higher final pyridine swelling values than the corresponding values in the as-received coal. We attribute the increase to the formation of new oxygenated functional groups on the surface of the coal. These groups provided additional polar groups that could strongly interact with pyridine, thus changing the thermodynamics of the coal-solvent interaction.

The oxidation in particular results in a considerable increase in swellability prior to thermal relaxation of the coal's structure (below 250°C). The thermodynamically favorable interaction of the new oxygen functional groups and pyridine in all probability overcomes some of the non-covalent interactions that are thermally labile at higher temperatures (though many are preserved). The structure of the coal must swell to accommodate the pyridine molecules that so strongly interact with the polar groups. The enthalpic penalty of breaking the non-covalent interactions (visible in the DSC spectra) is more than compensated for by the favorable interaction of the pyridine and coal. In addition, the very slow nature of the swelling in this low temperature regime (see Figure IV-1) also favors this explanation over an alternative hypothesis based upon the oxidation itself destroying some of the non-covalent interactions.

Once the thermally labile interactions are destroyed by heating the coal to over 300°C, the time dependence of swelling behavior is seen to change significantly; higher swelling is seen in shorter times. This is because the oxidized coal becomes quite extractable after thermal relaxation, just as in

the case when it is unoxidized (see Figure IV-1). The decrease in swellability with time is an artifact due to extraction of some of the coal. Temperatures above 350°C have not been explored in the case of the oxidized coal because the extraction already starts to become quite significant in the sample obtained at 350°C, and reliable swelling results became difficult to obtain.

The Effects of Oxidation on Swellability of Relaxed Coals

The main concern of this chapter is with what kind of sensitivity solvent swelling results have towards oxidation. The issue was explored with both as-received and heat-pretreated (relaxed) samples. The concern with the heat treated samples arises from two considerations. First, if solvent swelling is to be used as a measure of structural relaxation, there was a concern as to how carefully laboratory samples might have to be handled with respect to potential oxidation. Second, if thermal pretreatments are to be of practical interest in liquefaction schemes, there is interest in whether the pretreatments can or cannot be carried out in systems in which exposure to oxidizing species is tolerable.

Two coals, i.e., Upper Freeport and Pittsburgh No. 8 coals, were heat-treated to fully relax their structures. In the case of the Upper Freeport coal, this involved heating to 350°C, and in the case of the Pittsburgh No. 8 coal, to 300°C. These temperatures were chosen based upon the data presented in Chapter II [also 7,8,10]. The samples were preheated under flowing nitrogen, in order to exclude oxygen at this stage.

The preheating in this case was followed by aerial oxidation inside the DSC at 120°C for 15 hr with an air flowrate of 100 ml/min. Note again that in this case heat treatment *precedes* oxidation, the opposite of the situation in the experiments of Figure IV-1. The differences in swellability attributable to aerial oxidation were measured in pyridine and the results are shown in Figure IV- 2.

Figure IV-2 reveals several interesting results. While heat-treated-plus-oxidized Upper Freeport coal exhibited *higher* pyridine swellability compared to heat-treated-only coal, the opposite was observed in Pittsburgh No. 8 coal. Also, it appears that in the case of the Upper Freeport coal, short-time values of swelling ratio were quite similar, irrespective of oxidation, whereas the Pittsburgh No. 8 samples quickly show a difference. However, appreciable differences in pyridine swelling ratios, attributable to oxidation, start to appear with further swelling time in both the Upper Freeport and Pittsburgh coals. The apparent decrease of the pyridine swelling ratio with time in the results of Figure IV-2 is again caused by extraction of mass from the coals, as noted earlier.

The increase in swellability with oxidation of the Upper Freeport coal is modest at short swelling times. This is not inconsistent with the data of Figure IV-1. The structure is already fully relaxed by heat treatment, and the addition of oxygen functional groups does not provide pyridine an extra

"handle" for relaxing the structure, as it does in non-heated coals. The actual short-time swelling ratio is quite similar to that for heat treated, non-oxidized coal itself (around 2.22 at 350°C from Figure IV-1, compared to 2.25 for non-oxidized coal in Figure IV-2 and 2.29 for oxidized coal in Figure IV-2).

Since the decrease in apparent swellability with time is attributed to extraction of the coal, it appears that the unoxidized Upper Freeport coal is more extractable than the oxidized; starting from the same values, the unoxidized samples reach lower final apparent swellabilities, meaning that they lose more mass. In the case of the Pittsburgh coal, there is not a clear difference in extractabilities between oxidized and unoxidized.

Because both the oxidized and non-oxidized Upper Freeport samples swell equally readily to their quite comparable maximum values, the later differences in extractability are difficult to understand. The data might appear to indicate that in the oxidized coal, more of the coal matter is somehow only loosely bonded into the insoluble network structure. This binding does not influence the initial swelling of the coal, so this suggests that the coal is not actually more crosslinked (in which case the initial swelling ratio would also be reduced). We do not know the nature of the bonding that keeps the coal from being more extractable, whether it is covalent or non-covalent. There is another possibility to explain the observations, however. It is possible that the oxidized sample is actually more highly crosslinked, and the fact that it has comparable swellability to the unoxidized is a coincidence, resulting from a higher degree of oxidation of the surface, increasing the favorability of interaction with pyridine. Whatever the mechanism, there is evidence of a deleterious effect of 120°C aerial oxidation on the macromolecular structure of this coal, as regards any attempt to break down that structure or solubilize it.

In the case of the Pittsburgh No. 8 sample, oxidation is seen to be generally deleterious to swellability. The Pittsburgh coal has a significant concentration of polar functional groups already, so it does not benefit from added oxygen providing more strong interaction sites for swelling. Note by comparing these results with the results in Figure II-3 that the effects of heat treatment itself on the swellability in pyridine is not great. Reduced swellability therefore appears to be associated with oxidation. From the earliest point on, the curves for oxidized and non-oxidized Pittsburgh No. 8 samples track each other closely, meaning that comparable amounts of extractable are lost from both samples. The effect is not as large as in the Upper Freeport coal. This means that the incremental effect of aerial oxidation is not nearly as significant in the Pittsburgh No. 8 coal as in the Upper Freeport coal. The deleterious effect of oxidation is, however, inarguable.

Figure IV-3 shows the effect of aerial oxidation on THF swelling of heat-treated Pittsburgh No. 8 coal. The coal's structure was relaxed by heat treatment, as is evident from the fast swelling rate for the heat-treated coal compared to as-received coal. This, again, is consistent with the results from

Chapter II. In the case of the heat-treated-then-oxidized samples, no appreciable differences can be noted between THF swelling responses from 5 hour and 15 hour oxidized samples. All these samples swell very rapidly, and to a greater extent, than the untreated samples. After heat treatment, the time for samples to swell to equilibrium in THF is comparable to the time for swelling in pyridine.

We find it curious that in contrast to the results in pyridine, the swellability in THF is not strongly influenced by whether the sample is oxidized or not. Consistent with THF being a poorer solvent for this coal (note the lower swelling ratio compared to pyridine), the THF shows much less evidence of extraction, both by direct visual observation as well as based on the fact that the swelling ratio stays quite constant over long times. So it appears that with a "weaker" solvent, oxidation effects are not as notable because the extractability and swellability are not as great to begin with. This indicates the existence of important non-covalent interactions in the coal, for which pyridine is an effective solvent and THF is not. Moreover, these non-covalent interactions are influenced by oxidation of the structure, since the effectiveness of pyridine is reduced after oxidation of the structure. The obvious candidates for the non-covalent interactions are those involving polar groups (particularly hydroxyls), but other possibilities involving interactions between aromatic units with quinone functionality should not be overlooked.

The mass gain upon oxidation was determined for the Pittsburgh No. 8 sample shown in Figure IV-2. The oxygen uptake (assuming no loss of any material during oxidation) was 1.83 wt%. This corresponds to an addition of 1.1×10^{-3} mol O/g coal, or using a density of 1.3 g/cc for this coal, the oxygen uptake was 1.4×10^{-3} mol O/cc. To help put this figure in perspective, the uptake of pyridine by the coal is initially about 18.8×10^{-3} mol pyridine/cc. Thus there is not a major addition of potential pyridine-holding groups to the coal. The actual loss of pyridine uptake capacity as a result of oxidation is about 0.9×10^{-3} mol pyridine/cc, based on the earliest swelling points. The comparability of the equivalents of oxygen uptake and the loss of pyridine capacity is intriguing, but we cannot ascribe any significance to the comparability of these values at this time.

Figure IV-4 shows data on post-oxidative swelling for Illinois No. 6 coal. In this case, the samples were not heat-pretreated. The reason that heat pretreatment was not conducted is that, as seen in Chapter II, it has very little effect on the swelling behavior, except as temperatures approach those needed for pyrolysis. Additionally, the oxidation in this case was carried out in a tube furnace for 24 hours, at 115°C. The pyridine swellability is not significantly influenced by the oxidation of the samples, except for the fact that the oxidized sample swelled slightly more slowly at the start. On the other hand, the THF swellability was enormously reduced by the oxidation of the sample.

The fact that the pyridine swelling ratio is unaffected by oxidation means that the crosslink structure of the coal is not particularly affected by oxidation. The change in THF swellability can

then only be due to addition of new, strong non-covalent interactions in the coal. This could involve formation of new oxygen functional groups which do not, at this range of temperatures, contribute to covalent crosslinking, but could be involved in crosslinking through polar functional groups. Such crosslinking may or may not be important in the context of a real process environment, since these kinds of non-covalent crosslinks may or may not survive. Clearly in the presence of a good solvent such as pyridine, they would not. Depending upon the processing environment to which the coal is subsequently exposed, the situation might however change further, as will be noted in the next section.

The Effects of Temperature History on Oxygen Added by Oxidation

Figure IV-5 shows the effect of aerial oxidation on the DSC spectra of Upper Freeport coal. To prepare the samples for analysis, the coal was first heat-treated inside DSC up to 350°C. During this treatment, the water evaporation process at around 110°C as well as structural relaxation process around 310-350°C are both clearly visible (see thick-solid line (1) in Figure IV-5). Then the heat-treated coal sample was exposed to an air flow of 100 ml/min inside DSC for 12 hr at 120°C, followed by another two consecutive DSC scans up to 350°C (the first and second scans shown as a solid line (2) and a dotted line (3), respectively). A clear exotherm, extending from 150-230°C with maximum at around 195°C, can be seen in (2). There was an earlier report [11] of an exotherm at around 195°C in Upper Freeport coal, following long exposure to air. The difference DSC (shown as solid line (4) in Figure IV-5) illustrates more clearly the irreversible exotherm that results from the oxidations performed here, and it is quite clearly centered at 195°C. There can be no question that this exotherm represents a rearrangement of oxidation products in the coal, since it is only observed after oxidation.

It has already been concluded in connection with the data of Figure IV-2 that oxidation at 120°C must cause chemical reactions in the structure. The existence of the exothermic peak at 195°C suggests that a different set of oxidation processes can be expected above this temperature. It should also be noted that the search for oxidation effects by DSC can be misleading, if it implies that the peak at 195°C represents the *beginning* of oxygen functional group chemistry. The oxygen may well be already on the surface from a lower temperature, and merely rearrange to a different form at the higher temperature.

The DSC results on oxidized Illinois No.6 and Pittsburgh No.8 coals are shown in Figure IV-6. The difference DSC spectra clearly illustrate the exotherm around 200°C caused by added oxygen. It can be noted that the temperature range of the exothermic peaks is remarkably similar to that observed in the Upper Freeport medium volatile coal (see Figure IV-5). These observations strongly suggest that for the most part, the aerial oxidation process involves certain specific types of chemical

groups, irrespective of coal rank (and pretreatment conditions). The generality of this conclusion is only challenged by the data for Illinois No.6, which show a significant "tailing" of the exotherm to higher temperatures than those seen for the oxidative rearrangements in the other two samples.

Figure IV-7 shows the results of experiments intended to explore the effects of temperature of oxidation upon the conclusion that there is always an exotherm centered near 200°C. In this case, samples of Upper Freeport coal were air-oxidized at temperatures of 60°C and 80°C, in addition to the 120°C that had been explored earlier. The nature of the rearrangement exotherm was found to be a strong function of the previous oxidation temperature. Lower oxidation temperatures led to lower temperatures for the rearrangement exotherm.

It is significant that the exotherms always appear to begin at a temperature that corresponds to the previous oxidation temperature. This makes it clear that the rearrangement reactions actually include an enormous variety of processes, some of which can occur at the actual temperature of oxidation, and others of which are delayed until higher temperatures are reached. The integration of the exotherms also clearly indicates that the higher temperature oxidations created more oxygen-containing groups on the surface. The higher temperature exotherm peak for oxidation at 60°C yielded 3.5 J/g, that for 80°C yielded 4.5 J/g, and that for 120°C yielded 6.8 J/g.

Figure IV-8 shows the results of a TGA analysis of an Upper Freeport sample pre-oxidized at 125°C. Between 150°C and 250°C (the range of temperatures for the main exothermic rearrangement peak), the mass loss under nitrogen is only 0.1%. This means, using the above cited value, that the net heat effect is 6800 J/g mass loss. This is not a very large heat effect. If the main gaseous product were CO₂, then the net heat effect is about 150 J/mol CO₂ released.

Figure IV-9 shows the effect of post-oxidation desorption at the same temperature. The samples were initially oxidized under air, and then the air was replaced by nitrogen, while keeping temperature constant. It can be seen that the exotherms remain quite visible, regardless of nitrogen exposure. Thus the rearranging species cannot be removed by simple desorption; the rearrangement probably involves an oxygen-containing functional group.

IV.4. Conclusions

- Aerial oxidation of unheated Upper Freeport coal led to higher pyridine swellability values than those in the corresponding as-received coal. This is likely due to addition of oxygen functionality, which makes the thermodynamics of pyridine interaction with the surface of the coal more favorable. When the structure of the coal was thermally relaxed prior to oxidation, the effect of the oxidation on initial swellability was minimal. This serves as warning that measurements of swelling ratios cannot necessarily be used in a straightforward manner to study the effects of oxidation on crosslinking.

- Thermally pre-relaxed Upper Freeport and Pittsburgh No.8 coals and as-received Illinois No. 6 coal show an appreciable impact of 120°C aerial oxidation on solvent swelling behavior. The effects were quite different in different coals. Aerial oxidation appears to lead to lower pyridine extractability from Upper Freeport coal, though the structure of the coal did not appear to be more highly crosslinked. Actual crosslinking seemed to be promoted in Pittsburgh No. 8 coal, but pyridine extractability, THF swellability and THF extractability were unaffected. In Illinois No. 6 coal, the pyridine swellability was unaffected, but the THF swellability decreased sharply.
- The comparison of DSC thermograms obtained from as-received and oxidized coal samples at 8°C/min demonstrate that an exothermic peak centered around 195°C was caused by the added oxygen and, interestingly, does not depend upon coal rank. These observations might suggest that the oxidation is actually concerned with certain specific components in coal structure, irrespective of coal rank as well as pretreatment conditions. However, this must be considered in light of the result below.
- According to DSC thermograms obtained from oxidized coal samples, the Illinois No.6 coal appears to be attacked in a slightly different manner than the Upper Freeport and Pittsburgh No.8 coals. The exotherm centered at near 195°C leads into a much broader exotherm, extending to much higher temperatures.

In summary, it may be said that the effects of oxidation are in no sense "simple". In some cases, oxidation actually enhances swelling, whereas in most, it leads to an apparent increase in crosslinking. Effects on extractability, as might be of great interest in the context of liquefaction pretreatments, are difficult to reliably predict. Based upon the work performed here, however, there is generally little benefit to be derived from oxidation, before or after heat treatment. Again, the only "benefit" observed was in helping to relax the structure of high rank coals. This could be accomplished by heating in the absence of oxidation as well, without the deleterious effects on extractability.

Since there is thus little to be gained by deliberate oxidation, we would recommend against conditions that promote it. We also caution that it is apparent that major rearrangements of oxidation products take place in all coals, at temperatures of around 200°C. Therefore the conclusions drawn based upon our lower temperature studies might not apply to higher post-oxidation conditions, as are of interest in liquefaction. Since this was not a key focus of the present study, we did not pursue this question further.

IV.5. References

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Figure IV-1. Comparison of pyridine swelling ratios with heat-treatment temperature between as-received and air-oxidized Upper Freeport medium volatile bituminous coal.

Figure IV-2. Effects of aerial oxidation on pyridine swelling characteristics in heat-treated and oxidized Upper Freeport, Pittsburgh No. 8 coals.

Figure IV-3. Effects of aerial oxidation on changes of THF and pyridine swelling ratios with swelling time in as-received and heat-treated Pittsburgh No. 8 coal. The notation of 300°C in the figure denotes that the sample was preheated inside the DSC up to 300°C at 8°C/min under a nitrogen environment. Oxidation was performed inside the DSC at 120°C with 100 ml/min air for 5 or 15 hr.

Figure IV-4. Effects of aerial oxidation on solvent swelling behavior in Illinois No. 6 coal. Results are shown as a function of swelling time. Oxidation was performed in a tube furnace at 115°C, for one day, under room air.

Figure IV-5. DSC and difference DSC thermograms obtained at 8°C/min from Upper Freeport medium volatile bituminous coal. The experiment was performed as follows: First, as-received coal was heat-treated up to 350°C, the result of which is denoted as (1) in the figure. Second, the purge gas inside the DSC was switched from nitrogen to air (100 ml/min) and the sample was kept isothermal at 120°C for 12 hr. Third, the resulting oxidized sample was scanned twice in the DSC, the results of which are (2) and (3). The difference DSC thermogram of the two consecutive DSC thermograms (2) and (3) is denoted as (4).

Figure IV-6. First and second DSC thermograms as well as the corresponding difference DSC thermograms for oxidized Illinois No.6 and Pittsburgh No.8 coals. Oxidation condition was 120°C for 15 hr while the sample was kept under air flow of 100 ml/min inside the DSC.

Figure IV-7. Effects of air-oxidation temperature in the difference (1st-2nd) DSC thermograms obtained from Upper Freeport coal. DSC runs were performed at 8°C/min under nitrogen flow of 100 ml/min. Oxidized samples were prepared inside the DSC cell under the constant air flow of 100 ml/min for 18 hr.

Figure IV-8. Mass loss obtained during heating of air-oxidized Upper Freeport at 8°C/min. in inert gas. The sample had been oxidized at 125°C for 460 minutes in air, prior to performing this experiment.

Figure IV-9. DSC spectra obtained upon heating pre-oxidized Upper Freeport coal at 8°C/min. in inert gas. The coals were pre-oxidized for 18 hours at the indicated temperatures of 120°C and 80°C, and then heated in inert gas for 18 hours at the same temperatures. Following cooling, these samples were then subjected to the DSC experiments.

V. The Elastic Properties of Coals

V.1 Elastic Behavior of Coals Studied by Mercury Porosimetry

V.1.1 Introduction

Mercury porosimetry is a commonly applied technique for examining the pore structure of solids. The volume of mercury that can be forced into the pores of the solid in any particular range of pressure gives an indication of the porosity in a certain range of sizes. Application of the technique to coals presents certain difficulties. It is well established that the apparent increase in mercury uptake by coal at higher pressures (>100-200 atm) is actually due to the compressibility of coal structure. Because of this compressibility, the application of mercury porosimetry to pore characterization in coals has involved careful corrections, so that actual pore size distributions could be calculated.

The compressibility that is measured by this technique is the isothermal compressibility, formally defined by:

$$\kappa = -(1/V)(\partial V/\partial P)_T \quad (V.1)$$

This compressibility thus represents the fractional change in volume per unit change in pressure. This quantity is the reciprocal of the so-called "bulk modulus", B. As will be discussed below, these quantities are related to other common mechanical properties of the coal.

Thus the mercury porosimetry method gives an indication of the compressibility of bulk coal structure, and this can be an advantage in studying the structure of coal, since it can help elucidate an elastic model for macromolecular coal structure. Here the use of this technique for characterizing the macromolecular structure of coal is explored.

V.1.2 Experimental

The coals that have been examined in this part of the study include the same Illinois No. 6 and Pittsburgh No. 8 coals as have been presented in earlier chapters. Also, a series of four North Dakota lignites has been examined, as well as a sample of Powhatan No. 5 bituminous coal. The analyses of these last five coals were presented in Table II-2. Samples that were studied were generally fairly fine powders; the actual mesh sizes will be reported separately below.

Mercury "porosimetry" (compression) was carried out using a standard Quantachrome Instruments mercury porosimeter. This instrument can be used to scan mercury pressures up to

33,000 psia. Normally the instrument scans at 6,600 psia/min. In some tests, the scans were deliberately interrupted and samples held at a constant pressure. In a departure from "normal" practice, here both compression and decompression cycles were examined. The terminology "intrusion volume" will be used to denote the measured decrease in mercury volume with increase in applied pressure, recognizing that this term does not necessarily reflect the actual physics of the process, in that actual penetration of pores is not the process of interest. No special efforts were made to interpret the low pressure part of the intrusion curves, since the actual porosity information was of no interest here.

V.1.3 Results and Discussion

Figure V-1 shows typical results from mercury "porosimetry". The lower curves in each graph were obtained during the compression step while the upper curves were taken during the decompression step. In common application of the mercury porosimetry method, the volume "loss" during compression would normally be associated with intrusion of mercury into the coal (losses in pure mercury volume are positive "intrusion volumes", using the parlance of mercury porosimetry). Instead of interpreting the results in this manner, here we associate the loss of mercury volume with the compression of the sample, as has been established by others [1,2]. Of course it was necessary to verify that the apparent compression at high pressures was not an artifact of the system. A blank run ascertained that the compressibility of the measurement apparatus itself was negligible compared to that exhibited by the sample.

As a thermodynamic property, the bulk compressibility of a sample would not be expected to be path-dependent. Thus the hysteresis, such as displayed in Figure V-1, might be viewed as disturbing in this regard. The nature of the apparent hysteresis in the pressure range from 3,000 to 33,000 psia was examined by various techniques. A series of several consecutive compressions and decompressions were performed on a sample of Illinois No. 6 coal, and the results are given in Figure V-2.

After the first compression-decompression ("intrusion-extrusion") cycle, all subsequent intrusion-extrusion cycles were essentially identical, implying that the process had become reversible. The difference between the first and all subsequent cycles is attributed to an irreversible uptake of mercury in the pores of the coal. Note that the "intrusion volume" always returns to the same non-zero value after the first cycle. Since the first intrusion curve was not parallel to the second and subsequent intrusion curves not only in the low pressure range, but also in the 3,000 to 33,000 psia range, this suggests that there might be some irreversible changes (intrusion or compression) occurring in this range of pressure. In this respect, the results of this study are a bit different than those of Toda and Toyoda [1], who saw only purely reversible compression effects in

this higher range of pressure, even during the first scan.

The hysteresis loop obtained at high pressures may well be attributable to a kinetic effect, reflecting the speed with which the system could be compressed or relaxed. Several experiments were performed to test this issue. In one series, decompression of a freshly intruded sample was permitted to occur down to various pressures between 3,000 and 33,000 psia, followed immediately by recompression. The result was a very close retrace of the decompression curve between these pressures.

The above result implied that whatever causes the apparent hysteresis is fully reversible only at quite low applied stresses. Such behavior has been observed before in a different context, as will be discussed below. It seems to say that until a very low pressure is achieved, the system cannot revert back to a particular configuration. It should be recalled that we have presented evidence for the thermally assisted relaxation of structures that are equilibrated relative to at geological conditions, but not laboratory conditions (this is the reason for the DSC-revealed and solvent swelling- induced relaxations we have discussed earlier). Thus there is already evidence that certain coal structural configurations can be achieved which are metastable at laboratory conditions. While not truly equilibrium configurations, they appear to be such because the kinetics of relaxation are quite slow. In the case of the decompression experiments, the relaxation can perhaps occur at a measurable rate only if the driving force is high enough, as a result of the lowered pressure around the sample.

Further information as to the nature of the hysteresis came from another type of experiment. These tests involved permitting a sample to stand at 5,000 and 10,000 psia for two hours while continuously recording the "intrusion" or "extrusion" volume. The results indicated that there is apparently no kinetic effect associated with the decompression curves; "extrusion" values did not change during the period of holding a constant pressure. There however appeared to be some effect of holding time on compression values at high pressure. The longer that a sample was held at a particular pressure, the higher the "intrusion" value obtained, approaching the values of the decompression curve, but not reaching them. In any event, it is clear that the kinetics of relaxation are important.

Similar hysteresis was observed by another worker using very different experimental techniques. Brenner [3] has performed compressive testing of pyridine-swollen thin sections of coal. His tests were classical stress-strain measurements in which the load is applied in one coordinate direction, as distinct from the measurements of compressibility performed here. The unidirectional stress experiment provides the "tangent Young's modulus" or "dynamic Young's modulus," E ($\equiv$ tensile stress / tensile strain). The relationship between E and B is through the

Poisson ratio (ν) of the material, defined as the (change in width per unit width / change in length per unit length) in tensile-type experiments. The moduli are related by:

$$E = 3B (1 - 2\nu) \quad (V.2)$$

For organic liquids, the Poisson ratio is exactly 1/2 in value, and the relationship between the moduli is trivial, in that liquids cannot support a tensile stress. For polymers, ν can be significantly less than 1/2. For example, polyethylene has $\nu = 0.49$, PMMA has $\nu = 0.4$ and polystyrene has $\nu = 0.38$. The Poisson ratio for coals was estimated in one study to be fairly constant at 0.35, at least up to very high ranks of coal [4]. There was, however, some variability in values reported for coals by other workers; values were found to be in the range 0.37 to 0.44 [5]. This means that if the lower range of values for Poisson's ratio is correct, then value of Young's modulus, E , should be numerically quite close to the value of the bulk modulus B . Otherwise, E might be about 1/3 of B .

The measurements of Brenner [3] showed that the stress-strain curves of swollen coals are characterized by hysteresis, relative to compression and decompression. The slope of the compression cycle was always gentler than the slope of the decompression cycle at high stresses. This naturally means that E is greater during the decompression than during the compression cycle, at high load. At low loads, the opposite appears to be true. Our results for B follow exactly the same trend. At high loads (high pressures) the volume change with change in pressure is greater during compression than decompression, which means that B is higher for decompression than compression, at high loads. The hysteresis in the stress-strain curves is thus observed in two very different tests.

Brenner also noted that the recovery of the coal to its initial unstressed volume can be quite slow even at zero stress. This echoes our finding that there is a definite kinetic limitation in recovery of the material, and our results go further to suggest that recovery is essentially impossible, except for near zero stress. It is notable that Brenner performed his measurements on rubbery coals and obtained characteristics somewhat similar to what we observe with coals presumed to be in the glassy state.

Thus it is not clear whether the compression or decompression value of B is "correct". In light of this, Table V-1 gives values for both compression and decompression. The tabulated values are $(1/B\rho = \kappa/\rho)$, where ρ is the initial coal density. The results for Illinois No. 6 and Pittsburgh No. 8 show the extent to which the results are reproducible. It appears that values of (κ/ρ) have uncertainties of about 10% around a mean.

The values for the four lignites of Table V-1 are displayed for both the as-received (wet) coal and the same coal dried at near zero relative humidity at room temperature for several weeks. These results show the difference in elastic behavior of coals which are "plasticized" by water, and those that are dried, and thus more heavily non-covalently crosslinked. No clear trend of κ with drying is

evident. In some cases, the value of (κ/ρ) for dried coal is higher, in others, lower. It is, however, always true that the compression values are higher than the decompression values.

The results for the Pittsburgh No. 8 coal show that an extracted coal has a slightly higher compressibility than a raw coal. This may result from two contributions. Removal of extractable material from a matrix might be expected to create more voidage and, therefore, compressibility. In addition, the structure of the coal is relaxed by pyridine swelling.

There is not a very strong variation of compressibility with rank, as is apparent from a comparison of the results of the bituminous coals and the lignites. There is at most a factor of three spread in all compressibility values.

Finally, it should be noted that there are several more property relations that can be used to compare B to other measurable properties. The shear modulus of a material (G) is defined by (shear stress / shear strain) and is related to the other directly measured quantities as well:

$$E = 2G (1 + \nu) = 3B (1 - 2\nu) \quad (V.3)$$

These quantities can also be related to the speed of sound in a material. For longitudinal sound waves in a simple fluid, the velocity is related to B:

$$B = \rho u^2 \quad (V.4)$$

where u is the speed of sound and ρ is the density. For a rigid incompressible material, the propagation of sound occurs through a transverse wave, and the distortional wave velocity is simply related to another property, the shear modulus:

$$G = \rho u^2 \quad (V.5)$$

For real solid materials, the relationship between longitudinal wave velocity and bulk modulus must take into account the Poisson ratio of the material [5]:

$$B = \rho u^2 (1+\nu) / [3(1-\nu)] \quad (V.6)$$

All of the above properties have been reported by other workers for coals [e.g.4]. Generally speaking, all of the reported results on coals are self-consistent, and imply a very highly crosslinked structure for the raw coal. Attempts have been made at deriving the molecular weight of chain segments between crosslinks, M_c , using well-known expressions from rubber elasticity theory. One such form closely resembles the ideal gas law:

$$G = \rho RT / M_c \quad (V.7)$$

As has been shown by Larsen and Kovac [7], application of real measured values of G or E gave seemingly unrealistic values of M_c (values were of order 1 to 10). In that study E was typically of order 10^9 Pa, and thus from equation (V.3) and the values of ν reported above, G was of the same order of magnitude. In fact, by use of (V.3), and by using $\rho = 1.3 \text{ g/cm}^3$, it can be clearly seen that the results of Table V-1 also will yield estimates of E which are of exactly the same order of magnitude. Thus there is great consistency among all of the data that have been produced on the

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mechanical properties of coals, and all imply very high values of the moduli. Such high moduli in polymer systems are generally associated with the glassy state.

The problem associated with application of a theory that presumes the coal to be in a rubbery state to coal which is in fact in a highly glassy state speaks for itself. This is the reason for the inability to use (V.7) to calculate values of M_c . The coal is not rubbery, and its network structure is highly constrained in its movement, not so much because of covalent crosslinks, but rather, because of non-covalent interactions that effectively act as crosslinks.

It is clear that while water acts as a very effective relaxation agent for some coals, and greatly enhances rates of transport through the coal, the coal is still in a highly glassy state, even when moist. This is seen from all of the data of Table V-1 on the lignites. There is no dramatic orders-of-magnitude decrease in B as a result of presence of the plasticizer water.

With respect to the relaxations that can be induced in Pittsburgh No. 8 coal by pyridine swelling, it is seen that there is a small effect, but again, not orders of magnitude. The coal's structure remains glassy after the treatment. This comes as little surprise, since it is clear that coal does not become rubbery following solvent extraction or heating; it remains a brittle solid. It is in a rubbery-like state only in the presence of good swelling solvents. This is clearly seen in the experiments by Brenner, which gave moduli of order 10^6 Pa for pyridine immersed samples [3]. Such moduli are very typical for polymeric systems in which crystallinity is not high, and can be observed over a wide range of temperatures if the polymer is crosslinked. The fact that such values are obtained on pyridine-swollen coals gives confidence in the use of theories of solvent swelling on coals, since these generally assume the coal to be in a state such that the equations of rubber elasticity can be applied.

The above discussion leads to some firm conclusions regarding the state of coal network structure under various conditions. A coal's structure may be *relaxed* by solvent preswelling or by the action of heat, but that does not mean that its structure will be made permanently rubbery; quite the contrary, it remains glassy at room temperature. The structure will become rubbery only in the presence of a good solvent. The mere presence of a swelling solvent in the structure, e.g. water in lignites, does not assure the attainment of a rubbery state.

Considering the glassy nature of the coal in the compression tests that we have performed, it then comes as little surprise that there is a marked degree of hysteresis observed. The relaxation of the structure would be expected to be observable only over a very long timescale, if the driving force for relaxation is small. It is only when the structure is far out of equilibrium with respect to prevailing conditions that it will be driven towards a new configuration on the timescale of the experiments performed here.

V.1.4 Conclusions

It has been noted that there is no single, distinct measure of the bulk modulus of coals measurable in bulk compressibility tests. Consistent with other tensile modulus measurements, there is a hysteresis associated with the measurements of these moduli. The origin of the hysteresis is not yet firmly established, but it is in all probability associated with a time-dependent response of a network structure.

The mechanical properties of the coal are not very widely varying, based upon our measurements of the bulk moduli. There are not obvious trends with the presence of a plasticizing solvent in the coal, but there is a suggestion that extraction could affect values a bit.

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V.2. Effects of Thermal and Solvent Pretreatments on the Elastic Properties of Coal

V.2.1. Introduction

It is now well established that thermal pretreatment in a range of temperatures lower than those needed for pyrolysis can significantly affect the penetrability and swellability of coals. The present chapter is concerned with the effects of heat/solvent pretreatments on the elastic constants of the coal network structure. This, in turn, tells one about how the non-covalent interactions in coal are being broken down. Studies of the elastic properties of coal are nothing new [e.g. 1-10]. As noted above, because of the compressibility of coal, the application of mercury porosimetry to pore characterization in coal has involved careful corrections, so that the actual pore size distribution could be calculated [1,11,12].

It is known that dynamic mechanical methods are ca. 1000 times more sensitive for detecting molecular relaxations such as the glass transition temperature, T_g , than are differential scanning calorimetry (DSC)/differential thermal analysis (DTA) techniques [13]. This is not surprising, since the dynamic mechanical methods depend directly upon the state of the network structure, while the thermal techniques measure a heat effect in going from one state to another. A change of state in the network need not give a strong thermal signature. The change in solvent swellability is also a direct measure of a change in network structure, so it would be expected that the dynamic mechanical techniques should confirm trends from solvent swelling.

Weller and Wert [7-10] have extensively applied the torsion pendulum technique, one of the dynamic mechanical methods, for elucidating the elastic properties of coal in the temperature range below 200 °C. They employed square rods cut from whole coal. Since the relevant temperature range for the structural relaxations we are interested in is generally higher than 200°C, we decided to study the thermal structural relaxation at temperatures higher than 200°C by employing dynamic mechanical analysis (DMA). This technique involves a constant amplitude oscillation of the solid to determine stress-strain properties. The nature of the stress/strain measurements is different in our work than in Weller and Wert's, but the quantities that are measured are closely related.

V.2.2. Experimental

A DuPont 982 DMA device was employed for mechanical analysis. A detailed description of the

equipment has been given elsewhere [13,14]. Briefly, this instrument operates on the principal of inducing forced resonant vibratory motion with a fixed, selected amplitude. The operator of the instrument selects an amplitude to be maintained, based upon a preliminary analysis of the sample. For the coals studied here, a relatively "routine" amplitude of 0.2 mm proved suitable. There is not independent control of frequency in this instrument, but the operating range of the instrument is such that the frequency will generally be between 2 and 85 Hz. The actual measurement involves determination of the energy input to an electromechanical driver that is designed to maintain the amplitude constant. Thus the shear storage modulus is determined from the frequency of oscillation and the energy needed to drive the system gives a measure of the shear loss modulus. These moduli are "converted" into tensile moduli, using the usual relationship involving the Poisson ratio of the material (again, for coals, a value of around 0.35 is typical).

The samples for the DMA were prepared by pressing the as-received coal powder (-100 mesh) obtained from the Argonne Premium Sample Bank with a press normally used for making FTIR sample pellets, at 15 kpsi for 6-12 hr, which results in a sample of ca. 4 mm thickness with 12.8 mm diameter. Data were obtained at the heating rate of 4 °C/min under nitrogen flow of 200 ml/min.

Slippage of the samples from the clamps inside the DMA, especially during oscillation in the high temperature range (>300°C), was noted to be a main cause for irreproducibility, and special care was taken to make certain that the sample was tightly clamped. The pelletizing process used here clearly creates a solid tablet of different macroscopic mechanical properties than the original solid. The choice to work with samples prepared in this way was dictated by a desire to continue to use the Argonne Premium Coal Samples, that are generally only available in powdered form. The gross macroscopic mechanical properties of such pellets, e.g. tensile modulus, will clearly be different from those of a sample prepared, for example, by cutting a chunk from a virgin block of coal. In fact, any samples cut directly from coal could still be subject to naturally occurring heterogeneities in the coal, and thus mechanical properties are in that case still subject to large variations, depending upon the nature of the tests. This is not important for present purposes, because our goal is not to make use of macroscopic mechanical properties. Rather, we are here only interested in changes on the molecular level that manifest themselves as changes in a particular property.

For purposes of comparison, we examined the changes revealed by DMA in the context of changes earlier noted using thermal techniques, such as DSC and solvent swelling techniques. The detailed procedures for obtaining DSC and solvent swelling results have been reported earlier [15,16].

V.2.3. Interpretation of Results

Raw DMA results are obtained as the frequency of oscillation and the damping signal. Again, the frequency of oscillation is directly related to an elastic modulus of the sample, whereas the energy needed to maintain constant amplitude oscillation is a measure of damping within the sample [14]. Normally, the modulus is resolved into storage and loss moduli. The storage modulus, E' , corresponds to the perfectly elastic component whereas the loss modulus, E'' , represents the perfectly viscous component, reflecting the degradation of energy into heat. The dimensionless ratio of loss/storage moduli is defined as the damping factor, $\tan \delta = E''/E'$.

It is features that are clearly visible in the “ $\tan \delta$ ” or “loss modulus spectra” that are of significance in identifying events affecting the network structure. Both E'' and $\tan \delta$ can be used to reveal glass transitions, appearing as maxima in the spectra during the transition. Other types of transitions, in addition to the glass transition, can cause changes in E'' . This parameter merely serves as a sensitive indicator of a change in the ability of molecular segments to move, relative to one another. Examining this modulus as a function of temperature has been viewed as having analogy with scanning the absorption of a molecule across different infrared wavelengths. As a particular temperature is reached, a network structure abruptly moves into a different state, allowing a temporary increase in loss processes (E'') at the transition temperature. Above the transition temperature, the network is in a different state than before, but the extra, temporary degradation of mechanical energy input to irreversible heating processes does not continue. In contrast to this, the storage modulus (E') changes more monotonically with temperature. It may also show an abrupt change at a particular temperature, but the change is permanent.

It is thus the E'' or $\tan \delta$ behavior we choose to focus on here. We expect, based upon values reported in the literature [7,9], that the loss tangent for coals will not be very large, i.e. that $\tan \delta$ is of order 10^{-2} at frequencies between 1 and 10 Hz, even during transitions. This suggests that the loss to dissipation is generally not large, and that the value of E' should be a fair approximation to Young's modulus, E , which is an “infinite time” equilibrium value.

The tensile storage modulus for the coal samples is in absolute value comparable to what might be encountered in some glassy polymer samples. There was, however, a calibration problem identified only after these measurements were completed. We believe that the values reported here are probably somewhat too low. This is not of particular significance, since it is not the absolute values that we are interested in, so much as the temperatures at which transitions take place.

In Figure V-3, a first transition is seen near 60°C, for different samples of wet, as-received Pittsburgh high volatile bituminous coal. This transition is normally not visible in DSC, because it is buried beneath the water evaporation peak. The position of this peak is sensitive to the presence

of moisture, as is seen from Figure V-4. This behavior is typical of the effects of a "plasticizing agent" in a polymer. The molecular motions of the coal chains are enhanced at low temperatures when water is present, and internal hydrogen bonding of the coal itself is suppressed by the opportunity to hydrogen bond with a solvent (in this case, water).

The large peak in Figure V-3 that is revealed by $\tan \delta$ above 200°C coincides with a transition shown both by DSC analysis of this coal and by a change in tetrahydrofuran (THF) swellability (see Figure II-3). This transition involves an irreversible relaxation of the coal structure [16,17]. Note how dramatically the $\tan \delta$ value increases, compared to the modest clues to as to transition provided by both DSC and solvent swellability changes. The $\tan \delta$ values do not show a definite peak in our work only because pyrolysis occurs prior to the end of relaxation, and the structure continues to irreversibly change.

Figure V-5 illustrates the behavior of Upper Freeport medium volatile bituminous coal in DMA. The tensile storage modulus exhibits a continuous decline with temperature, except for two regions of more rapid decline in modulus. The loss modulus, and thus $\tan \delta$, both suggest that there is a low temperature event, again probably associated with moisture in the coal, at below 100°C. The main relaxation of structure starts to occur from 240°C, as observed in both tensile storage modulus and $\tan \delta$. This observation augments the DSC and solvent swelling results (see Figure II-6) for the same coal, in that Upper Freeport coal showed the characteristics of a relaxed coal structure such as increased swellability in solvents and endothermic peak. In the DSC, the coal exhibited a distinct endothermic peak centered around 350°C which was started from around 310°C, whereas solvent swellability increased significantly above 250°C. It is thus confirmed by DMA that properties that depend directly upon the macromolecular structure (such as DMA and solvent swellability) are more sensitive indicators of irreversible structural relaxations than is DSC. This is of little surprise, because direct measurement of macromolecular structure properties should be more sensitive than an indirect measurement of changes through a thermal signal.

V.2.4. Conclusions

Two bituminous coals were subjected to DMA analysis and the results were compared our earlier reported DSC and solvent swelling results. Results from different techniques appear to point to the same basic conclusions with regard to transitions, although there are subtle differences between the results of different techniques. The transition related to coal moisture is more visible in DMA and solvent swelling techniques than in DSC analysis. DMA confirms that solvent swellability is a more sensitive index of macromolecular changes than is DSC. The importance of observations made by several different techniques in order to discern transitions accurately has been

noted. This study confirms the usefulness of applying different techniques simultaneously for this purpose.

We noticed that good reproducibility in DMA depends upon the reproducibility of forming pellets, in our case. A main problem was small cracks generated while the pellet was released from the press.

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Table V-1. Summary of results on the compressibility of coals.

<u>Coal</u>	<u>Pretreatment</u>	<u>Compressibility (cc/g-atm. x 10⁵)</u>	
		<u>Compression</u>	<u>Decompression</u>
Glenn Harold (lignite)	As-received	1.82	0.84
	Dried	1.12	0.62
Gascoyne (lignite)	As-received	1.53	0.70
	Dried	1.40	0.70
Freedom (lignite)	As-received	1.40	0.98
	Dried	1.40	1.40
Beulah (lignite)	As-received	1.68	0.35
	Dried	1.96	1.26
Illinois No. 6 (hvb)	As-received	2.57	0.82
		2.98	0.99
		<u>2.92</u>	<u>0.93</u>
	Mean values	2.82	0.91
Pittsburgh No. 8 (hvb)	As received	0.91	0.65
		<u>1.18</u>	<u>0.59</u>
	Mean values	1.05	0.62
	Pyridine extracted	1.81	0.99
Powhatan No. 5 (hvb)	As-received	1.23	0.77

Figure V-1. Typical mercury porosimeter results on coal, showing mercury intrusion as a function of applied pressure.

Figure V-2. Intrusion-extrusion cycles in mercury porosimeter for Illinois No. 6 coal (-20+100 mesh).

Figure V-3. DMA spectra of Pittsburgh No. 8 coal samples. The samples were pressed from -100 mesh powder at 15 kpsi for the indicated times. The samples were either predried or used as-received. The heating rate for all experiments was $4^{\circ}\text{C}/\text{min}$.

Figure V-4. Effect of sample drying on the tensile loss modulus of Pittsburgh No. 8 coal observed by DMA. The samples were pressed from -100 mesh powder at 15 kpsi for 10 hours. The heating rate was 4°C/min.

Figure V-5. DMA spectrum of Upper Freeport coal. The sample was pressed from -100 mesh powder at 15 kpsi for 12 hours. The heating rate for the experiment was 4°C/min.

VI. USE OF SOLVENT SWELLING FOR COAL MACROMOLECULAR ANALYSIS - A REVIEW OF THERMODYNAMICS

VI.1. INTRODUCTION

VI.1.1 Use of Solvent Swelling for Analysis of Coal Structure

Recently, a considerable amount of attention has been directed at understanding how the macromolecular structure of coal influences its reaction behavior. The fact that coal must have a macromolecular structure has been recognized for some time, and has been embodied in many of the "classic" models of coal structure (e.g. refs. 1-5). Van Krevelen² and Kreulen⁶ recognized the colloidal nature of coals and used this to explain many important features of their behavior. Wolfs et al.⁷ demonstrated that certain polymeric substances were good analogs for coal, with respect to pyrolysis behavior. This work remains the cornerstone for many of the sophisticated models of coal pyrolysis behavior today. The development of models of fluidity has long been based on "depolymerization" as a key step (e.g. ref.8). And of course extraction of soluble material from coal has been understood for many years as the segregation of small soluble components from an insoluble matrix which can also be broken down to some extent by thermal decomposition.⁹

An improved level of understanding of the macromolecular structure of coal has been developed over the last few years, in part because a number of new tools (mostly borrowed from the polymer field) have been successfully applied to studies of the structure. The review by Green et al.¹⁰ summarized much of the development of the coal macromolecular concept, as it exists today, and discusses many of the techniques that have been applied in studying the problem. This section is concerned with the use of one of the techniques borrowed from polymer science, solvent swelling¹¹, as a method for characterizing coal's macromolecular structure.

It has been recognized for some time that coals have a macromolecular structure that permits swelling in appropriate solvents (e.g. refs. 12-16 and the reviews 10 and 17). In spite of many attempts to carefully apply the technique of solvent swelling to elucidation of the

macromolecular structure of coals, there remain many significant unanswered questions regarding the technique, particularly with respect to the models used to quantitatively describe the behavior. It has been recognized by many workers that the use of specifically interacting solvents (polar, hydrogen bonding) makes the use of classical solvent swelling theory inappropriate to the extent that the assumption of regular solution theory governing the coal-solvent interactions is invalid^{12,16,18}. Some recent measurements suggest that the inadequacy of the swelling models to describe certain phenomena may indeed have to do with the handling of specific interactions in both mixing and elastic free energy calculations, and these will be described below.

There is little doubt that an improved knowledge of the macromolecular structure of coals is both desirable and necessary, since recently an enormous amount of effort has been directed at putting the qualitative picture of coal thermolysis, viewed as a network depolymerization⁷, onto a quantitative basis²⁰⁻²⁶. A key requirement of all these modeling efforts is accurate knowledge of the coal network's fragmentation behavior. Thus far the models of initial network structure used as input to the degradation models have been largely based upon various experimental observations concerning the extractability or fluidity of the pyrolyzing coal. Development of a more complete understanding of the pyrolysis behavior requires much more complete knowledge concerning the identity and density of cleavable and uncleavable linkages in coal.

The swelling of coals by solvents has also been extensively examined in recent years, because of what the swelling process might reveal about other aspects of coal and its processing. For example, swelling studies have helped understand the nature of solvent transport within coal²⁷⁻³⁵, about changes in coal structure that occur during reactions of coal³⁶⁻⁴², and about how coal retains moisture³³. Additionally, solvent preswelling of coals has been suggested as being of interest as a pretreatment strategy⁴³. Thus the solvent swelling behavior of coals is an important aspect of its utilization and might lead to new, more effective processing strategies if an improved understanding of the behavior were available.

VI.1.2 The Thermodynamics of Interaction of Swelling Solvents with Coal - Broad Outline

The theory of solvent swelling in polymer networks has been well described elsewhere^{11,44-46}. The starting point for most solvent swelling models is the fact that at true

swelling equilibrium, the Gibbs free energy of the system must be at a minimum. It is classically *assumed* that the change in the Gibbs free energy of the solvent-polymer system during swelling is made up of two contributions --one due to elastic deformation of the network, and the other due to mixing of the components. Thus the total free energy change upon mixing of coal and solvent ($\Delta G \leq 0$) is given by:

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}} \quad (\text{VI.1})$$

Equilibrium is thus formally determined by the minimization of the free energy with respect to extent of swelling, which is equivalent to minimization with respect to moles of solvent uptake, n_s . This equivalence arises from the fact that the swelling is associated with the change in the macromolecular network structure required to accommodate solvent molecules, as opposed to creation of any significant open volume. Thus at equilibrium:

$$(\partial \Delta G / \partial n_s)_{T,p} = (\partial \Delta G_{\text{mix}} / \partial n_s)_{T,p} + (\partial \Delta G_{\text{el}} / \partial n_s)_{T,p} = 0 \quad (\text{VI.2})$$

It is in the details of calculating the individual contributions of mixing and elastic deformation that several well-known models of swelling differ from one another. The theories of swelling as they apply to coal will be reviewed and developed in more detail in another paper. For present purposes, it is sufficient to assume that there are two separable contributions that determine the free energy change upon swelling. There have been performed separate measurements of the enthalpy of solvent/coal mixing processes, and of the elastic properties of coal. The intent here is to consider how these results contribute to the understanding of the swelling process in coals.

VI.1.3 Specifically Interacting Solvents and Their Behavior in Swelling Coals

It is well-known that there are some "special" solvents that are much more effective for swelling coal than are many others. For example, pyridine is generally a far better swelling solvent for virgin coals than is benzene, due to the existence of "specific" interactions involving the lone pair in pyridine. It has been shown¹⁸ that reducing the hydrogen bonding character of some coals renders non-specifically interacting solvents far more effective than they otherwise are. The classical theories of solvent swelling have not been developed with such a situation in mind.

Rather, the assumption has always been made that the network interacts non-specifically with the solvent, that is, all atoms in the network structure of coal will interact equally with a solvent molecule. Clearly this situation is not satisfied if there are, for example, large numbers of clearly identifiable hydrogen-bonding and non-hydrogen-bonding sites in the network, and any the solvent can "choose" between them. In destroying the heterogeneity of sites in the network, such as by reacting away strong hydrogen bonding sites, the "ideal" case of non-specific interactions is approached.

It is, however, clear that hydrogen bonding interactions cannot be the only specific interactions that exist in coals. For example, the unique ability of CS₂-containing mixtures to swell and solvate certain high rank coals that cannot otherwise be swollen in hydrogen bonding or electron donor solvents⁴⁷ suggests a unique set of specific interactions within the coal, perhaps involving aromatic-aromatic interactions³⁵. Other possible non-covalent bonding interactions in coal (e.g. charge transfer) have also been recently explored and concluded to be important in some cases⁴⁸.

Consequently, it is difficult to formally apply classical solvent swelling theory to the behavior of unmodified coals in "good" swelling solvents, since all of these systems have the potential for exhibiting several specific interactions. It is the purpose of this analysis to consider how these types of systems would be expected to behave in swelling experiments.

Since hydrogen bonding is a commonly suggested type of specific interaction within coal^{18,49}, the discussion is first turned to the thermodynamics of hydrogen bonding systems. It is well established that the free energy ΔG_{hb} for hydrogen bonding interactions (in non-coal systems) is often linearly related to the enthalpy ΔH_{hb} for the interaction, if families of similar hydrogen bonding bases are employed⁵⁰. This means that the ΔS_{hb} have similar values in families of such bases. Moreover, the range of ΔS_{hb} values obtained with different types of bases is not great, and there appears to be a general, albeit crude, monotonic relationship between ΔG_{hb} and ΔH_{hb} for a wide variety of bases^{50,51}.

For present purposes, the significance of the above result is that the *enthalpy* of mixing might then be a principal parameter that defines differences in ΔG_{mix} behavior for different hydrogen-bonding solvents. This helps explain why correlations of swelling data with what amount to different measures of the enthalpy of mixing, are moderately successful, as can be seen, for example, in the data of Figure VI-1⁵². The original data are here replotted in terms of molar uptake of solvent per unit volume of coal rather than swelling ratio, as will be further

discussed below. The uptake is calculated from $[(Q-1)/V_s]$, where Q is the measured volumetric swelling ratio (=swollen coal volume/initial coal volume) and V_s is the molar volume of the solvent.

The above successful attempt at correlating the effectiveness of solvents for swelling a coal involved a parameter that characterizes the enthalpy of interaction of electron donors (hydrogen bond acceptors) with arbitrary electron acceptors (hydrogen bond donors). The scale used for that purpose was Gutmann's "Donor Number" (DN)⁵¹. The donor number is a measure of electron donating ability relative to an arbitrarily chosen electron acceptor (SbCl_5). Thus the Donor Number scale is an arbitrarily defined scale of base strength, in the sense of a Lewis base. The higher the donor number, the stronger the base. It can be seen from Fig. VI-1 that for the particular Polish bituminous coal in question, there appears to be a threshold electron donor strength that determines the ability of the solvent to swell the coal to a condition approaching a limiting value of $[(Q-1)/V_s]$, or what appears to be a full saturation of a certain number of sites in the coal. More direct evidence in support of a saturable number of specific interaction sites will be offered below.

A somewhat different approach was used by another group in order to illustrate the importance of specific interactions in swelling of coals. It has been shown¹⁸ that the extent to which solvents exceed an expected regular solution theory extent of swelling correlates with $\Delta H_{f,pfp}$, the heat of hydrogen bonding of the solvents with *p*-fluorophenol⁵⁰. This parameter is also clearly a measure of the base strength, and again is in fact a calorimetric measure of interaction with a particular electron acceptor. While it cannot be said that exactly the same type of interactions are possible with the coal as with *p*-fluorophenol, the strength of coal-solvent interactions is probably correlated with *p*-fluorophenol-solvent interactions. The results thus imply that if energetically favorable enough interaction sites are available within the coal, uptake will occur onto these sites, regardless of whether the solvents have a good match with the coal, in terms of ordinary dispersion-type interactions. Apparently the stronger the possible interaction of the solvent with specifically interacting electron-accepting sites, the greater the number of sites that will interact. This in all likelihood means that there exists a competition, for interaction with coal electron acceptors, between the added electron donor and native electron donors in the coal. This point will be further discussed below.

Hall *et al.*⁵³ showed a relatively less well-defined, though still quite evident, trend

of swelling of coal with DN, but preferred a correlation with pK_b instead. The good correlation with pK_b , for which a different set of solvents with a narrow range of solvent molar volume values was examined, leaves little doubt about correlation with base strength. Base strength is, in broadest definition (Lewis base) a measure of the ability of the solvent to donate electrons to a Lewis acid. Thus DN and pK_b unquestionably also measure related quantities.

In a review of linear solvation energy relationships, Kamlet et al. note the proliferation of arbitrary measures of polarity, acidity, and basicity, and note that quite often the measures are correlated⁵⁴. This may be seen in Figure VI-2. We have used the presently available set of overlapping data^{50,51} to derive the following correlation between $\Delta H_{f,pfp}$ and DN:

$$\Delta H_{f,pfp} = 0.6835 + 0.3063(DN) - 0.002775 (DN)^2 \quad (VI.3)$$

A large portion of the data could quite reasonably be correlated linearly, but a second order polynomial fits the data better. Both DN and $\Delta H_{f,pfp}$ are experimentally determined parameters, measured with respect to a very different reference acid or electron acceptor in each case.

The above results all strongly suggest a correlation between solvent swelling of coal and the enthalpy of formation of hydrogen bonds or other electron donor-acceptor interactions between the solvent and the coal. From this follows a conclusion that the factor that distinguishes effective specifically interacting solvents from other less effective solvents is a favorable enthalpy of interaction with the coal. As noted above, since most of the solvents in question are of comparable size, it is logical that the entropic effects of mixing any given amount of the solvents with the coals must be of comparable magnitudes, and the differences between solvents are mainly due to enthalpic factors.

The mixing enthalpy is a *net* enthalpy; and must naturally include the enthalpy required to dissociate any coal-coal interactions and solvent-solvent interactions, in addition to the enthalpy of forming the new coal-solvent interactions. It is possible for the net enthalpy of mixing to be zero or even positive (endothermic), since the always-positive entropy of mixing could still dictate that the free energy of mixing ($\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$) be negative. In fact, in "standard" non-specifically interacting solvent swelling theory, it is precisely the entropy of mixing which is assumed to drive the swelling process, since exothermic mixing processes are not expected. It is also worth recalling that the *elastic* free energy change upon swelling is virtually always positive, and must be offset by a negative mixing free energy for any swelling to occur. Fortunately, the enthalpic effects associated with the deformation of the network structure itself, as would contribute to the elastic free energy change, can usually be neglected, and the elastic free

energy change is calculable from entropic considerations.

Attention is now turned to the consequences of existence of specific interactions on the solvent swelling behavior of coals. There have been concerns raised as to whether theories that have as their starting point an assumption of non-specific interactions can be used to quantitatively describe the swelling behavior of coals. We consider the role of strong, specific interactions in more detail.

VI.2. EXPERIMENTAL

In order to establish several key points in the model for coal swelling, it was necessary to perform a variety of experiments involving the mixing of coals with specifically interacting solvents. Several experiments addressed directly the swelling behavior of coals. The solvent swelling procedures employed in this study have recently been described in detail³¹. The technique is an adaptation of earlier reported methods^{55,56}. It involves the simplest technique for measuring the extent of swelling-- measurement of the solvent induced height change in a column of coal held in a constant diameter glass tube. The method has been adapted for performing diffusion rate studies at various temperatures^{31,32}.

The technique involved immersion of prepared, sized, coal samples in pure solvents. The measurements were performed in constant diameter tubes of 3 mm inner diameter, and about 5 cm in length. These tubes permitted such measurements to be made with modest quantities of sample (50 to 100 mg). After placing a coal sample into a tube, it was first centrifuged for 3 minutes (at 7500 rpm in a roughly 30 cm diameter horizontal rotor) to permit accurate measurement of the initial height of the coal sample. Solvent was then added and the contents vigorously stirred with a thin rod. The extent of equilibrium swelling was determined at various temperatures, after permitting the sample to equilibrate for at least a day, and was always rechecked later to assure that equilibrium had been achieved. Before swelling measurements were made, the samples were again centrifuged for 3 minutes. The extent of volumetric swelling is proportional to the increase in height of the column of coal.

It was sometimes necessary to add fresh solvent to the tubes if the amount of extractable material was large; this was done by carefully removing the contaminated solvent, after centrifugation, using a syringe or small pipette, and then adding the fresh solvent. Measurement of

the extent of swelling was then repeated after equilibration. The removal of what in some cases could have been a significant mass of the starting coal with the extract can be expected to significantly affect the reported swelling ratio. The swelling is effectively reported on a starting coal volume basis, rather than on a dry residue basis. Studies in which the coals are exhaustively pre-extracted will give results on a dry residue basis. The two sets of results are not quantitatively directly comparable. Since the points to be made in this study were not influenced by the choice of basis, the results are given on a dry, unextracted coal basis. Such a basis would be clearly unacceptable were the aim to *quantitatively* characterize the macromolecular structure of the network.

No corrections have been made to the swelling results to account for the mineral content of the coal. The mineral matter would presumably be unswellable, and its contribution to the dry and swollen volumes should be subtracted, as it has in careful work⁵⁶. In practice, this has been seldom done. The correction is given by⁵⁶:

$$Q_{\text{drmmf}} = (Q_{\text{measured}} - y)/(1-y) \quad (\text{VI.4})$$

where $y = [(\rho_{\text{dry coal}}/\rho_{\text{minerals}})] \times [\text{mass fraction minerals in coal}]$. As can easily be verified, the difference in swelling ratio will be only a few percent for coals that contain a typical 10% by mass of mineral matter, since $(\rho_{\text{dry coal}}/\rho_{\text{minerals}})$ is around 0.5⁵⁶. No corrections have been made for the filling of pores by solvent, since this would not be expected to affect the calculation of the swelling ratio by an immersion technique⁵⁶. This correction has been suggested as important in work that infers the swelling ratio from gravimetric measurements⁵⁶⁻⁵⁹. There is a difficulty with such corrections, since they are sensitive to the severity of the drying procedures used in preparing the coal; it has been shown that the residual porosity in dried lignite is a function of the temperature and time of drying of the sample^{33,60}. Thus the direct immersion technique is preferred for studies of swelling.

Some measurements were made of the heat of mixing of coal and solvents. These were performed in a Microscal flow calorimeter. All results reported here were obtained at near ambient temperature (298 K). For these experiments, a sample (<100 mg) of prepared coal was placed in a cell through which a solvent or solvent mixture is continuously flowed. In the experiments of interest here, the composition of the solvent mixture was abruptly changed, and the resulting heat effect of mixing was measured. The measurement cell was calibrated by dissipating a known amount of heat from a precision resistor embedded within the cell.

In the experiments of interest here, the main carrier solvent was a normal alkane

(either hexane or heptane), which give a very minimal heat of mixing with the coal. Mixtures containing different amounts of specifically interacting solvent were introduced after the samples are equilibrated in pure alkane carrier solvent. In all cases, several cycles were studied which involved switching back and forth between a pair of solvents, and measuring the heat release or heat absorption involved in doing so. Only experiments which displayed a high degree of repeatability and reversibility in the heat effects are reported here. It should also be noted that a high degree of swelling of a sample in the measurement cell was unacceptable, in that the solvent flowrate could not be maintained. This meant that the experiments had to be performed with pairs of solvents that did not cause more than 10 to 15% swelling relative to the initial volume. This required a tedious process in which samples were preswelled to a certain extent prior to insertion into the sample cell.

The analyses of the coals examined in this study are provided in Table VI-I. Except where otherwise noted, the coals were ground and sieved to the size range 53-88 μ m. It must be noted that there was a significant sensitivity of results to sample preparation conditions. Generally, all samples were predried in a vacuum oven at 373 K for three hours, prior to testing. An episode during which air leaked into the vacuum oven during drying gave a dramatic demonstration of the sensitivity of swelling behavior to oxidation. Swellabilities of the oxidized samples of Pittsburgh No. 8 coal were dramatically reduced, in some cases. The solvents were all purchased as standard reagent grade, and used without further purification.

VI.3. RESULTS AND DISCUSSION

VI.3.1 Swelling Experiments in Linear Alkyl Amines

It has earlier been noted that the swelling of coals in linear alkyl amines gave volumetric swelling which was roughly proportional to the molar volume of the amine⁶¹. The results of similar experiments conducted as part of this study, shown in Figure VI-3, provide a similar conclusion, for a lignite and a bituminous coal. These results came from experiments in which the raw coals were swollen in a series of alkyl amines. Thus there is a generality of the earlier result across a broad range of ranks from high volatile bituminous down to lignite.

Such results have been interpreted in terms of specific interactions between the coal and solvent, since the same number of moles of solvent were taken up by the coal, regardless

of the length of the linear alkyl chain attached to the amine functional group⁶¹. It is logical to conclude that the active functional group is the amine, and that this group is in some sense titrating certain groups in the coal. The DN values of these particular linear alkyl amines have not been determined, but it would be expected that the values would be quite high, since ethylamine has a DN value of 55 and t-butylamine has a value of 57. In terms of the hierarchy of basic solvents, these alkyl amines are clearly stronger than pyridine (DN=33.1)⁵¹. On the basis of behavior such as that seen in Figure VI-1, we would conclude that the alkyl amines are then strong enough electron donors that they would find interaction with all available sites.

VI.3.2 Implications of Linear Alkyl Amine Swelling Results for Standard Solvent Swelling Theories

One aspect of the results in Figure VI-3 is that they can in no way be interpreted in terms of any of the classical solvent swelling theories. The simplest illustration of the difficulty is available from the Flory-Rehner theory expression that relates molecular weight between crosslinks (M_c) to the swelling ratio ($Q=1/v_c$, where v_c is the volume fraction of network chains in the swollen sample, using the nomenclature commonly employed in the polymer literature), viz^{44,45}:

$$M_c = \frac{\rho_c V_s v_c^{1/3} [2 v_c^{2/3} / \phi - 1]}{[\ln(1 - v_c) + v_c + \chi v_c^2]} \quad (\text{VI.5})$$

The parameter ρ_c is the raw coal density (typically 1.3 g/cc), ϕ the functionality of crosslinks (probably 3 or 4, referring to how many chains come together at a single point), χ is a measure of the enthalpy of mixing⁴⁴, and V_s is, again, the molar volume of the solvent. This expression is derived for certain assumptions concerning the network behavior ("phantom network", subject to Gaussian chain statistics). This is unimportant for present purposes, since other assumptions concerning the nature of the network lead to the same conclusions.

The enthalpy of mixing per mole of added solvent ($\Delta H_{\text{mix}} = RT\chi v_c$) is always positive (endothermic) for non-specific interactions, and thus χ is normally a positive number. The value of χ is generally not known *a priori* and is difficult to measure in the coal-solvent system. Values of χ have been reported to range between -0.4 and 0.8 for typical pairs of solvents and coals, over a range of temperatures^{16,62-64}. The reporting of negative values in and of itself is a

warning that specific interactions are involved. This raises a question as to whether merely allowing for exothermic mixing processes is sufficient to "correct" models such as (VI.5) for the case of specifically interacting solvents. It will be seen that this procedure is *not* satisfactory for describing the complicated thermodynamics of coal swelling.

A linear relationship between Q and V_s cannot be predicted from (VI.5) for realistic values of the parameters, if χ is taken as constant. The results are shown in Figure VI-4 for "typical" values of χ . The trend of all of the predictions is, in fact, in the opposite direction from the data. Additionally, it was necessary to assume very low values of M_c (about 200 daltons) to obtain "realistic" values of V_s from this calculation. Such low values are typical of single aromatic clusters^{65,66}, and if correct, would imply a very highly crosslinked structure. The fact that the trend with molar volume is incorrect of course means that the model is inapplicable in any case.

It might be hypothesized that the observed linear trend of Q with the molar volume of solvent is a consequence of some systematic variation of χ with molar volume. Published heat of immersion data⁶⁷ do not support this, as can be illustrated by another simple calculation. It has been reported that the enthalpy of immersion of the same Pittsburgh No. 8 coal as studied here in *n*-hexylamine is -49.09 cal/g coal, while the heat of immersion in *n*-butylamine is -54.90 cal/g coal. For a Beulah-Zap sample, the same values are -16.14 and -94.35 cal/g coal, respectively. The definition of χ suggests that it can be directly calculated from these enthalpy of immersion data. Since $(Q-1)/V_s$ is the equilibrium molar uptake of solvent per volume of dry coal, then $(Q-1)/V_s \rho_c$ is the molar uptake per unit mass of dry coal. By multiplying ΔH_{mix} with this quantity, the heat of immersion per unit mass of dry coal results. Substituting for ΔH_{mix} the expression involving χ , the final result is that:

$$\chi = [Q h V_s \rho_c] / [(Q-1) RT] \quad (VI.6)$$

where h is the measured enthalpy of immersion of the coal in the solvent. The values of χ obtained by this procedure are unusually high (-39 for *n*-butylamine and -7.8 for *n*-hexylamine, given the results for the North Dakota lignite, and comparable values are derived for the Pittsburgh No. 8 coal). This would imply that ΔG_{mix} is dominated by the enthalpy of mixing, with χ assumed to be a large negative constant, such that $|\chi v_c| \gg |\ln(1-v_c) + v_c|$. This would allow recasting (VI.5) into the following form:

$$V_s = (\chi M_c / \rho_c) / [Q(.667 - Q^{.667})] \quad (VI.7)$$

in which $\phi=3$ has been assumed, and $v_c=1/Q$. Again this does not represent a linear relationship

between Q and V_s . Moreover, the observed values of Q (around 2), and a value of χ of the order calculated from heat of immersion data (-10), and a molar volume of order those of the linear alkyl amines tested (100 daltons), implies that M_c/ρ_c would be of order 20. Since the density of coal is of order 1.3 g/cc, the value of M_c would be unrealistically low (of order 10 daltons). Thus the classical model of coal swelling, based upon non-specific interactions, fails in several respects. It is clearly necessary to search for an alternative.

VI.3.3 The Evidence for Specific Interaction Sites in Coals

It has been pointed out that there appears to be a particular number of sites in the coal that are capable of amine uptake⁶¹. This conclusion is here examined in the context of other results. It would then be reasonable to assume that all the linear alkyl amines are equally effective in disrupting intracoal hydrogen bonds and/or other non-covalent interactions, and forming new coal-solvent interactions. From the above cited data on the enthalpies of immersion, it is apparent that the ability of the alkyl amines to find the interaction sites cannot depend upon the absolute value of the interaction enthalpy, since these varied widely. Rather, it once again appears that there is a certain threshold value of mixing enthalpy, beyond which it is assured that solvent interaction with all sites is favorable.

If all of the amines interact with the same sites whose number per unit volume of coal is n_s^* , a constant, then the volume of solvent imbibed at equilibrium is simply $(n_s^*V_s)$, and the equilibrium swelling ratio is given by:

$$Q = [(n_s^*V_s) + V_0]/V_0 = (n_s^*/V_0)V_s + 1 \quad (\text{VI.8})$$

where V_0 is the volume of dry coal. This means that the quantity $(Q-1)/V_s = n_s^*/V_0$ should be a constant. This is the reason we prefer to present swelling ratios in terms of $(Q-1)/V_s$ for the purposes of this analysis. The observed linear variation of swelling ratio with the molar volume of the solvent is of course also implied in (VI.8).

The actual results of a regression of the data in Fig. VI-3, as well as those of reference 61, yields linear relationships of the form:

$$(Q-1) = \alpha V_s + \gamma \quad (\text{VI.9})$$

where the individual values of α and γ are shown in Table VI-II. The lignite and the subbituminous coals show higher values of the slope $\alpha (=n_s^*/V_0)$ than do the bituminous coals. This could logically reflect the fact that the higher oxygen contents of the lower rank coals correlate

with a higher content of amine binding sites.

The magnitude of the α values suggests that all of the coals have about 10^{-2} eq/cc of specifically interacting, amine binding sites. If the raw coal density is taken to be a typical 1.3 g/cc, and if it is assumed that each specifically interacting site is associated with a nitrogen or oxygen heteroatom, then the specifically interacting nitrogen plus oxygen contents of these samples would have to be in the neighborhood of 11 to 12 wt %. This is possible in the lower rank samples, but not so in the Bruceton and Pittsburgh No. 8 samples (and is not so, even if account is taken of the small sulfur contents of these samples). Green and West⁶¹ had already noted that the phenolic hydroxyl contents of the Illinois No. 6 and Rawhide samples are not high enough to explain the interactions in terms of simple hydrogen bonding at such sites. It remains unclear what other specifically interacting sites are involved with the amines.

There is a possibility of solvent interaction with mineral components; it has been reported that clay minerals can swell in pyridine⁶⁸. Also, minerals have been noted to affect the heat of mixing of coals and solvents⁶⁹. Another possibility for coal-solvent interactions beyond simple hydrogen bonding involves electron donor-acceptor interactions of the aromatic clusters present in the higher rank coals. Aromatics are unquestionably capable of hydrogen bonding types of interactions, behaving as weak bases (electron donors)⁷⁰. They can also serve as electron acceptors, relative to a strong enough donor. While it is unlikely that any such very strong donors exist in the coal structure, they may not really be needed for such interactions to exist, because the aromatic structures will likely be substituted. In particular, the aromatic structures will quite likely contain electron withdrawing groups (mainly oxygen substituents). The ability of quinones and hydroquinones to participate in electron donor-acceptor complexes is well established⁷¹. Such complexes need not exhibit simple 1:1 stoichiometry with electron donors, so the magnitude of α in the bituminous coals must be considered in light of this fact as well. The potentially important role of aromatic-aromatic interactions has been recently discussed by Larsen and Wei⁷² and Nishioka and Larsen⁷³.

Turning to the parameter γ , equation (VI.8) suggests that it should have a value of zero. The implication of a $\gamma > 0$ is that even if a solvent of zero molar volume were used, some swelling would be observed. It might be most appropriate to dismiss a non-zero value as a failing of a very simple model that would not necessarily be expected to extrapolate well beyond the range of the measurements. The positive γ values might, however, have physical significance. The fact

that the values are all positive may reflect the fact that the amines cause swelling in two ways. In addition to the swelling caused by the absorbing of molecules of finite size, is the swelling that results from the dissociation of coal-coal bonding interactions, accompanied by the relaxation of the network structure. In the case of the lignite, the act of drying the sample in preparation for the swelling measurements involves a collapse of the structure, to the extent of about 30%^{33,60}. The measured value of γ for the lignite (0.36) suggests that the fully relaxed state of the network structure is closer to that which exists prior to drying. The removal of the water causes formation of strong internal coal-coal hydrogen bonding interactions that can actually stress the network structure in the direction of compression.

The possibility that the unstressed network structure of lignites is closer to that of the natural moist state, in which true coalification occurs, is quite reasonable. This fully relaxed network state is not the normal state for a dry coal because of the strong tendency to form internal non-covalent bonding interactions. The values of γ also suggest that higher rank coals also relax somewhat in response to the action of the specifically interacting solvents in disrupting non-covalent interactions, but the amount is small in comparison to the final degree of swelling of the coals. In the case of higher rank coals, the extent of shrinkage upon drying is only a percent or two³³. Thus the stresses that are revealed by positive γ values in higher rank coals are probably not caused by the sample drying, but are of natural origin, in the process of coalification. Again, this is consistent with other observations that imply that stresses present in raw bituminous coals are irreversibly removed by swelling in good solvents^{18,73-75} or that the structures of bituminous coals are irreversibly relaxed by heat^{34,35}. The fact that the coal's network structure may not be fully relaxed prior to solvent exposure has not been included in any of the usual theories of solvent swelling applied to coal. Again, the magnitude of the effect is not large in bituminous coals, but could be significant in lignites.

There is another interesting sidelight to the observation that the network structure of coals might not be fully relaxed in an ordinary dried state. It has recently been suggested³³ that since the structure of coal in a dried state is "collapsed" as a result of moisture removal, surface areas measured at low temperatures on dried coals cannot accurately indicate the accessibility of the coal to a good solvent, or its accessibility to gases under high temperature conditions (which result in thermal relaxation of its structure). This view is consistent with results that show that specifically interacting solvents give higher apparent surface areas than do poor non-specifically

interacting solvents⁷⁶. The interpretation of surface area measurements on dried raw coals is further clouded by the possibility that the species selected for surface area determination may also be soluble in the coal structure, without swelling it very much⁷⁷, perhaps because they are able to reach "closed" porosity in the interior of the structure⁷⁸. When the coal is fully relaxed, the concept of "closed" porosity might not be of great significance. These considerations all point to the importance of recognizing the possible relaxations of coal structure in considering the accessibility of the coal to reagents, and again raise a serious question about whether it is ever meaningful to perform classical gas-adsorption surface area measurements on dried raw coals.

VI.3.4 Correlation of Swelling with Heats of Immersion

It appeared from the behavior of the coal shown in Figure VI-1 that there should be a correlation between the heat of interaction of solvents with the coal and the volumetric molar uptake of solvents. To test that hypothesis more directly, the swelling behavior of Pittsburgh No. 8 solvent was examined in a series of solvents, for which heat of immersion data were available. The results are shown in Figure VI-5, in terms of the usual molar uptake of solvent per volume of coal. It is clear that generally the solvents characterized by higher heats of immersion gave the higher extents of swelling. The fact that the curve shows a maximum shows, however, that solvent uptake can depend upon more than the enthalpies of interaction with the coal. Figure VI-6 shows that there is a good correlation between the donor number and the heats of immersion in the solvents of Figure VI-5, so it does not appear that the particular choice of correlative parameter (heat of immersion as opposed to donor number) is responsible for the unusual shape of the curve in Figure VI-5.

We believe that in the case of the data of Figure VI-5, the pyridine, ethylenediamine and dimethylsulfoxide may have had available a non-specific interaction swelling route in addition to the specific swelling route; once all of the specific interaction sites are filled, further addition of a solvent is possible, based upon non-specific swelling mechanisms. The favorability of such a mechanism would depend upon the match in solubility parameters of coal and solvent. Such combined effects have been documented in other cases⁷⁹.

Again, apart from the maximum in Figure VI-5, the results of Figure VI-5 do generally follow the trend of Figure VI-1 quite well. Figures VI-1 and VI-5 suggest that in two bituminous coals, the molar uptake of solvent is largely determined by the enthalpy of interaction

of solvents with electron acceptor groups in the coals. This behavior is not limited to bituminous coals. Similar behavior can be found for a lignite, as seen in Figure VI-7. It is notable that the apparent "outlier" at high donor number is heptylamine. It has been shown that steric factors can play an important role in determining swelling behavior in alkyl amines²⁹. It is likely that the heptylamine cannot access all specifically interacting sites.

All of the results suggest that a consistent pattern of behavior is seen over a broad range of ranks. Three other data sets, taken from the literature are shown in Figures VI-8 through VI-10. Most data appear to follow the trends outlined above. In Figure VI-9, however, the fact that the poor electron donor, benzene, could significantly swell the coal while other poor donors could not is again ascribed to good solubility parameter match, in a sample that had previously had coal-coal specific interactions disrupted by pre-extraction. This highlights the sensitivity of swelling behavior to sample preparation conditions. In Figure VI-10 the solvent that shows an unusual maximum is methanol, again likely to have had a good solubility parameter match with the coal in question.

We have not yet extended these studies to extensive testing of higher ranges of rank (low and medium volatile bituminous coals). These coals require thermal pretreatments to "relax" their structures, before showing significant swelling behavior³⁵. It was possible with a special combination of solvents (CS_2 with any of a number of good electron donors) to also "relax" the medium volatile bituminous coal, leading to subsequently enhanced swelling in ordinary solvents. This was perhaps the most extreme case thus far encountered of very specific interactions required in order to swell a raw coal. The implication is the same, that depending upon the strength of non-covalent interactions that exist in the coal, there is a minimum solvent strength that is needed to disrupt these and swell the coal.

VI.3.5 The Effect of Solvent Activity on Swelling

Generally speaking, the lower the concentration of a component of a liquid mixture, the lower its thermodynamic activity and related to this, the lower the chemical potential of the species in the solution. By diluting a strong swelling solvent with a weakly swelling solvent, then the effects of activity on swelling behavior could be examined. A series of experiments has recently been reported in which pyridine solubles were deliberately added to pyridine, and the effect on coal swelling measured. It was clearly seen that the reduction in activity caused by the addition was related to a decrease in coal swellability⁸⁰.

A quantitatively "cleaner" method of varying activity of a swelling agent involves performing the swelling using only solvent vapor, since activity can be directly related to vapor pressure. Unfortunately, vapor swelling results are difficult to obtain and interpret, and the decision was made to continue using liquid phase swelling techniques for this part of the study, in spite of the fact that the activities could not be accurately calculated in all cases.

The results of several different experiments on Beulah lignite are shown in Figures VI-11 through VI-13. The experiments involved using mixtures of pyridine/n-heptane (Figure VI-11), 1-propanol/n-heptane (Figure VI-12) and n-butylamine/n-hexane (Figure VI-13) to swell the coal at room temperature. A large ratio of solvent to coal was used in all of these experiments, so the concentrations are accurately reflected in the data, even if there was different uptake of the two solvents by the coal. It is quite clear that the behavior is non-linear, with respect to the concentration of the specifically interacting components (pyridine, propanol and butylamine).

The coals were not measurably swellable in pure hexane or heptane. Even when the role of specific interactions is minimized, as by acetylation of the oxygen functional groups, the solubility parameter mismatch between a low rank coal and such linear alkanes is quite large, and the alkanes are not effective swelling agents⁶⁸. This means that the uptake of the alkane by the coal, even in the presence of a specifically interacting solvent, is in all likelihood very small.

The results of Figures VI-11 through VI-13 should also not be confused with similar-looking data on pyridine-chlorobenzene mixtures, published some years ago⁷⁹. In that study, it was noted that chlorobenzene could also be a good swelling solvent, except for its inability to participate in specific interactions in the coal. Here, the alkanes are not good swelling agents in any case. This was verified by direct measurements. Thus the results of Figures VI-11 through VI-13 should be interpreted as the uptake of specifically interacting solvents as a function of their concentration in the mixture.

What is implied by all three figures is that there is an increased extent of swelling with increase in activity of the specifically interacting solvent. The data are again shown in terms of molar uptake, rather than straight swelling ratio. It is important to note that there was in no case a simple "titration" of specific interaction sites on the coal. Otherwise there would have been observed a constant extent of swelling (solvent uptake) regardless of the concentration of the specifically interacting solvent. This means that the interaction of these solvents with the coal is not energetically favorable enough so as to assure filling of all specific interaction sites.

It is interesting to note that the data of Figures VI-11 through VI-13 can be crudely correlated by straight lines, if swelling is plotted against the logarithm of concentration as the independent variable. This is illustrated in Figure VI-14, which shows the data of Figures VI-11 through VI-13 replotted. While the fits are in some cases good and in other cases fairly crude, this correlation might offer explanation as to what governs equilibrium in the swelling process. This will be further discussed below.

VI.3.6 Heat of Mixing Measurements

The heat of mixing was measured for two of the systems discussed in the previous subsection. Figure VI-15 shows the heat release upon switching a dried Bulah lignite sample from n-heptane to a mixture of 1-propanol/n-heptane. The heat of immersion of coals in n-alkanes is generally not very high^{81,82}, at most a few J/g for much higher rank coals than are of interest here. The higher rank coals would be expected to have a better match with alkane solvents because of their less polar surfaces. Additionally, our attempts at direct measurements of the heat of immersion of the lignite into alkanes, by switching from a gas to liquid solvent environment, suggested that this value was too small to measure reliably with our equipment. Thus the heat effect of interaction of the pure alkane solvents with the coal appears small in comparison with the heat effects reported in Figure VI-15 and the measured effects are associated with the specifically interacting solvents (as the swelling data themselves also suggest).

The heat of mixing of the lignite and propanol mixtures is exothermic, but not very large. What is, however, striking, is that a significant portion of the heat is released when the sample is exposed to very low concentrations of propanol. Comparison with Figure VI-12 shows that a very small extent of swelling is associated with a very large amount of heat release.

Figure VI-16 shows the cumulative heat release curve as a function of pyridine concentration in pyridine/n-heptane mixtures. The overall heat of mixing of this sample with pure pyridine is about 100 J/g, consistent with earlier published results for a similar sample⁶⁷. The results on heat of mixing are shown in Figure VI-16 together with the relevant swelling results of Figure VI-11. It is possible to calculate from these two slopes, assuming a dry coal density of 1.3 g/cc, the mixing enthalpy per mole of pyridine uptake. The result is 4.0 kJ/mol exothermic. Such a value is lower than what might be inferred from Figure VI-2 for good electron donors interacting with good acceptors; for $DN > 30$, $|\Delta H_{f,fp}| > 25$ kJ/mol. The explanation appears to be that while the pyridine forms new hydrogen bonding-type interactions, it must break other pre-existing

interactions to do so (see below).

The above cited results seem to suggest that the extent of solvent swelling does *not* correlate with the heat of mixing, in that the bulk of the heat release occurs very early during the swelling process. This would appear to be at odds with the conclusion which was reached earlier (from, for example, Figure VI-1 or Figure VI-5). The resolution of the apparent contradiction is hypothesized to derive from the fact that the major part of the measured heat release occurs as a result of interactions of specifically interacting solvents with "free" sites. The free sites are those which would, for example, hydrogen bond to something else in the coal, but are precluded from doing so for steric or stoichiometric reasons. The thermodynamic driving force for "filling" such sites is quite large, due to the very favorable enthalpy of doing so.

Clearly, however, there is much specific site uptake of specifically interacting solvents well after the energetically attractive free sites are filled. If the remaining specifically interacting sites are not free, but are instead initially non-covalently bonded to other sites in the coal, there is a need to break these coal-coal specific interactions, in order to form the new coal-solvent interactions. Such processes are not nearly as energetically as favorable as those involving "free" sites, since the enthalpy involved in forming the new interaction must take into account the dissociation energy of the coal-coal interactions. In terms of the results of experiments in which the concentration of the swelling agent is varied, at low concentrations the number of favorable interaction sites is small, and these consist mainly of the energetically very favorable free sites. As the concentration of swelling agent is increased, progressively less favorable sites become filled, and swelling continues but the enthalpic effects become smaller. This does not yet explain why the extent of filling of less favorable sites depends upon concentration. This will be addressed in the next section, after presentation of relevant modeling considerations.

Finally, as regards the apparent contradiction between correlations such as those in Figure VI-1 and the fact that most heat release occurs very early during swelling, the following should be considered. It is only certain good electron donor solvents that can form very favorable interactions with specific acceptor interaction sites. The energetic favorability is directly measured during the titration of "free" sites. If, however, the solvent is unable to form favorable enough interactions with specific sites, the energy barrier associated with breaking the existing non-covalent coal-coal interactions cannot be balanced by the favorable enthalpy of new interactions. In the absence of the new favorable coal-solvent interactions, the enthalpy of mixing would be large

and endothermic, and the free energy of mixing would not be sufficiently negative to drive the swelling process forward. Therefore, there is in actuality no contradiction between the results from the two different kinds of experiments; the information they provide is complementary.

VI.4.0 MODELING THE SOLVENT SWELLING OF COAL

The driving force for diffusional transport of solvent into the particle is a solvent chemical potential gradient. Interaction of a specifically interacting swelling agent with the surface of a dry coal serves to lower the chemical potential of the solvent, relative to its state in the surrounding fluid phase. The coal imbibes the swelling solvent until this is no longer true. A negative ΔG_{mix} drives the process forward. The favorable mixing process is eventually halted either because the mixing interactions become unfavorable (specific interaction sites are used up, and dispersion interactions are unfavorable) or because of the influence of $\Delta G_{\text{elastic}}$ (the solid is unable to accept any further solvent that tries to enter because of the large free energy penalty due to stretching the network further). In either case, the chemical potential of the solvent *in the coal* is raised by the fact that there is an unfavorable free energy consequence of adding more solvent to the coal. The formal thermodynamic definition of chemical potential of solvent in the coal network, relative to some reference condition, is given by $(\partial \Delta G / \partial n_s)_{T,p}$, and ΔG must include both elastic and mixing contributions.

The elastic free energy term is always positive, and as noted above, can determine when $(\partial \Delta G / \partial n_s)_{T,p}$ becomes positive upon more addition of solvent to the coal. The elastic free energy term is a function of the degree of network deformation and is not a function of solvent-coal interaction *except to the extent that the latter can influence disruption of non-covalent network crosslinking*. This latter point represents a significant departure from the classical solvent swelling theory, in which there is no allowance for non-covalent crosslinks. Clearly the more non-covalent crosslinks removed by the solvent, the less rigid the network, and the less the elastic free energy penalty associated with deforming it.

Is there evidence that solvents can act to disrupt non-covalent network interactions? The role of hydrogen bonding interactions as non-covalent crosslinks has been called into question⁸³. Still, there is little doubt that non-covalent interactions do exist in coals, and that they can be broken by both solvents and heat. The evidence is provided by a wide variety of observations, including those that show swellability in solvents can be enhanced by heat pretreatment or solvent pretreatment³⁵ or that transport rates through coal can be greatly enhanced

by pre-exposure to hydrogen-bonding solvents³³. It is also possible that extraction-induced increase in residue rigidity⁸⁴, relative to raw coal, is a manifestation of formation of new, stable non-covalent crosslinks during extraction⁸⁵. *Therefore, non-covalent crosslinks appear to play a role in limiting coal solvent swelling, and that certain solvents are more effective at disrupting these crosslinks than are others.*

It is logical to believe that there are non-covalent crosslinks within the coal network involving electron donor-acceptor processes for which a suitably strong solvent electron donor can substitute. For example, there are nitrogen bases within the coal, of pyridinic structure, that can form fairly strong interactions with phenolic hydroxyl functionalities. The interactions may be dynamic - for example, at any time a particular nitrogen functionality might be in closer proximity to (and interacting more strongly with) any of a number of neighboring hydroxyls. The options for finding different interaction possibilities are, however, limited by the rigid structure of the coal network structure. The rigidity is conferred by the covalent crosslinks acting in concert with large numbers of other similar non-covalent interactions. Such rigidity is common in many polymer systems that have strong non-covalent interaction possibilities, even when actual three-dimensional covalent crosslinking is not present (e.g. cellulose).

When a solvent such as pyridine is introduced, the degrees of freedom available to the network chains increase significantly. The hydroxyls have many new options for energy minimizing interactions that do not involve coal nitrogen functional groups. The network structure of coal can under those circumstances even become much less rigid, exhibiting even rubbery elastic characteristics⁸⁶. Free energy requirements for moving apart the different parts of the coal network are greatly reduced, because a large number of enthalpically significant non-covalent interactions no longer need to be broken to do so; the free energy penalty is only that associated with the entropic aspects of deformation of a less crosslinked network.

VI.4.1 Modified Theory of Solvent Swelling in Specifically Interacting Media

It has been suggested by the data presented above that the specifically interacting solvent will "seek out" the energetically most favorable specific interaction sites first - those that for reasons of stoichiometry or geometry cannot be involved in intracoal interactions. These sites will

involve a very favorable ΔG_{mix} . Interaction with these "free" sites will still require expansion of the network structure to accommodate the interacting solvent volume, and thus the balance between mixing and elastic free energies comes into play immediately. It is quite possible that in order to gain access to larger numbers of highly favorable mixing interactions, some non-covalent bonding interactions would have to be disrupted. To disrupt these might not be particularly favorable energetically, but their removal will reduce the energy penalty for swelling the network significantly.

The above physical picture can be represented in the following more quantitative terms. Equation (VI.1) may be rewritten as:

$$\Delta G = n_f \Delta G_{\text{mix},f} + n_b \Delta G_{\text{mix},b} + \Delta G_{\text{el}} \quad (\text{VI.10})$$

where n_f is the number of moles of solvent interacting with "free" specific interaction sites, n_b is the number of moles of solvent interacting with non-covalently bonded sites, thus breaking the crosslink, noting also that $n_s = n_f + n_b$ is the total solvent uptake. The ΔG_{mix} terms refer to the free energy contributions of the interactions with free and non-covalently bonded sites. It is useful to recognize that the clean accounting for different interaction sites implied by (VI.10) is in fact quite idealized, since the mobility of solvent molecules within the particle would not allow for a hard and fast accounting of different types of interactions. Still, the model is useful insofar as it accounts in some average way for the energetic consequences of the different possible interactions.

The entropic consequences upon ΔG_{mix} of addition of n_s solvent molecules does not depend upon the particular nature of the interactions; the calculation would still follow from Flory lattice theory⁴⁴. Thus this contribution can be separated from the enthalpic contribution to ΔG_{mix} . The enthalpy of interaction with free sites will be different from the enthalpy of interaction with bound sites, and will as shown above be a function of the total solvent uptake. For simplicity, it is assumed that the partial molar enthalpy of interaction, ΔH_{mix} , includes both contributions, though the net exothermicity of the free site interactions will clearly be greater. In that case, (VI.10) may be rewritten as:

$$\Delta G = -T\Delta S_{\text{mix}} + n_s \Delta H_{\text{mix}} + \Delta G_{\text{el}} \quad (\text{VI.11})$$

Differentiating with respect to n_s as in (VI.2) and setting equal to zero, again results in the criterion of equilibrium:

$$T (\partial \Delta S_{\text{mix}} / \partial n_s)_{T,P} - \Delta H_{\text{mix}} - (\partial \Delta H_{\text{mix}} / \partial n_s)_{T,P} = (\partial \Delta G_{\text{el}} / \partial n_s)_{T,P} \quad (\text{VI.12})$$

The three terms on the left hand side are always positive, since entropy increases with mixing, and the assumption has been made that the specific interactions are always exothermic (as we have

experimentally observed). The details of the calculation of the right hand side will be outlined in a forthcoming paper. Here, a simplified example can be considered. For this purpose, a very simple network model is considered, the so-called "phantom network" of Flory⁴⁴. In this case, the free energy of elastic deformation can be estimated from:

$$\Delta G_{el} = (V_0 \rho_c RT / 2 M_c)(v_c^{-2/3-1}) \quad (VI.13)$$

where all symbols have been defined above and $\phi=3$ was assumed. In the usual application to solvent swelling theory, M_c is a constant, and differentiation with respect to n_s yields:

$$(\partial \Delta G_{el} / \partial n_s)_{T, P} = \rho_c RT V_s v_c^{1/3} / (3 M_c) \quad (VI.14)$$

When crosslinks are dissociated by solvent, then M_c is not a constant. This results in a term of the following form being added to the right hand side of (VI.14):

$$- (V_0 \rho_c RT / 2 M_c^2)(v_c^{-2/3-1})(dM_c/dn_s) \quad (VI.15)$$

It has previously been shown⁸⁷ that:

$$dM_c/dn_s = 3f M_c^2 / 2 V_0 \rho_c \quad (VI.16)$$

in which f is the fraction n_b/n_s . Then (VI.14) becomes:

$$\begin{aligned} (\partial \Delta G_{el} / \partial n_s)_{T, P} &= \rho_c RT V_s v_c^{1/3} / (3 M_c) - (3f RT / 4)(v_c^{-2/3-1}) \\ &= RT v_c^{1/3} [\rho_c V_s / 3 M_c - (3f / 4)(v_c^{-1} - v_c^{-1/3})] \end{aligned} \quad (VI.17)$$

It is instructive to consider that the first term of (VI.17) is positive, as expected. Since $0 < v_c < 1$, then the second term is always negative, meaning that it reduces the rate at which elastic free energy is increased by addition of solvent. It is not yet possible to say what the value of f is, without further information. Clearly f is not constant in that "early" in the swelling process, the solvent preferentially finds and saturates the "free" specific interaction sites, as indicated by the release of a heat of mixing.

It is difficult to say *a priori* at what value of n_s the equality in (VI.12) is actually satisfied, since this depends in a complicated way upon when all the specific interaction sites are exhausted, such that the second and third terms of the left hand side term vanish, and upon the magnitude of $(\partial \Delta G_{el} / \partial n_s)_{T, P}$. It is clear that as non-covalent interactions are removed, the molecular weight between crosslinks in the network increases, and the structure becomes more elastic.

VI.4.2 Implications of the Modified Swelling Theory

The results from the swelling experiments in linear alkyl amines can now be reconsidered. The equilibrium appears to be determined by the point at which specific interaction sites are exhausted. The question is whether equilibrium is established by the fact that the left hand side of (VI.12) suddenly decreases or the right hand side suddenly increases, when the specific interaction sites are used up. There is a reason to believe that both occur simultaneously. Surely the ΔH_{mix} will suddenly be less favorable when the interactions go from specific to non-specific in nature. Likewise, the ability to incrementally stretch the network per unit of free energy is significantly decreased when the ability to cleave non-covalent bonding interactions is used up (i.e. when f suddenly becomes zero in (VI.17)). The fact that two important factors both dramatically change in an unfavorable direction at the same time could explain why the equilibrium is achieved at a constant value of n_s , in spite of observed great differences in actual values of ΔH_{mix} ^{67,88} and V_s for the different alkyl amines. The absolute values of $(\partial \Delta G_{\text{el}} / \partial n_s)_{T,P}$ and $(\partial \Delta G_{\text{mix}} / \partial n_s)_{T,P}$ are not as important as is the fact that the curves of these functions vs. n_s cross at the same n_s . The predicted behavior is shown for a set of reasonable set of parameter values in Figure VI-17.

The results of Figure VI-17 come from assuming that the network has as a basic building block size 100 daltons, and that each of these building blocks is linked by a non-covalent crosslink to another, in the dry state. It is assumed that the actual molecular weight between covalent crosslinks is 2000 daltons. Then, initially, before the uptake of any solvent ($v_c=1$), it may be seen from (VI.14) that:

$$\begin{aligned} [\partial(\Delta G_{\text{el}}/RT)/\partial n_s]_{T,P} &= \rho_c V_s v_c^{1/3} / (3 M_{c0}) \\ &= 0.347 \end{aligned} \quad (\text{VI.18})$$

where typical values of $\rho_c=1.3$ g/cc and $V_s=80$ cc/mol (as for pyridine or THF) have been assumed. Now it is further assumed that equilibrium swelling occurs when all non-covalent crosslinks are dissociated at $Q = 2.5$ (or $v_c = 0.4$). For simplicity only, it is assumed that f is a constant, such that integration of (16) is straightforward:

$$\begin{aligned}
 M_c &= [1/M_{c0} - 3 f n_s / (2V_0 \rho_c)]^{-1} \\
 &= [1/M_{c0} - 3 f (Q-1)/(2 V_s \rho_c)]^{-1} \quad (VI.19)
 \end{aligned}$$

From this, f may be estimated to be 0.439 (again, f is the fraction of imbibed solvent molecules that act to actually dissociate non-covalent crosslinks). Using this value, the free energy upon elastic deformation can be estimated as:

$$[\partial(\Delta G_{el})/RT]/\partial n_s]_{T, P} = v_c^{1/3} [(V_s \rho_c) / 3M_{c0} - (f/2)(2.5/v_c - 1 - 1.5 v_c^{-1/3})] \quad (VI.20)$$

This is the origin of the curves in Figure VI-17.

The failure of solvents that have an endothermic or mildly exothermic value of ΔH_{mix} to promote a high degree of swelling is probably mostly attributable to their inability to lower $(\partial\Delta G_{el})/\partial n_s]_{T, P}$. It should be recalled that there is always an entropic driving force for mixing of coal and solvent, even if ΔH_{mix} is not significantly exothermic. Mixing enthalpies would have to be significantly endothermic to make the mixing term itself unfavorable. Note that all the solvents in Figure VI-5 mixed exothermically with the coal, and so this is apparently not the case. Thus the limiting factor in that case was the elastic free energy requirement for swelling.

The elastic free energy requirement does not depend upon the strength of coal-solvent interactions, except to the extent these interactions determine the dissociation of the non-covalent crosslinks. It is clear from results such as those in Figure VI-17 that the ability of the solvents to dissociate crosslinks is a key criterion for reaching significant degrees of swelling. Note that those results show but a modest decrease in M_c up to a fairly significant degree of swelling (or value of n_s), but that the effect on the elastic free energy is enormous, even when M_c appears to be only slightly increased.

The experiments in which the solvent activity was varied can also be reconsidered in light of the modified theory. It has already been noted that the results suggest that a simple, energetically very favorable titration is not all that is involved, in that not all specifically interacting sites are filled at low solvent activities. This could be seen, for example, in Figure VI-16, which showed that the mixing was exothermic throughout the concentration range studied.

Furthermore, the distinction between strong and weak swelling agents is not seen in the basic rules governing swelling equilibrium, but only in the extent of swelling. This can be seen by comparing the data of Figures VI-11 and VI-12, for pyridine and propanol. The curves have

very similar shapes, but the final extent of swelling, both in terms of absolute value of Q as well as in terms of $(Q-1)/V_s$ is different for the two solvents.

The chemical potential difference between the specifically interacting solvent in the coal (μ) and the solvent outside the coal (μ^0) is given by:

$$\mu - \mu^0 = (\partial \Delta G / \partial n_s)_{T,P} \quad (VI.21)$$

where as usual, $\Delta G = \Delta G_{mix} + \Delta G_{el}$. This means that a change in μ^0 will always be reflected in μ , since the criterion of equilibrium is $\mu = \mu^0$. For any particular specifically interacting solvent, the relationship between n_s and μ is not changed by varying solvent concentration. The different swelling ratios obtained at different concentrations are dictated by the change in μ^0 forcing a change in μ , and thus the equilibrium value of n_s .

The calculation of the free energy of the elastic deformation of the network, via (VI.20) or any other related expression, is unaffected by the change in solvent concentration. The left hand side of (VI.12), which determines the equilibrium, would generally be expected to be influenced in all terms, if there is a significant ΔH_{mix} of the two solvents. If the equilibrium swelling occurs at a point well beyond where free site filling ends, then $(\partial \Delta H_{mix} / \partial n_s)_{T,P} = 0$ is a fair approximation, since as was determined above, the enthalpy effects become small and not a strong function of uptake. Then swelling equilibrium is apparently determined by the relative magnitude of the other two terms on the left hand side of (VI.12).

The above issue can be addressed quantitatively using Flory lattice theory for the configurational entropy⁴⁴:

$$(\partial \Delta S_{mix} / \partial n_s)_{T,P} = R [\ln(1-v_c) + v_c] \quad (VI.22)$$

What this means is that the relative magnitude of the entropic to enthalpic term in (VI.12) is given by:

$$[\ln(1-v_c) + v_c] / (\Delta H_{mix} / RT) \quad (VI.23)$$

In the case of the propanol/heptane solution, the value of the ratio is infinite, since ΔH_{mix} is close to zero. Thus entropy will clearly dominate in that case. It was above determined that for pyridine, $\Delta H_{mix} = -4000$ J/mol. For a typical extent of swelling at which this heat was observed, $Q=1.3$ or $v_c=0.77$, the ratio is of order unity, meaning that neither term clearly dominates.

In the case of entropic domination of the free energy of mixing, the only possible effect of specifically-interacting solvent concentration comes from the fact that the entropy change associated with removal of solvent from the solvent mixture and insertion into the coal matrix

would be affected. The effect of diluting the specifically interacting solvent with a noninteracting solvent is to decrease the entropic benefit of the mixing process, since the solvent starts in a more disordered state. We strongly suspect that the latter is key in the propanol results. This suspicion is supported by the fact that the correlation of $(Q-1)/V_s$ with the logarithm of specifically interacting solvent concentration is linear, as seen in Figure VI-14. This is because the partial molar entropy of the specifically interacting solvent in an ideal solvent mixture decreases linearly with the logarithm of its mole fraction. Therefore, the entropic driving force for solvent to enter the coal should increase with the logarithm of its mole fraction in solution, as observed.

Of course none of the mixtures used here are truly ideal. The propanol/heptane mixture can, to a first approximation, be claimed to follow *regular* solution behavior. This system exhibits a non-zero excess molar volume of mixing⁹⁰, but the values are considerably smaller than, for example, those typically seen for much less ideal solutions, such as methanol in water. Thus regular solution behavior is roughly approximated, meaning that the partial molar entropy of the propanol is linear in logarithm of mole fraction.

In the case of the pyridine/heptane system, the solutions clearly follow regular solution theory in approximately the correct range of temperatures⁹¹. Thus the linear correlation of swelling with logarithm of concentration in this system also appears to support the same physical picture as for the propanol/heptane system. The difference in this case is the larger value of ΔH_{mix} which was obtained calorimetrically. From measured heat of solution values, the partial molar enthalpy of mixing of pyridine in n-heptane is approximately⁹²:

$$\Delta H(\text{J/mol}) = 8192 (1-x)^2 - 1105 (1-x)^3 \quad (\text{VI.24})$$

where x is the mole fraction of pyridine. This expression gives 4.7 kJ/mol at $x=0.2$, which composition is in the mid-range of the data shown in Figure VI-16. The similarity of the above value to the measured heat release during swelling (4.0 kJ/mol) strongly suggests that the measured heat effect is actually mainly a result of removal of pyridine from the solution, into much more favorable contact with functional groups in coal.

The swelling processes in the case of the pyridine/n-heptane mixtures appear, on the basis of Figure VI-14, to be entropically controlled even in the face of fairly large enthalpies of mixing. The fact that the mixing term is not clearly dominated by either enthalpy or entropy (on the basis of the ratio in (VI.23)) could help to explain the slightly greater scatter in the case of pyridine vs. propanol.

To summarize, there appears to be only a small distinction between strong and

weak solvents in trends of swelling with activity. This strongly suggests that the final equilibrium is largely determined by the first term of the left hand side of (VI.12). In other words, *swelling is entropically driven to a limit determined by the elastic behavior of the coal network, taking into account the dissociative processes that specifically interacting solvents can participate in.* This physical picture will be developed more formally, with other models for the elastic behavior of coal, in a forthcoming publication.

It should be noted that the above analysis has treated coal as essentially a homogeneous system, which it surely is not. It has been recently postulated that phase separation could be an important aspect of coal swelling⁹³. There is unquestionably a naturally imposed phase separation, due to the different macerals present in coals. These macerals would surely behave as distinct phases. To ask whether or not a further phase separation occurs with respect to each of these macerals is to heap several layers of complexity onto what is still a very tenuous theoretical foundation. We prefer to develop the foundation further without yet building in this complexity.

Finally, a very different type of swelling model has been recently advanced, based upon the concept of "disinterspersion" of network chains in good solvents⁹⁴. Essentially, the model postulates that the network consists of fairly stiff member, which cannot change conformation significantly during swelling. This would fundamentally alter the calculation of elastic deformation of the network, and represents a significant departure from the Flory formalism used in the present discussion. In adopting this different theoretical viewpoint, the need to have a solvent that is able to "replace" coal-coal interactions with coal-solvent interactions, remains. Therefore the results presented here concerning the correlation of swelling with measures of the enthalpy of interaction would be consistent with the alternative model as well.

VI.5. SUMMARY

It has been found that the swellability of coals in specifically interacting solvents is a strong function of the electron donating capacity of the solvents, as measured by two very different scales. The two scales are seen to be closely related. The swelling also correlates with the heat of immersion of coals in solvents, and thus it appears that it is the enthalpy of interaction of specifically interacting solvents with surface functionalities in coal that determines swelling behavior. There is generally a particular number of specific interaction sites in the coal that

determine the maximum extent of swelling, though there is the possibility of non-specific interactions contributing to further swelling, beyond this "titration endpoint". Variation in swelling with solvent activity appears to be a function of the fact that the process is entropically driven, beyond a very early stage when interaction of "free sites" in the coal dominates. The dissociation of non-covalent crosslinks is an important feature of the swelling process.

VI.6. REFERENCES

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Table VI-I
Analyses of the Coals Studied

<u>Sample</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>Ash</u>	<u>O</u>	<u>Moisture</u>
North Dakota Lignite	65.6	3.6	1.1	0.8	11.0	17.9	26.0
Pittsburgh No. 8*	74.2	4.1	1.4	2.3	13.2	4.8	1.7

•All analyses on a dry weight percent basis, except moisture, which is the ASTM as-received value.

• Oxygen values are by difference.

* Argonne National Laboratory Premium Coal Sample.

Table VI-II
Values of the Parameters α and γ in Equation VI-9

<u>Coal</u>	<u>α (mmol/cc)</u>	<u>γ (dimensionless)</u>
N.D. Lignite	14.	0.36
Rawhide Subbituminous*	14.	0.10
Pittsburgh No. 8	11.	0.18
Illinois No. 6*	11.	0.11
Bruceton*	9.	0.13

* Data from ref. 61.

Figure VI-1. Solvent swelling behavior of a Polish bituminous coal. Data from reference 52 replotted in terms of a molar uptake of solvent per unit dry coal volume.

Figure VI-2. Correlation of solvent Donor Numbers⁵¹ and their heats of mixing with p-fluorophenol⁵⁰.

Figure VI-3. Swelling of several coals in linear alkyl amines. Closed squares and solid line- Pittsburgh No. 8 bituminous coal; solid triangles and solid line- Beulah, North Dakota lignite. The amines examined were n-propyl-, n-butyl-, n-pentyl-, and n-hexylamine. Data from reference 61 shown as open points and dotted lines; triangles- Rawhide subbituminous coal; squares- Illinois No. 6 bituminous coal; diamonds- Bruceton bituminous coal.

Figure VI-4. Relationship between volumetric swelling ratio (Q) and solvent molar volume (V_s), based upon Flory-Rehner theory of solvent swelling. Dashed curve- $\chi = -0.4$; solid curve- $\chi = 0$; dotted curve- $\chi = +0.4$.

Figure VI-5. Relationship between solvent swelling behavior and heat of immersion data⁶⁷ for Pittsburgh No. 8 coal. The solvents include, in order of increasing heat of immersion, toluene, acetonitrile, methanol, dimethylsulfoxide, pyridine, ethylenediamine, n-hexylamine, and n-butylamine.

Figure VI-6. Relationship between enthalpy of immersion of Pittsburgh No. 8 bituminous coal in various solvents⁶⁷ and solvent Donor Numbers⁵¹. The same solvents are considered as in Figure 5. Actual Donor Number data were not available for n-hexylamine, and n-butylamine, but it was estimated that the values should be similar to those of t-butylamine (DN=57) and ethylamine (DN=55).

Figure VI-7. Solvent swelling behavior of Beulah lignite in a series of solvents at room temperature. The solvents tested and their Donor Numbers were nitrobenzene (4.4), acetonitrile (14.1), dioxane (14.8), acetone (17.0), ethylacetate (17.1), methanol (19.0), diethyl ether (19.2), ethanol (20.0), isopropyl alcohol (20.0), tetrahydrofuran (20.0), dimethyl formamide (26.6), N-methylpyrrolidinone (27.3), dimethylsulfoxide (29.8), water (33), pyridine (33.1), ethylenediamine (55). Additionally, the following solvents were tested, and approximate values of Donor Number assigned based upon comparison with other known materials: n-butylamine (57), n-hexylamine (57), n-heptylamine (57), toluene (0), cyclohexane (0). Donor Numbers from reference 51.

Figure VI-8. Swelling behavior of Illinois No. 6 bituminous coal in a series of solvents at room temperature. Data from references 28 and 29. Solvents included methanol (19), ethanol (20), benzene (0.1), n-propylamine (57), n-butylamine (57), n-hexylamine (57), pyridine (33.1), acetone (17.0), tetrahydrofuran (20.0), dimethylsulfoxide (29.8), and ethylenediamine (55). Donor numbers indicated in parentheses, and assigned as described previously.

Figure VI-9. Solvent swelling behavior of pre-extracted Illinois No. 6 bituminous coal in a series of solvents at room temperature. Data from reference 18. Solvents included benzene (0.1), acetonitrile (14.1), dioxane (14.8), acetone (17.0), diethyl ether (19.2), tetrahydrofuran (20.0), dimethylsulfoxide (29.8), and pyridine (33.1). It should be noted that the pre-extraction greatly enhanced benzene swellability compared to that in the raw state, but that swellability in “poor” solvents (e.g. n-pentane, n-heptane, methylcyclohexane, cyclohexane) remained very small. These latter solvents would also be expected to have near zero donor numbers.

Figure VI-10. Solvent swelling behavior of pre-extracted Hebe low rank coal in a series of solvents at room temperature. Data from reference 16. Solvents included benzene (0.1), nitrobenzene (4.4), dioxane (14.8), acetone (17.0), methanol (19.0), ethanol (20.0), dimethylformamide (26.6) and pyridine (33.1).

Figure VI-11. Swelling of dried, pyridine pre-extracted Beulah lignite in pyridine/n-heptane mixtures at ambient temperature.

Figure VI-12. Swelling of dried, pyridine pre-extracted Beulah lignite in 1-propanol/n-heptane mixtures at ambient temperature.

Figure VI-13. Swelling of Beulah lignite in n-butylamine/n-hexane mixtures at ambient temperature.

Figure VI-14. Swelling of Beulah lignite in the same mixtures as shown in Figures VI-11 through VI-13. Solid squares-pyridine; open squares-propanol; triangles- n-butylamine.

Figure VI-15. Heat release from dried Beulah lignite upon exposure to indicated concentration of 1-propanol in n-heptane, at ambient temperature.

Figure VI-16. Heat release from, and swelling of, dried pre-extracted Beulah lignite upon exposure to different concentrations of pyridine in n-heptane. The reported heat release values are referenced to a zero taken at a pyridine mole fraction of 0.087. The experiments were performed at ambient temperature. The open symbols and dotted line refer to ΔH_{mix} , and the closed symbols and solid line to $(Q-1)/V_s$. The slope of the correlation line for the heat of mixing data is 9.44 J/g-coal, and the slope of the correlation line for the swelling data is 3.06 mmol/cc coal.

Figure VI-17. Predictions of the solvent swelling model, assuming dissociation of crosslinks by specifically interacting solvents. Heavy solid line shows predictions of M_c . Thin solid line shows actual course of $(\partial \Delta G_{el} / \partial n_s)_{T,P}$ according to the model. The dashed line shows the value of $(\partial \Delta G_{el} / \partial n_s)_{T,P}$ in the absence of any non-covalent crosslink dissociation, and the dotted curve shows the behavior in the fully dissociated state. Note that in fact the region between about 1.7 and 2.5 swelling ratio is unstable, and that the system will be driven to full swelling at 2.5.

VII. PRACTICAL IMPLICATIONS OF THE PRESENT RESULTS FOR LIQUEFACTION PRETREATMENT

VII.1 INTRODUCTION

There have recently been reported the results of many studies on the possibly beneficial effects of pre-liquefaction treatments on yields. The pretreatments have been categorized as affecting either mass transfer during liquefaction ("Type I") or affecting the liquefaction chemistry more directly ("Type II")¹. In practice, distinguishing between the two effects might be quite difficult, but the broad characterization of the main effects is nevertheless useful. We will consider the results of the present study in light of these characterizations.

VII.2 STEAM PRETREATMENTS

One important class of pretreatments that has captured much attention in recent years involves steam or liquid water presoak, prior to liquefaction or pyrolysis. The interest in this technique was sparked by reports of significant enhancement of pyrolysis liquid yields during steam pyrolysis, or following steam pretreatment². Other reports of effects on extraction, pyrolysis, and liquefaction have followed³⁻¹¹. It is fair to say that there is not yet an entirely clear picture that has emerged from these studies.

There appears to be little doubt that steam treatment serves to alter the chemical, and thus physical, structure of coals. This has been concluded on several bases. First, it is clear that thermal treatment in inert gas does not give similar results to steam treatment under identical thermal conditions². The steam treated material is chemically very different from the raw material⁴. Hydrothermal treatment has, in some respects, been said to mimic coalification itself¹⁰. Lower rank coals can become more like higher rank coals, in that hydroxyl content is lost, and the coals become more aromatic⁷. Another important facet of the pretreatments in liquid water is removal of certain inorganic species⁸. These can play an important role in retrogressive reactions during liquefaction¹²⁻¹⁵.

As the above results would suggest, there are many profound changes in structure that can be caused by steam treatment. It is little wonder that the mechanism of subsequent effects remains unclear. Moreover, there is not even a unique measure of benefit of steam pretreatment. In one case, the yield of pyrolysis tars achieved a maximum while toluene solubles from liquefaction reached a minimum, as a function of pretreatment conditions⁹. The simple notion that steam pretreatment

affects only one aspect of the thermal degradation processes is clearly not supported.

It may be recalled that in the present study, there was no dramatic relaxation event near the 340°C that has been identified as offering significant opportunities for enhancing liquid yields from Illinois No. 6 coal². Indeed, this is consistent with the observation that treatment in inert gas at that temperature did very little to help increase yields. As was noted in Chapter II, in connection with Figure II-4, the temperature range in which steam pretreatment has been seen to be effective *does* correspond with the regime in which irreversible structural changes are evident from DSC and solvent swelling. In fact, it appears as though there could be crosslinking occurring in that very range of temperatures. This was supported by other work as well⁴. It then seems quite plausible that the steam chemically reacts with the coal and prevents certain chemical pathways leading to crosslinking.

To further explore the effects of such pretreatments, we treated Illinois No. 6 coal at 285°C in liquid water at 1000 psig for one hour. Following the pretreatment, the sample was cooled, under water, to room temperature, and then dried at room temperature, under vacuum, before swelling tests were performed.

The 285°C temperature is below that suggested as essential for observing large effects on yields of pyrolysis liquids² or liquefaction products⁵, but slightly higher than the temperature reported to be needed in order to observe effects on the products of liquefaction⁵. Some results of this work are shown in Figure VII-1. For reference, an Illinois No. 6 coal which has been heat treated to 285°C in inert gas gives a pyridine swelling ratio of 3.0 and a THF swelling ratio of 2.3, after 7 days of swelling. Thus, surprisingly, it appears that water pretreatment has apparently crosslinked the structure, relative to what happens in inert gas. Still, the initial swelling in pretreated coal is fast, just as in the coals not treated in water. Therefore there is not a dramatic alteration of structure in the direction of increased mass transport resistance.

It has been reported that the pyridine swelling ratio of coal treated at 300°C under high pressure inert gas is less than the pyridine swelling ratio of the same coal treated under 735 psig of steam. This is opposite the trend that we observed under similar, though not identical, conditions. The reasons for the difference are not understood. Whether it has to do with the fact that our experiments were performed in a liquid water environment, as opposed to steam, is unclear. Also, our inert gas treatment took place at atmospheric pressure; it is possible that higher pressures promote secondary reactions which promote greater crosslinking.

There was concern that the reported sensitivity to oxidation could influence results of tests performed by different workers. To briefly test the effects of oxidation on our samples, we deliberately air oxidized samples at 115°C for one day. The effects of oxidation are seen to be dramatic in some respects. The oxidation greatly decreased the initial rates of swelling. This is

perhaps attributable to the formation of new, strong non-covalent bonding interactions due to polar surface groups created by the oxidation. To overcome these new intracoal interactions requires a longer duration of solvent soaking. The oxidation does not, however, result in new permanent crosslinks in the structure. This is seen from the fact that pyridine swelling reached the same final swelling equilibrium value, regardless of oxidation. The fact that the THF swelling did not achieve the same final value after oxidation is understood in terms of the strength of the new groups introduced by oxidation. They are quite strong non-covalent bonding functional groups. The pyridine is able to overcome their intracoal bonding interactions, whereas the weaker THF is not.

The above result might come as a surprise to those used to thinking in terms of the deleterious crosslinking effects of oxygen. Just as was concluded in Chapter IV, however, the crosslinking effect can be very real, but not manifested until the coal is raised in temperature to a point at which the oxygen functional groups rearrange. Support for the proposed high temperature rearrangement process is given in Figure VII-2, showing the DSC difference spectra of oxidized raw and water-treated coals. The behaviors are very similar. Both coals show a rearrangement centered at around 200°C. Thus the structure of the coal can be altered well before actual liquefaction temperatures are ever reached. The above result again shows the danger in applying a single, very arbitrary test (solvent swelling) to characterize the state of the coal under conditions far removed from those of the test.

In summary, we believe that we understand some aspects of the complicated picture that the literature presents with respect to the effects of water or steam pretreatment of Illinois No. 6. While some minor effects on structure may be observed below 340°C, major chemical changes to the coal require temperatures above this value. There are measurable (crosslinking) effects on structure even at around 285°C, but the impact appears to not be great on subsequent liquefaction behavior. This might be attributable to the fact that the new crosslinks cannot survive the subsequent liquefaction conditions, but this has not been established. In the search for effects of oxidation on crosslinking, measurement of macromolecular network structure by solvent swelling might provide a misleading picture, insofar as the crosslinks might only be developed by subsequent higher temperature processing.

It is also fair to note that the initial interest in steam pretreatment arose from a perceived opportunity to significantly enhance liquid yields from pyrolysis or liquefaction. Apart from the early results that led to the flurry of research activity on this topic, there have been few major breakthroughs towards this goal. Pyrolysis tar yields can be measurably increased in not only the Illinois No. 6 coal, but in other low rank coals as well^{9,10}. These increases are, however, not so large as to make the processes interesting as a direct source of liquid fuels. The effect of hydrothermal pretreatments on yields of desirable liquefaction products can also be seen, but again,

are not large enough to motivate taking steps towards a new process based upon the pretreatment. For lignites, it appears that demineralization or even cation exchange might offer more exciting possibilities¹¹. Based upon our work and that of others, we cannot at present identify any new promising pathways, based upon a fundamental alteration of the macromolecular network structure by steam or water pretreatment.

VII.3 SOLVENT SWELLING PRETREATMENTS

There have been a number of recent reports concerning the benefits of coal preswelling on pyrolysis and liquefaction yields¹⁶⁻²⁶. Considering first the pyrolysis processes, it is difficult to cleanly separate out the effects of the swelling per se from other effects in some of these studies. For example, the swelling is only a vehicle for introducing catalyst deeply into a particle in one case¹⁸. We anticipated a similar use for solvent swelling in the discussions in Chapter III of this report. The challenge may be to find the right solvent combination of solvent (s), coal and catalyst, so that the catalyst is itself soluble or dispersible enough in an effective swelling agent. In any case, the effects from the work that has been thus far carried out using this methodology have not been very large¹⁸.

The use of methanol swollen coal in pyrolysis had some small beneficial effect on yields, particularly benzene, toluene, and xylene yields¹⁷. The overall conversion of the coal to liquids was modestly increased, but the total char yields were practically unaffected. In another study, preswelling the coal in tetralin served to not only open up the structure of the coal, but to also put a hydrogen donor into intimate contact with the coal. There were reported significant increases in total volatiles yields, and in particular, tar yields¹⁶. Still, the benefit to the overall performance is at best incremental.

It is easy to understand why the mere preswelling of coals would not by itself help much in a pyrolysis environment. First, as our results have clearly indicated, the relaxation of coal structure that can be accomplished by the use of solvents will generally also be accomplished equally or more effectively by heating itself, prior to entering the active pyrolysis zone. It is possible that if the heating were to be carried out very rapidly, the thermally-induced pre-relaxation might be kinetically limited, and not achieved prior to the onset of pyrolysis. Moreover, if the solvent is of fairly low molecular weight, it can be lost during the heatup of the system.

Many of the same arguments apply to liquefaction processing. If the liquefaction is carried out above 350°C, then for all but the very highest rank coals, there should be complete thermal relaxation prior to liquefaction. The main benefit of preswelling would again be seen in "Type I" contexts, in which the mass transfer can be improved at a critical early stage of the process. This has

been observed by several groups of workers¹⁹⁻²⁶. The effect has been attributed in various cases to swelling, or more vaguely, to the presoaking in solvent, which enhances mass transport. The role of swelling on catalyst dispersion has again been highlighted²³. It is also quite probable that the beneficial effects of staged heating of the liquefaction mixture really has to do with allowing the swelling and relaxation to occur prior to the active pyrolysis stage²⁷. This appears to be the key; relaxation must occur prior to the onset of reactions that involve competition between liquefaction and retrograde reactions. There is, however, a limit to how far this strategy can be practically taken, since 100% conversions have not been routinely achieved.

The above discussion highlights the need for consideration of the kinetics of relaxation. We can consider this issue in the context of our results on thermally-induced changes in the macromolecular structure of coals. As was noted in Chapter II, the apparent activation energy for relaxation of Pittsburgh No. 8 coal was about 50 kcal/mol, and that for Upper Freeport was 80 kcal/mol. In a study of the relaxation of Pittsburgh No. 8 coal by pyridine solvent, we found that the activation energy range was from 14 to 16 kcal/mol²⁸. The characteristic timescale for relaxation was a few minutes at the elevated temperatures at which the thermal relaxation measurements were performed, and a half hour at room temperature, at which the solvent swelling tests were performed. Using these values leads to a crude estimate of activation energy which is consistent with neither of the values cited above. What this very strongly implies is that there are two very different mechanisms at work, and that relaxation of the structure could be governed by either one, in different pretreatment schemes.

What may be concluded, then, is that there are actually two relaxation pathways available. Since the solvent swelling pathway is not very highly activated, the long timescales seen at near room temperatures might well apply at liquefaction conditions as well. On the other hand, the thermal pathway is characterized by kinetics not unlike those for the degradation reactions themselves, and would naturally be competing with the liquefaction reactions and the retrogressive reactions, but for the fact that relaxation occurs at slightly lower temperatures. This explains the efficacy of staged temperature liquefaction, that assures that the relaxation can occur prior to the main reactions of interest.

VII. 4 REFERENCES

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Figure VII-1. Effects of water pretreatment on solvent swelling behavior of Illinois No. 6 bituminous coal. The results marked "Oxid" refer to samples that were air-oxidized at 115°C for one day.

Figure VII-2. Differential Scanning Calorimetry spectra of oxidized and water pretreated and oxidized Illinois No. 6 bituminous coal. The curves marked 1 and 2 refer to the first and second scans. The curve marked 1st-2nd is the difference of the two spectra. All spectra were obtained at 8°C/min, under inert gas purge.

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