FINAL REPORT

**A NEW MODEL OF COAL-WATER
INTERACTION AND RELEVANCE FOR
DEWATERING**

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EXECUTIVE SUMMARY

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This project was concerned with developing an improved understanding of how moisture is held in coals. There is a concern that the historically held view, that capillary condensation in pores plays a significant role, could not be correct, since the coal shrinks and swells in response to moisture loss and gain. Thus there is no well-defined pore system for holding the moisture. This appears true for a range of ranks from lignite to high volatile bituminous coal. Instead, it appears that something more like classical swelling of coals in solvents is responsible. This study examined this hypothesis by various means, considering both the mixing thermodynamics of coal and water (or coal and other swelling solvents) and by examining coal's elastic response. The conclusion is that water does indeed behave like many other swelling solvents, but is a somewhat poor swelling solvent. The structure of the water swollen coal appears to remain fairly glassy, implying that many non-covalent crosslinks remain unbroken. The water interacts with coal only at certain types of adsorption sites. This is consistent with a second historical view that polar functionality is responsible for water retention. The filling of these sites, somewhat surprisingly, appeared to involve a strong enthalpic driving force, rather than the entropic driving force that characterizes solvent swelling in other solvents. The practical importance of these results for thermal dewatering processes is that the historical view is supported. That is, that pyrolytic polar group removal is necessary. An alternative suggestion, based upon attempts to further crosslink coal, has not received support.

I. Project Overview

This project is concerned with a basic scientific question concerning the properties of coal— to what extent is the ability of coal to hold moisture a manifestation of the well-known ability of coal to swell, when exposed to good solvents? The question implies that the long-held belief that coal holds a significant portion of its moisture by classical capillary condensation processes, is possibly in error. This seems to be a very real possibility for low rank coals- i.e. lignites. To explore this hypothesis further requires an examination of the basic phenomena governing the swelling of coals in good solvents. This is the focus of the first part of this project.

The possibility that coal holds a significant portion of its moisture by solvent swelling mechanisms leads to an interesting technical issue. It is well known that simple drying of low rank coals at minemouth is ineffective because the process is reversible, to a significant degree. The economic advantages of pre-shipment drying have however dictated a search for "permanent" drying procedures. These have been developed by largely empirical means, and involve mild pyrolytic treatments of the coals in oil, steam or liquid water itself. The idea has always been to pyrolytically remove oxygen groups, which are assumed to be those that hold water most strongly by hydrogen bonding. The treatments have been designed to minimize tar formation and decrepitation of the particles, both highly undesirable. In relation to the present new hypothesis concerning water retention, it is likely that a sound approach to permanent drying would involve highly crosslinking the coal at mild drying conditions. The crosslinked coal could not swell sufficiently to hold much water. It is identifying processes to achieve this goal, that constitute the objective of the second phase of this work.

To accomplish the stated goals of the project requires an initial examination of the factors that govern the solvent swelling of coals. Thus this report will begin with an examination of the thermodynamics of coal swelling. A preliminary examination of this topic was reported in the first quarterly, but we have over the course of this project developed a firmer, more quantitative understanding of the issues that are involved in this process. Following this introductory discussion of the thermodynamics, attention is turned in later chapters to a discussion of

techniques for measuring the factors that determine the thermodynamics. Specifically, Chapters 3 and 4 consider measurements of the elastic properties of coal. Chapters 5 and 6 consider the free energy and heat of mixing of coal with solvents (water included).

II. The Thermodynamics of Swelling of Coals by Solvents

II.1.0 INTRODUCTION

II.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. The present paper 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.

II.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:

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

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:

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

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.

II.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 communication 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 II-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. II-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 II-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:

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

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.

II.2.0 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:

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

where $y = [(\rho_{\text{dry coal}}/\rho_{\text{minerals}})]$ [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 II-1. 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.

II.3.0 RESULTS AND DISCUSSION

II.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 II-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 II-1, we would conclude that the alkyl amines are then strong enough electron donors that they would find interaction with all available sites.

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

One aspect of the results in Figure II-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}:

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

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 (II.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 (II.5) for realistic values of the parameters, if χ is taken as constant. The results are shown in Figure II-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:

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

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 (II.5) into the following form:

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

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.

II.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:

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

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 communication. The observed linear variation of swelling ratio with the molar volume of the solvent is of course also implied in (II.8).

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

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

where the individual values of α and γ are shown in Table II-2. 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 (II.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.

II.3.4 Correlation of Swelling with Heats of Immersion

It appeared from the behavior of the coal shown in Figure II-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 II- 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 II-6 shows that there is a good correlation between the donor number and the heats of immersion in the solvents of Figure II-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 II-5.

We believe that in the case of the data of Figure II-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 II-5, the results of Figure II-5 do generally follow the trend of Figure II-1 quite well. Figures II-1 and II-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 II-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 II-8 through II-10. Most data appear to follow the trends outlined above. In Figure II-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 II-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.

II.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 II-11 through II-13. The experiments involved using mixtures of pyridine/n-heptane (Figure II-11), 1-propanol/n-heptane (Figure 12) and n-butylamine/n-hexane (Figure II-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 II-11 through II-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 II-11 through II-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 II-11 through II-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 II-14, which shows the data of Figures II-11 through II-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.

II.3.6 Heat of Mixing Measurements

The heat of mixing was measured for two of the systems discussed in the previous subsection. Figure II-15 shows the heat release upon switching a dried Beulah 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 II-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 II-12 shows that a very small extent of swelling is associated with a very large amount of heat release.

Figure II-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 II-16 together with the relevant swelling results of Figure II-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 II-2 for good electron donors interacting with good acceptors; for $DN > 30$, $|\Delta H_{f,pfp}| > 25$ 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 II-1 or Figure II-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 II-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.

II.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.

II.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 (II.1) may be rewritten as:

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

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 $\Delta \bar{G}_{\text{mix}}$ 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 (II.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, (II.10) may be rewritten as:

$$\Delta G = -T\Delta S_{\text{mix}} + n_s \Delta \bar{H}_{\text{mix}} + \Delta G_{\text{el}} \quad (\text{II.11})$$

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

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

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:

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

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:

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

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 (II.14):

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

It has previously been shown⁸⁷ that:

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

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

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

It is instructive to consider that the first term of (II.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 (II.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.

II.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 (II.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 (II.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 II-17.

The results of Figure II-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 (II.14) that:

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

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:

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

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:

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

This is the origin of the curves in Figure II-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 $(\partial \Delta G_{\text{el}} / \partial n_s)_{T,P}$. It should be recalled that there is always an entropic driving force for mixing of coal and solvent, even if $\Delta \bar{H}_{\text{mix}}$ 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 II-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 II-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 II-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 II-11 and II-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:

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

where as usual, $\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}}$. 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 (II-20) or any other related expression, is unaffected by the change in solvent concentration. The left hand side of (II-12), which determines the equilibrium, would generally be expected to be influenced in all terms, if there is a significant $\Delta\bar{H}_{\text{mix}}$ of the two solvents. If the equilibrium swelling occurs at a point well beyond where free site filling ends, then $(\partial\Delta\bar{H}_{\text{mix}}/\partial n_s)_{T,P=0}$ 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 (II-12).

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

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

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

$$[\ln(1-v_c) + v_c]/(|\Delta\bar{H}_{\text{mix}}|/RT) \quad (\text{II-23})$$

In the case of the propanol/heptane solution, the value of the ratio is infinite, since $\Delta\bar{H}_{\text{mix}}$ is close to zero. Thus entropy will clearly dominate in that case. It was above determined that for pyridine, $\Delta\bar{H}_{\text{mix}} = -4000 \text{ J/mol}$. 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 II-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:

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

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 II-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 II-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 (II.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 (II.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. The implications of the different theories will also be the subject of a forthcoming paper.

II.5.0 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.

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Table II-1
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 II-2
Values of the Parameters α and γ in Equation II.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 II-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 II-2. Correlation of solvent Donor Numbers⁵¹ and their heats of mixing with p-fluorophenol⁵⁰.

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

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

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

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

Figure II-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 II-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 $(\partial \Delta G_e / \partial n_s)_{T,P}$ according to the model. The dashed line shows the value of $(\partial \Delta G_e / \partial n_s)_{T,P}$ 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.

III. ELASTIC PROPERTIES OF COALS - A STUDY BY MERCURY POROSIMETRY, AND ITS IMPLICATIONS

III.1 INTRODUCTION

Mercury porosimetry is a widely used technique for examining the pore structure of solids¹. The method has found frequent application in examination of coals²⁻⁵. Recently, questions have been raised about the interpretation of surface area and porosity measurements on raw coals, since they do not have a rigid pore structure, but rather behave as a colloidal gel, with water as the solvent^{6,7}. The "porosity" which is determined by mercury porosimetry and gas adsorption techniques is generally of interest with respect to rates transport of chemical species through the coal during high temperature processing. Such porosity values might not be a quantitatively reliable basis for calculating transport rates, however, because the structure of the coal gel can be profoundly altered by heating and/or solvent exposure well before any reactions take place (the same is not the case for a highly heat-treated char which has a much more rigid structure). Nevertheless, mercury porosimetry is still widely applied to raw coals. Some aspects of the measurements, and what they can reveal about the macromolecular structure of coals, will be examined here.

In the classical application of the mercury porosimetry technique, the volume of mercury that can be forced into the pores of a solid in any particular range of pressure gives an indication of the porosity in a certain range of sizes. When the technique is applied to coals, quantitative interpretation of the results presents several difficulties. One problem is associated with the fact that the "pores" are not truly cylindrical, but rather slit-shaped⁵. Another is the fact that the *apparent* increase in mercury uptake by coal at higher pressures (>10 MPa) is actually due to the compression of coal structure. Because of this, the application of mercury porosimetry to pore characterization of coals has usually involved corrections for this compression. The need for the compressibility correction has normally been operationally defined by a region in which mercury uptake curves are more or less linear in applied pressure²⁻⁴.

The compressibility of a solid is formally defined by:

$$\kappa = -(1/V)(\partial V/\partial P)_T \quad (\text{III.1})$$

where V is sample volume and P is 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.

III.2 EXPERIMENTAL

The coals that have been examined in this part of the study include two Argonne Premium Coal Samples⁸ - Illinois No. 6 and Pittsburgh No. 8. Additionally, 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 coals are presented in Table III-1. Samples that were studied were generally fairly fine powders, -20 +100 mesh in size.

Mercury "porosimetry" (compression and decompression) was carried out using a standard Quantachrome Instruments mercury porosimeter. This instrument can be used to scan mercury pressures up to 227 Mpa (33,000 psia). Normally the instrument scans at 45.5 MPa/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 "uptake volume" will be used to denote the measured decrease in mercury volume with increase in applied pressure. It is recognized that this term does not necessarily reflect the actual physics of the process, in that actual penetration of pores is not the main process of interest. No interpretation of the low pressure part of the intrusion curves will be presented, since the actual porosity information is of no interest here.

III.3 RESULTS AND DISCUSSION

Figures III-1 through III-3 show typical results from mercury "porosimetry". The zero mercury uptake reference point was defined at an initial applied mercury pressure of 0.4 MPa.

Figure III-1 shows the effect of sample drying on the results that are obtained. The dried lignite samples (whether dried at room temperature or at 373 K) show a higher uptake of mercury at low pressures. Upon drying, the lignite "gel" structure collapses, but significant amounts of mesoporosity and macroporosity survive and are, in fact, created by the drying. Overall, the Glenn

Harold lignite structure shrinks by almost 40% by volume upon drying, so the changes in the porous structure are profound, and it is presumably not a simple matter of removing water from pre-existing pores that results in the greater mercury uptake ⁶. The other notable feature in these results is that there is always a hysteresis evident in the compression-decompression cycles. This hysteresis was also noted in all other results obtained in this study.

In this study, the main focus is on the high pressure, fairly rectilinear portions of the compression curves. In the case of the Glenn Harold lignite, this region is seen to begin at almost 50 MPa. In as-received Pittsburgh No. 8 coal (Fig. III-2), the linear portion of the curve obtains at about 100 MPa, whereas in the as-received Powhatan No. 5 coal (Fig. III-3), it was also seen above 50 MPa. There was a fair deal of variability observed in this onset point. As noted above, it has been customary to associate the uptake of mercury in this high pressure range with the compression of the sample. A blank run ascertained that the compressibility of the measurement apparatus itself was negligible compared to that exhibited by the sample in this range.

As a thermodynamic property, the bulk compressibility would not be expected to be path-dependent. Thus the observed hysteresis, such as displayed in Figures III-1 through III-3 and seen in all other experiments we performed, must be viewed as inconsistent with simple interpretations of the high pressure behavior in terms of simple reversible compressibility.

Hysteresis behavior is not uncommon in mercury porosimetry work¹. A classical explanation of this sort of behavior is the so-called "ink-bottle" model. According to this model, pores have narrow necks that preclude their filling until high pressures, but have wide bodies, which prevents their emptying until low pressures. Alternatively, hysteresis has been explained by differences in advancing and receding mercury contact angles in the solid.

Thus there is a fundamental inconsistency not only between the usual, simple interpretation of the high pressure compression behavior in coals and the existence of hysteresis behavior, but also between the generally accepted models of hysteresis, which are based upon pore penetration, and the conclusion that pore penetration is not significant in determining uptake at high pressures. While we have serious reservations about the value of quantitative measurements of the pore structures of raw coals and thus do not seek to clarify these issues for that purpose, we do believe that these

results help illustrate some interesting features of coal network structure behavior.

The nature of the apparent hysteresis in the pressure range from 20 MPa to 227 MPa was further 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 shown in Figure III-4. It should be noted that in this case, the starting sample was "wet" (as received) and so there is little penetration of "porosity" evident in the first cycle. Again, this is of little concern here, where porosity was not the main issue of interest. The same decompression cycle was always traced out. Such behavior has also been observed in a very different kind of materials (e.g. alumina-silica gel¹). Also, after the first compression-decompression cycle, all subsequent compression-decompression cycles were essentially identical, implying that the process had become reversible.

The fact that pre-drying of a sample does not alter the above conclusions is borne out by the results of Figure III-5, obtained on a pyridine pre-extracted and pre-dried sample. Here, a more "normal" pore penetration behavior is seen, together with irreversible uptake. Again, all decompression curves are coincident, and all subsequent compression curves are likewise coincident.

Since in the undried sample of Figure III-4, the first compression curve was not parallel to the second and subsequent compression curves not only in the low pressure range, but also in the linear 20 to 227 MPa range, this suggests that there are irreversible changes occurring in this range of pressure. These might have little to do with actual pore filling, and could even involve loss of some of the moisture from the sample. Since this was not a key aspect of the present study, no attempts were made to verify this hypothesis.

In Figure III-5, all uptake curves are coincident above about 80 MPa. In classical porosimetry, the difference between the first and all subsequent compression cycles is often attributed to an irreversible uptake of mercury in the pores of the coal. The fact that the uptake curves for the first and subsequent cycles coincide in the high pressure range is not at variance with this. The classical interpretation would be that the pores were all irreversibly filled during the first cycle, and the high pressure behavior is attributable to the reversible compression of the sample. There is, however, also the possibility of permanent damage to the pore structure, as has been established to occur in

other materials^{1,9}. There is no way to easily distinguish from these results whether there has been irreversible filling of pores or actual physical damage. Again, the classical interpretation of the high pressure behavior disregards the existence of the hysteresis loop.

Since there is a high degree of reversibility shown on repeated cycles, the major high pressure-induced changes that occur on the second and third compression cycles, and give rise to hysteresis, are not due to any permanent alterations in the gross macroscopic structure of coals (i.e. collapse of macroscopic voids). Also, as has been noted before, the relative linearity of the uptake with pressure in the high pressure region (in virtually all cases) seems to argue in favor of the uptake involving compression rather than true pore penetration. It is more likely that reversible changes in structure are being caused on a molecular level. The coal material itself can be reversibly pushed into a tighter packing arrangement by the applied pressure. The resulting hysteresis behavior could be attributable to the slow kinetics of relaxation of some parts of the structure, upon decompression. It might even be that a certain critical driving force, that depends upon external pressure, is needed in order for relaxation to occur.

We have recently presented evidence for thermally- or solvent- assisted relaxation of raw coals. It appears that coal structure is initially at equilibrium relative to its geological conditions of formation, but not to laboratory conditions^{10,11}. While not truly equilibrium configurations relative to laboratory conditions, the as-mined configurations *appear* to be such because the kinetics of relaxation are immeasurably slow unless the structures undergo significant perturbations. We caused these perturbations by heating or solvent exposure of the samples. In the case of the present decompression experiments, the relaxation of some high pressure-induced configurations can perhaps occur at a measurable rate only if the driving force is high enough, as a result of a much lowered pressure around the sample.

It was thus hypothesized that the hysteresis loop obtained at high pressures may well be attributable to a kinetic effect, reflecting the speed with which the coal network relaxed during decompression. Several experiments were performed to test this hypothesis. In one series, decompression of a freshly compressed sample (227 MPa) was permitted to occur down to various pressures between 20 and 227 MPa, followed immediately by recompression. The result was

always a very close retrace of the *decompression* curve between these pressures. This demonstrated that there is a reversible component of compression (uptake does continually decrease with decrease in pressure) that acts independently of some more difficult-to-reverse component.

On the other hand, decompressing the samples to ambient always closed the hysteresis loop, after the first compression/decompression cycle (see Figures III-4 and III-5). The kinetics of restoring the coal structure to near its new atmospheric pressure equilibrium state can be quite fast near ambient pressure, i.e. no delay was needed before starting the next cycle in the case of Pittsburgh No. 8 coal, and a few hours of ambient pressure exposure are needed for Illinois No. 6 coal.

Further information as to the nature of the hysteresis came from another type of experiment. These tests involved permitting a sample to stand at 34.5 or 68.9 MPa for two hours while continuously recording the "uptake" or "extrusion" volume. The results indicated that at these intermediate pressures, there is apparently no measurable rate of mercury extrusion; "uptake" values did not significantly 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 "uptake" value obtained, closing about a quarter of the gap between the decompression and compression curves. Thus it appears that the magnitude of the compression value is determined by two factors - the pure, bulk compressibility and the kinetics of some kind of slow structural reorganization.

A similar hysteresis behavior was observed by another worker using very different experimental techniques. Brenner¹² 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:

$$E = 3B (1 - 2\nu) \quad (\text{III.2})$$

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 coal¹³. 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 ¹⁴. If the lower range of values for Poisson's ratio is correct, then value of E should be numerically quite close to the value of the bulk modulus B , and in any case E will always be of the same order of magnitude as B .

The measurements of Brenner¹² 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 slow or impossible even at zero stress. On repeated cycles, the recovery to the new volume can be fast 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, however, 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.

The above observations raise the question as to whether our compression or decompression value of B is "correct". Similar questions come up often in mechanical testing of polymeric materials, in which the time history of testing is important. The behavior we observe is characteristic of a macromolecular network with high internal viscosity. This normally forces distinguishing between dynamically and statically determined mechanical properties, and the "correct" value depends entirely upon the intended use of the data. In the case of coals, there is the

question of whether to use the compression or decompression value of B to “correct” classical porosimetry results. Use of the initial compression may be justified. The slow relaxation upon decompression gives a lower apparent high-pressure compressibility, but the compression upon initial intrusion would, however, not be subject to the same kinetic limitations, as noted above.

Table III-2 gives values for both compression and decompression values of compressibility that we obtained from the highest pressure linear portions of the respective curves. 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. For comparison, if a coal density of 1.3 g/cc is assumed, then our apparent values of B from the *compression* cycles range from 2.6 to 8.5 GPa, which are in good agreement with the values obtained by others of 4.3 to 13 GPa², 4.6 to 9.0 GPa³, and 7.7 GPa⁴.

The values for the four lignites 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 internal voidage and, therefore, compressibility. In addition, the structure of the coal is relaxed by pyridine swelling¹⁵.

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.

The shear modulus of a material (G) is defined by (shear stress / shear strain) and is related to the other previously quantities as well:

$$E = 2G (1 + \nu) = 3B (1 - 2\nu) \quad (\text{III.3})$$

As has been shown by Larsen and Kovac¹⁶, application of measured or estimated values of G or E for coals to rubber elasticity models gave seemingly unrealistic values of molecular weight between crosslinks. In their study E was typically of order 10^9 Pa, and thus from equation (III.3) and the values of ν reported above, G was of the same order of magnitude. In fact, by use of (III.3), and by using an approximate value of density, $\rho=1.3 \text{ g/cm}^3$, it can be clearly seen that the results of Table III-2 also will yield estimates of E or G which are of the same order of magnitude.

Thus there is great consistency among all of the data that have been produced on the 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 state¹⁷. Even in the presence of water, a known plasticizing agent for transport in coals⁷, the coals are seen to be glassy, rather than rubbery. This is of little surprise, considering that the fracture behavior of wet lignites is still much more glassy than it is rubbery.

Coal 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 samples¹². 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 crosslinked¹⁷. 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. From our results, it is clear that coal remains quite glassy at room temperature, even after pyridine extraction. The structure will be rubbery only in the presence of a good solvent. Also, 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 in the compression-decompression cycles. The relaxation of a glassy structure would be expected to be observable only over a very long timescale, if the driving force for relaxation is small. Again, the creep behavior of coals is known to be characterized by long timescales^{18,19}. It appears that only when the structure is far out of equilibrium with respect to prevailing conditions, will it be driven towards a new configuration on the timescale of the experiments performed here.

III.4 CONCLUSIONS

It has been noted that there is no single, distinct measure of the bulk modulus of coals measurable in mercury porosimetry experiments. As with other modulus measurements on coal, there is a hysteresis associated with these measurements of bulk modulus. The hysteresis is presumably associated with the time-dependent reorganization of its macromolecular network structure, in response to the applied stresses.

The above results confirm what has been inferred from other types of measurements on the porosity and surface areas of coals. It has been concluded that because coal behaves as a viscoelastic gel (as opposed to a rigid solid) on the timescales of interest, then many of the "classical" characterizations of porosity might provide a misleading picture of the structure of coals. Here, it has been specifically concluded that "corrections" for coal compressibility, commonly used in mercury porosimetry work on raw coals, are subject to some uncertainty from this source. At the higher temperatures of actual coal processing, and especially in the presence of solvents, there is an even greater uncertainty concerning the applicability of these measurements, since the physical structure of the coal can be dramatically altered^{6,7,10,11}.

The apparent bulk moduli of coals do not vary widely with rank. The pre-extraction of the coal or presence of water in the coal affect the moduli by only a small amount. Water is an effective swelling agent for low rank coals, swelling lignites by 30 to 40%, relative to a dry state⁷. There is, however, no evidence from the values of bulk modulus obtained here that the rubbery state of the coal, as is attainable in pyridine swelling of higher ranks, exists in the wet lignites. We therefore indirectly support earlier workers²⁰ in their conclusion that the effect of moisture content on dynamic moduli is small.

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Table III-1--Ultimate Analyses of 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
Pittsburgh No. 8 HVBit. ^a	75.5	4.8	1.5	2.2	9.3	6.7	1.7	1.7
Illinois No. 6 HVBit. ^a	65.7	4.2	1.2	4.8	15.5	8.6	8.0	10.3
Powhatan No. 5 HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1	2.0

•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.

a- Argonne National Laboratory Premium Coal Samples⁸.

Table III-2--Summary of Compressibility Measurements

<u>SAMPLE</u>	<u>Pretreatment</u>	<u>Compressibility, κ/ρ (cc/g-Pa $\times 10^{10}$)</u>	
		<u>Compression</u>	<u>Decompression</u>
Beulah lignite	As-received	1.7	0.35
	Dried ^a	1.9	1.2
	"	<u>1.4</u>	<u>0.69</u>
	(Mean)	1.7	0.95
	Heated ^b	2.2	0.90
Freedom lignite	As-received	1.4	0.97
	Dried ^a	1.4	1.4
	Dried ^c	1.4	0.83
	Heated ^d	1.7	1.0
Glenn Harold lignite	As-received	1.8	0.83
	Dried ^a	1.1	0.61
	Dried ^c	1.8	1.0
Gascoyne lignite	As-received	1.5	0.69
	Dried ^a	1.4	0.69
	"	1.4	0.69
	"	<u>1.4</u>	<u>0.42</u>
	(Mean)	1.4	0.60
	Dried ^e	1.2	0.69
Pittsburgh No. 8 HVBit. ^a	As-received	0.90	0.64
	"	<u>1.2</u>	<u>0.58</u>
	(Mean)	1.1	0.61
	Pyridine Extracted	1.8	0.98
Illinois No. 6 HVBit. ^a	As-received	2.54	0.81
	"	2.95	0.98
	"	<u>2.89</u>	<u>0.92</u>
	(Mean)	2.79	0.90
Powhatan No. 5 HVBit.	As-received	1.2	0.76

a. Room temperature dried for 30 days at 0% relative humidity.

b. Heated at 573 K for 30 minutes.

c. As in a., plus 30 minutes at 373 K.

d. Heated at 573 K for 24 hours.

e. Dried at 373 K for one hour.

Figure III-1. Results of first compression-decompression cycles on Glenn Harold North Dakota lignite. Mercury uptake is relative to a zero uptake reference point at an applied mercury pressure of 0.4 MPa. The sample marked 100% RH, 298 K refers to a sample equilibrated over pure water at 298 K for 30 days; the sample was not dried prior to analysis, but there was a possibility of moisture loss, relative to the as-mined condition, due to the difficulty of maintaining true 100% relative humidity in a chamber which had to be periodically opened. The sample marked 0% RH, 298 K was dried at room temperature for 30 days over concentrated sulfuric acid. The sample marked 0% RH, 298 K+0% RH, 373 K involved room temperature drying as described above, followed by one hour at 373 K. Arrows on the curves indicate whether the experiment involved compression or decompression.

Figure III-2. The results of a single compression-decompression cycle performed on Pittsburgh No. 8 high volatile bituminous coal. The sample was used as-received.

Figure III-3. The results of a single compression-decompression cycle performed on Powhatan No. 5 high volatile bituminous coal. The sample was used as-received.

Figure III-4. The results of multiple compression-decompression cycles performed on Illinois No. 6 high volatile bituminous coal. The sample was used as-received (undried). The arrows indicate whether the experiment involved compression or decompression. All decompressions followed the same path. Long dashes- first compression; short dashes, second compression; dotted curve, third compression.

Figure III-5. The results of multiple compression-decompression cycles performed on Pittsburgh No. 8 high volatile bituminous coal. The sample was pyridine extracted and dried at 373 K prior to analysis. The arrows indicate whether the experiment involved compression or decompression. All decompressions followed the same path. Long dashes- first compression; short dashes, second compression; dotted curve, third compression.

IV. THE ELASTIC PROPERTIES OF COAL STUDIED BY DYNAMICAL MECHANICAL ANALYSIS

IV.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) techniques¹³. 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 Wert⁷⁻¹⁰ 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.

IV.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 ($>300^{\circ}\text{C}$), 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}.

IV.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 sample¹⁴. 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 δ " 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 IV-1, 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 IV-2. 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 IV-1 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 IV-3). This transition involves an irreversible relaxation of the coal structure^{16,17}. For convenience, the DMA and DSC difference spectra are plotted together on Figure IV-4. 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 near 275 to 300 °C. 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 IV- 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 IV-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.

Finally, Figure IV-7 shows the combined DMA and DSC results for heating of Powhatan No. 5 coal. There is an interesting event that reveals itself in the DSC as an irreversible endotherm near 300 °C. There is no clear behavior in the DMA spectrum at that point, but rather, a general rise in the $\tan \delta$ curve around that point. This illustrates the difficulty faced by researchers who seek to rely upon only one particular tool to identify phenomena in coal. The evidence for significant events may be much clearer using one tool than another, and different analysis tools work better for different samples. Generally speaking, DMA spectra are only obtainable and useful at temperatures below those needed for pyrolysis.

IV.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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Figure IV-1. 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°C/min.

Figure IV-2.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 IV-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 IV-4. Details of the DSC difference spectrum and the DMA spectrum for Pittsburgh No. 8 coal. The DSC curve was obtained at 8 K/min and the DMA at 4 K/min.

Figure IV-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.

Figure IV-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 IV-7. Difference DSC spectrum and DMA spectrum for Pocahontas No. 5 HVB coal.
The difference DSC spectra were obtained at 8 K/min, and the DMA at 4 K/min.

V. THE ROLE OF WATER IN COAL STRUCTURE

V.1. INTRODUCTION

This study is concerned with a basic scientific question concerning the properties of coal— to what extent is the ability of coal to hold moisture a manifestation of the well-known ability of coal to swell, when exposed to good solvents? The question implies that the long-held belief that coal holds a significant portion of its moisture by classical capillary condensation processes, is possibly in error. This seems to be a very real possibility for low rank coals. The question addressed here is- to what extent do coals of any rank exhibit the kind of shrinking/swelling colloidal behavior of concern?

The fact that coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain is well established¹⁻⁴. The fact that water can be held by polar groups within the structure of coal also is well documented⁵. There is considerable experimental evidence that there are at least two mechanisms by which water is held in coals. Differential scanning calorimetry (DSC) has suggested that water is held in a tightly bound "unfreezable" form as well as in a bulk "freezable" form^{6,7}. Another study, based on proton NMR examination of the water associated with a brown coal, reached similar conclusions⁸. The water is present in a free phase and a bound phase, the latter water molecules having some "mobility" and an ability to exchange with one another on a timescale of a typical experiment (order of fractions of a millisecond). The apparent freezing temperature of the bulk water is a bit below 273K (consistent with other results^{6,7,9}), and decreases with heat treatment of the coal⁸.

There has also been indirect evidence from dehydration experiments to support the view that water exists in several forms in coal. Variations in the extent of shrinkage brown coal per unit of moisture removed have been interpreted in terms of the role of different types of moisture in coal¹. The isosteric heat of moisture sorption on coals has been observed to be a function of amount of water in the coal¹⁰. The fact that hysteresis in coal moisture sorption

isotherms must be determined by shrinkage and swelling effects¹¹ complicates interpretation of such data, however. Perhaps one of the simplest illustrations of the multifaceted nature of water in coals has been provided by the observation that the dehydration behavior as a function of time is not particularly simple¹²⁻¹⁴. There is a suggestion from recent data that the process of moisture loss may be second order¹³ or of apparent order between 1.3 and 2.4 relative to remaining water in the case of bound water¹⁴.

It thus appears that water is retained tightly and in several forms in coals and that coal behaves like a swellable colloid in the presence of water. These two facts have not yet been merged into a unified theory of water retention in coals. Here we examined quantitatively the question of the shrinkage phenomenon that occurs upon drying. Is it simply a matter of removing the volume of the water, irrespective of the nature of water-coal interactions? This certainly seems to be the case in lignites, in which the microporosity disappears upon drying. The consequence of this would be that coal-coal interactions most likely replace coal-water interactions.

V.2. EXPERIMENTAL

The data to be considered in this paper were obtained by a very simple technique. The data were all obtained on the coals shown in Table V-1. There were many different sources for these samples, and the samples were available in many different conditions. Some had been carefully stored in large lump form, and were ground immediately prior to use. These had dried to only a limited extent prior to testing. Others had been stored in various ground forms, and had dried somewhat before use. The conclusions concerning shrinkage upon drying were not found to be particularly sensitive to the initial condition of the samples used for the tests. This will be established below. This does not, however, imply that the changes that occur upon drying are minor; quite the opposite is true, as we have already noted⁴.

The measurements to be reported here involved drying the coals in a vacuum oven, so as to prevent oxidation during drying. The samples were typically ground to less than 600 μ m particle diameter and measured into thin glass tubes, quickly centrifuged so as to settle the

samples, and then they were placed into the vacuum oven at either room temperature (298K) or at 373K. The samples were then tracked with respect to mass loss and volumetric shrinkage. The precision of the volumetric shrinkage measurements is no better than 2% (absolute), the mass loss measurements are good to 0.1%.

V.3. RESULTS

The volumetric shrinkage of the samples was excellently correlated with the moisture loss from the samples. This is readily seen from Figure V-1, which was obtained by drying the coals of Table V-1 at 373 K. The correlation for the data can be expressed as:

$$\text{Volumetric Shrinkage (\%)} = -0.162 + 0.863 (\text{Moisture Loss, \%})$$

A second series of measurements was performed on a Beulah lignite (the first sample in Table V-1). The lignite was allowed to partially dry at room temperature over various aqueous solutions of differing dessicant strength (e.g. H_2SO_4 , KCl, see ref. 4). The partially dried samples were then subjected to the same type of tests described above, both at room temperature and at 373 K. These results are shown in Figure V-2. The same type of linear trend is seen as in Figure V-1. There is a bit of a tendency for the shrinkage to be larger on the initially wetter samples dried at 298 K, but the differences are small enough so that their significance is open to question, given the uncertainty in the measurements.

As before, the correlation shown in Figure V-2 is seen to be well approximated by a linear relationship:

$$\text{Volumetric Shrinkage (\%)} = a + b (\text{Moisture Loss, \%})$$

In the case of the results of Figure V-2, $a = 0.803$, $b = 0.900$. Other similar tests were performed at room temperature with Gascoyne lignite ($a = -0.182$, $b = 1.00$), with Freedom lignite ($a = 0.230$, $b = 1.07$) and with Glenn Harold lignite ($a = 0.386$, $b = 0.938$). These results suggest that earlier reported shrinkage data⁴, which were obtained by measurements on larger blocks of coal, might have been influenced by the existence of residual mechanical stresses within the large sample blocks. The earlier results had not as clearly defined a linear

relationship between moisture removed and volumetric shrinkage, but were otherwise in reasonable agreement with the present results.

The volumetric shrinkage relationship shown above may be recast as:

$$(M_c + M_w)/(V_c + V_m) = a' M_c/(V_w - V_p) + (a' + b) M_w/(V_w - V_p)$$

where M_c is the mass of dry coal and M_w is the mass of water in the sample, the V 's refer to the volumes that these materials occupy, and V_p is the volume of porosity created upon drying. It should be noted that in this representation, the numerical value of b is as above, and $a' = a/100$. For all reasonable values of the parameters, the first term on the right hand side is generally small compared to the second, and will be neglected. Also $b \gg a'$. The left hand side is the bed-moist bulk density of the coals, and has been earlier measured to be of order 1.2 g/cc⁴. This leads to the conclusion that:

$$1/(1.2) = 0.833 \text{ cc/g} = 1/b - V_p/(bM_w)$$

where the density of the water in coal is taken to be roughly its bulk density (1 g/cc). Thus the porosity of the dried sample may be calculated from:

$$V_p/M_c = (M_w/M_c) (1 - 0.833 b) \text{ cc/g}$$

For a typical initial lignite moisture content of 30%, $M_w/M_c = 0.43$, and the porosity of the dried coal would be estimated as between 0.11 cc/g for the Beulah lignite and 0.05 cc/g for the Freedom lignite. The calculations are crude, but the results are in quite reasonable agreement with measurements of the porosity of dried lignites¹⁵. The ratio of volumetric porosity development to volumetric moisture loss is given by an expression $[1 - bf_m/f_v]$, where f_m is the mass fraction moisture in the coal, and f_v is the volume fraction of moisture in the coal. Again, linear volume additivity will almost surely not apply, but this equation suggests that for reasonable estimates of the parameters (f_m/f_v should be just a bit more than unity) and the measured values of b , the porosity development will not be nearly as great as the volumetric loss of moisture. Applied to a high volatile bituminous coal of 1.5% moisture content and initial density of 1.3 g/cc, the final porosity prediction would be unreasonably low (0.005 cc/g), so the conclusion is that the porosity had to already be present, rather than being created by moisture loss. This is obvious if one considers even from a simple volumetric pore filling perspective how much porosity could be created by loss of 1.5 % moisture in the form of 1

g/cc bulk water; there is not nearly enough volume lost so as to create porosity of order 0.1cc/g, as is typically reported¹⁵.

What the above results imply is that the lower rank coals will behave quite like ordinary colloidal gels. They cannot completely collapse to a zero porosity solid upon drying. The higher rank coals also show distinctly colloidal shrinkage behavior, but have in coalification collapsed to a point at which open porosity has already been created. The fact that the structure of the coals in all cases significantly expands to accommodate moisture suggests that simple capillary condensation models of moisture retention are inadequate for describing the thermodynamics of the situation. There must be significant thermodynamic consequences associated with the elastic deformations of the coal's network structure that are not properly allowed for in a capillary condensation approach. Such issues have been reviewed in connection with solvent swelling measurements of coal structure (see Chapter II and ref. 16).

V.4 THE SOLVENT SWELLING BEHAVIOR OF COALS AND ITS RELATIONSHIP TO MOISTURE RETENTION

The fact that water is a good swelling agent for low rank coals has led us to suggest that the moisture content of coals is essentially controlled by solvent swelling type processes. We have proposed that the swelling of coals in good solvents is governed by a process that has been hypothesized to involve a titration of specific interaction sites (see Chapter II or ref. 17). The swelling of coals in specifically interacting solvents is better examined in terms of the swelling number (N_s) than the volumetric swelling ratio (Q) itself; $N_s = (Q-1)/V_s$, where V_s is the molar volume of the solvent, and thus N_s represents the number of titratable sites per unit volume of coal. Thus N_s simply represents the molar uptake of solvent per unit volume of dry coal. The values of N_s are shown for four solvents in Table V-2 (the solvent swelling ratios were measured as described elsewhere¹⁸). Not shown are data on toluene and hexane, which are ineffective in these lignites (both give $N_s=0$).

It appears on the basis of these data that the electron donor strengths of DMSO, pyridine

and n-butylamine are all high enough so that the coal-coal interactions are dissociated. There is no systematic variation in solvent uptake with donor number for these solvents. Furthermore, as Chapter II showed, their donor number are all above the generally observed threshold values. The swelling number variation observed for the strong solvents of Table V-2 no doubt has origin in factors other than electron donor strength discussed earlier e.g. solubility parameter match.

Water, for which a reliable donor number has not been established, might be near the threshold electron donor strength or below it. It might give a lower swelling number than do the other higher donor number solvents because of an inability to dissociate some coal-coal interactions that the other solvents can. Alternatively, it might be that water, pyridine, DMSO and butylamine all interact with all specific interaction sites, and that water merely is a poorer solvent for non-specific interactions with the coal, because of its large solubility parameter, compared with the other solvents. We favor the first explanation for reasons based upon the heats of wetting, to be discussed in a later chapter.

We also feel that the experiments in which swelling was performed in ethanol support the view that water is not an effective swelling agent because of a low electron donor ability. Ethanol is also a relatively weak electron donor, but has solubility parameter which is closer to that of the other solvents than water. The ethanol is, however, an extremely poor swelling agent for the coal. The absolute extent of swelling is comparable to that provided by water, but the molar uptake is considerable lower in all cases. This strongly suggests that water is not as low in donor number as the low end of the range suggested for it in Table V-2. Water binds to more specific interaction sites than does ethanol, or in cases not shown here, does THF.

In that case, the difference between water and the other better swelling solvents is understood in terms of a distribution of different sorption site strengths within the coal, which results in some coal-coal interactions that water cannot effectively solvate. There is a competition between solvents and inherent electron donors in the coal for electron acceptor sites in the coal.

The actual, absolute swelling ratios for the different solvents are also shown in Table V-2.

These values are for coals that had been dried for 3 hours at 100°C, so there is some loss of moisture capacity in the coals, compared with the values shown in Figure V-1. Since the comparison of swelling ratios is performed on a consistent basis, this is unimportant. It is clear that in absolute terms, swelling in water is quite modest (<20%) compared to swelling in stronger solvents, which often give values in excess of 100%. Thus the limiting factor in moisture retention is clearly not the ability to stretch the network structure to accommodate the water, since this stretching occurs to a much greater extent with other solvents. It is clearly the thermodynamics of solvent swelling that limits the extent of swelling, and this is related to solvent strength.

As noted in previous chapters, the presence of moisture does not assure the attainment of a rubbery state. It was noted that wet lignite had bulk compressibility of a rigid, crosslinked solid. While water is clearly a swelling solvent for coal, it is not nearly as good as pyridine, for example. As noted above, pyridine has the ability to plasticize coal to the extent that it becomes a rubbery solid.

V.5 CONCLUSIONS

The results of this part of the study confirm that lignites have highly deformable gel-like structures, that shrink and swell roughly in proportion to the amount of moisture that they gain or lose. There is little basis for claiming that capillary condensation plays a major role in moisture retention by lignites. The same general behavior is exhibited by higher ranks as well, though the fraction of true porosity appears to be larger in those coals.

On the basis of solvent swelling measurements, it appears that water might not be able to "titrate" as large a number of specific interaction sites in coal as are other solvents. In terms of the proposed strategy of using crosslinking reactions to render the structure of low rank coals less swellable, and thus less prone to moisture regain, the present results suggest that this process occurs already in ordinary drying. It appears that some very difficult-to-dissociate coal-coal interactions are created upon the first drying the coal. Whether these are covalent crosslinks or non-covalent crosslinks is difficult to assess from the present data. Because in

our earlier work⁴ we found that the loss of moisture retentive capacity occurred even upon room temperature drying, under which conditions we feel reactions to be unlikely, we believe that the crosslinks are at least partly of a non-covalent nature.

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Table V-1--Ultimate Analyses of 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 ^a	65.6	3.6	1.1	0.8	11.0	17.9	29.4	29.4
Freedom lignite ^a	63.5	3.8	0.9	1.4	6.1	24.3	27.9	18.7
Glenn Harold lignite ^a	61.1	4.4	0.8	0.4	7.4	25.9	34.5	34.5
Gascoyne lignite ^a	60.9	4.2	0.6	1.4	8.2	24.7	30.7	28.9
Beulah lignite ^b	65.9	4.4	1.0	0.8	9.7	18.2	32.2	8.5
Texas lignite (PSOC1036) ^c	61.5	4.7	1.4	1.3	12.5	18.5	31.8	11.4
Belle Ayr Subbit.	69.3	4.4	1.0	0.5	10.3	14.5	30.3	20.9
Big Brown Subb.(PSOC785) ^c	62.8	4.6	1.1	1.1	12.6	17.8	27.8	12.3
Montana Subbit.(PSOC837) ^c	57.8	4.3	0.8	0.7	11.9	24.6	17.0	13.7
Bruceton HVBit. ^d	80.4	5.3	1.6	1.0	4.6	6.7	1.7	1.5
Powhatan HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1	2.0

•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.

a- Grand Forks Energy Research Center lignite sample bank.

b- Argonne National Laboratory Premium Coal Samples.

c- Pennsylvania State University Coal Sample Bank.

d- U.S. Bureau of Mines Standard Sample.

**Table V-2 -- Relative Swellabilities of Lignites in Different Solvents
(in mmol/gram dry coal)**

<u>Coal</u>	<u>Water</u>	<u>DMSO</u>	<u>Pyridine</u>	<u>n-Butylamine</u>	<u>Ethanol</u>
Beulah	10.5 (1.19)	12.9 (1.92)	11.2 (1.9)	12.5 (2.24)	3.4 (1.18)
Freedom	8.8 (1.16)	17.0 (2.24)	10.1 (1.8)	13.1 (2.30)	3.9 (1.23)
Glenn Harold	7.7 (1.14)	15.2 (2.09)	12.3 (2.0)	15.1 (2.50)	1.7 (1.10)
Gascoyne	7.7 (1.14)	13.7 (1.98)	9.9 (1.8)	18.0 (2.82)	0.9 (1.05)
Electron Donor Strength*	18-33	29.8	33.1	57	20
Solubility Parameter (cal/cc) ^{1/2}	23.5	13.0	10.7	-	12.8

• Values in parentheses are actual measured swelling ratios (mean values in some cases).

* Values from V. Gutmann, *Electrochimica Acta*, 21, 661 (1976) and *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, 1978, with the value for n-butylamine estimated from values for similar compounds.

Figure V-1. Volumetric shrinkage upon drying for coals of various rank, ranging from bituminous to lignite (see Table V-1 for coals; includes all except the Wyodak and Pittsburgh No. 8). All drying experiments performed in a 373 K vacuum oven.

Figure V-2. Volumetric shrinkage of Beulah lignite upon drying at two different temperatures. Each point represents the result of a separate experiment in which the lignite started with a particular moisture content, as indicated on the abscissa. The shrinkage value reported is that for drying from the starting moisture content to a fully dry state.

VI. THE DRYING BEHAVIOR OF LIGNITES AND ITS IMPLICATIONS FOR MOISTURE RETENTION THEORIES

VI.1. INTRODUCTION

The fact that coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain was clearly established in the previous chapter and in other works¹⁻⁴. We have hypothesized that water behaves as a typical specifically interacting swelling solvent, consistent with earlier conclusions that it is the polar groups in coal that hold most of the moisture⁵. Despite the fact that there is considerable experimental evidence for at least two mechanisms by which water is held in coals (tightly bound "unfreezable" and bulk "freezable"^{6,7}, or "mobile" and "bound"⁸), we saw little evidence for this multiform retention in the shrinkage and swelling behavior.

There has also been indirect evidence from dehydration experiments to support the view that water exists in several forms in coal. Slight variations in the extent of shrinkage brown coal per unit of moisture removed have been interpreted in terms of the role of different types of moisture in coal¹. The isosteric heat of moisture sorption on coals has been observed to be a function of amount of water in the coal¹⁰. The fact that hysteresis in coal moisture sorption isotherms will be affected by shrinkage and swelling effects such as we observed complicates interpretation of such data, however¹¹. The dehydration behavior of coals as a function of time is not particularly simple, also possibly indicating different types of sites¹²⁻¹⁴.

In this chapter, we present results of experiments that we use to explore these issues further.

VI.2. EXPERIMENTAL

The data to be considered in this chapter were obtained by a variety of techniques. The data were all obtained on the North Dakota lignites shown in Table V-1 of the previous

chapter. These samples had been stored in lump form, in the presence of a small amount of liquid water, to minimize drying and oxidation prior to use.

The measurements reported here involved drying the coals in two ways. The first involved placing finely ground, wet samples into controlled temperature, zero relative humidity containers, and then periodically weighing, to obtain simple mass loss kinetics, as a function of temperature. In another experiment, a sample of finely ground wet Beulah lignite was placed in a thermogravimetric analysis (TGA) system, and the kinetics of mass loss monitored as a function of decreasing relative humidity in the chamber; the sample was permitted to equilibrate at one relative humidity, then the new, lower humidity was induced (using salt solutions in the chamber), and the mass loss was monitored until a new equilibrium was established.

Classical water sorption isotherms were measured on finely ground samples, by ordinary gravimetric techniques.

Finally, differential scanning calorimetric (DSC) measurements were performed on Beulah lignite samples, to verify the concept of a distribution of sites for holding moisture in the coal. These experiments were performed by placing initially wet Beulah lignite samples into DSC pans that had holes in them to provide facile loss of water from the pans. Samples were heated up to a particular temperature, cooled, and reheated to a higher temperature, to explore the magnitude of mass loss and heat effects associated with moisture loss in various temperature intervals.

VI.3. RESULTS

In our earlier work, we reported on the kinetics of shrinkage of large block samples of lignites⁴. We have here measured crudely the kinetics of drying of bed-moist samples of four North Dakota lignites. The samples were ground to less than 74 μm particle size, and mass loss rates were measured in zero relative humidity environment at a constant 333 K or 323 K. The results of sample mass (M) with time (t) were seen to follow a first order mass loss law: $dM/dt = -k M$, which implies that a plot of $\ln (M/M_0)$ vs. t is linear with slope $(-k)$. The values of k are given in Table VI-1, together with apparent activation energies (E) for the

drying. No evidence of multistep drying kinetics were seen in these experiments, which only followed moisture loss to 85% of original levels. The drying rates are much higher than those reported for a similar Beulah-Zap sample in one study¹³, and much lower than those reported in another¹⁴. The origin of the discrepancy is unclear, except that in ref. 14, the rate was not modeled as first order in remaining moisture. The value of activation energies are quite variable, and their interpretation is uncertain to say the least. The higher values are very surprising. We believe that the interpretation of drying kinetics in terms of a simple first order model may be inappropriate in any case, as will be discussed further below.

More precise measurement of drying rates of the same Beulah sample of Table VI-1 were performed in a thermogravimetric (TGA) device operated at 303 K. These measurements were performed by introducing controlled relative humidity conditions into the chamber, then following mass loss to constant (apparent equilibrium) values, before introducing the next lower humidity conditions. The results are shown in Fig. VI-1. They shown distinctly two-stage drying behavior. Below about 75% relative humidity, the rates are much lower than above that value. This apparently supports the multistep behavior suggested by others¹⁴, but the rate is first order in remaining moisture in the low humidity regime. The low humidity rates are not well predicted extrapolation of the drying rate from the values in Table VI-1; much lower values would be predicted. This suggests that it is highly dangerous to attempt to fit simple models to such drying rate data. The drying of coals probably involves the removal of moisture from a wide range of sites, characterized by a distribution of activation energies.

It has been noted [e.g.15] that the moisture loss from coal increases with drying temperature, even above 373 K. This supports the idea that there is a distribution of energies associated with water retention and that some water is held more strongly in coal than in pure bulk water. Just how much more strongly is revealed by other types of experiments. Sorption isotherms were measured as earlier described⁴ for the lignites of interest and results are given in Fig. VI- 2. The fact that the isotherms do not shift at all (Beulah) or very little with temperature means that the isosteric heat of moisture vapor sorption is close to the heat of condensation of pure water (i.e. 42.7 kJ/mol).

The isosteric heat is generally determined from:

$$[\partial \ln (P/P_0)/\partial T]_n = (q_{st} - q_{cond})/RT^2 \quad (VI.1)$$

where P/P_0 is the vapor pressure of water relative to saturation (i.e. relative humidity), T is temperature, the subscript n implies evaluation of the derivative at constant moisture loading, q_{st} is the isosteric heat (positive is exothermic) and q_{cond} is the (positive) latent heat of condensation of water and R is the gas constant. It should be recalled, however, that unlike most solid systems to which this sort of analysis is applied, the concept of an isosteric heat here must recognize that there is more than a simple surface condensation involved, in that the material is swelling.

When there is a shift between 303 K and 323 K the results imply isosteric heats of order 70 kJ/mol or less. In fact, there is reason to believe that the apparent shift in the isotherms could be an artifact of thermally induced crosslinking even at these low temperatures; the solvent swellability of these coals is significantly reduced by drying at 373 K for one hour¹⁶, and we have noted significant decreases in both pyridine and DMSO swellability of the coals upon 333 K drying (though the isotherm determinations at 303 K have not been performed following heating, to verify this hypothesis). The low values of isosteric heats agree well with earlier studies^{10,11}. They also agree well with the low heats of immersion measured on a subbituminous coal (order 10^{-2} kJ/mol)¹⁷, since such measurements would be net of the heat of condensation of water.

The broad range of sites involved in holding moisture is also suggested by DSC scans of undried coals. Typically, there is a broad endotherm centered at temperatures above 373 K and often not completed until about 473 K [e.g. 18]. Great care must be exercised to not create a diffusional resistance within a typical sample holder, which would create the impression of high temperature water loss, but mass loss clearly does occur at temperature above 373 K¹⁵. Such DSC data showing a broad temperature range for moisture loss have recently been interpreted in terms of a diffusion controlled release of moisture¹³. We propose that a distribution of activation energies for moisture loss may fit such data as well, and would be consistent with the picture of different types of water-coal interactions, as suggested by the other data above.

The results of our measurements of thermal effects in drying of the Beulah lignite are shown in Figs. VI-3 and VI-4. These experiments involved heating the coal in steps from ambient to 100°C, cooling, then heating from ambient to 150°C, measuring the incremental mass loss and heat effect between 100°C and 150°C (see Fig. VI-3). Another sample was subjected to the same heating and cooling regimen, and then cooled again, before heating from ambient to 200°C (this is actually the experiment shown in Fig. VI-3). Finally a sample was subjected to the same regimen, and then cooled and reheated and from ambient to 250°C. The results of this experiment, as well as the superposition of other cycles through lower temperatures are shown in Fig. VI-4, which attests to the reproducibility of the effects.

Heat effects were measured for each stage of heating, and the mass loss for each was measured in selected experiments. The integral of the endotherm associated with any stage of moisture loss, divided by the amount of moisture loss, gave the net heat of evaporation per mass of water during any stage. These results are plotted in Fig. VI-5, and have been corrected for mass loss which occurs at ambient prior to the heating of the sample. They confirm that the moisture loss continues well beyond 100°C, and that the moisture is held progressively more tightly, as the temperature needed for driving it off increases. The behavior of the moisture in this sample is incidentally quite "normal" with respect to giving a very low enthalpy of fusion, relative to the heat effects associated with drying the sample^{6,7}. This point is qualitatively made in Fig. VI-6, which shows a very small enthalpy of fusion peak at near 0°C, compared to the large heat of evaporation peak near 100°C. The water is tightly held in this coal-water system, and is not generally in the form of bulk water.

The magnitude of the heat effect in the last stage of "drying", as represented in Fig. VI-5, appeared to be too high, and may involve more than physical moisture loss. The evaporation of bulk water involves the heat effects shown on Fig. VI-5. Clearly, the effects are much larger than bulk water evaporation at temperatures above 150°C. It is believed that the large heat effects may possibly involve endothermic reactions resulting in loss of H₂O or CO₂ by pyrolysis. This latter possibility was explored by analyzing the products of drying under identical conditions, and indeed CO₂ was found.

It was already earlier established that the drying of these lignites in the temperature range from 100°C to 300°C involved processes that decrease the swellability of the lignites in good solvents (e.g. pyridine¹⁶). It is quite likely on the basis of these results that the coal is undergoing crosslinking reactions. Thus "drying" is not an accurate term for describing the changes that occur above 100°C. The question is really whether one can ever separate true drying from the reactions. Chances are that it will not be possible, if elevated temperature drying is used.

It appeared on the basis of the data presented in Chapters II and V that the stronger the electron donor, the higher the uptake of solvent. This is understood in terms of a distribution of different sorption site strengths within the coal, and a competition for sites with inherent electron donors in the coal. Thus there is independent evidence from the DSC results that arguably supports the existence of a distribution.

It is hypothesized that the retention of moisture in lignites involves a solvent swelling type of behavior, governed by the nature of different specific interaction sites within the lignites. The net enthalpy of interaction of liquid water with the coals is not large, whereas the interactions are comparable in strength to intermolecular interactions in bulk water, as suggested by the high temperatures needed to dry coals. This means that during wetting of a dry coal, the exothermic wetting process must be counterbalanced by endothermic processes involving the dissociation of strong non-covalent bonding interactions in the dry coal. It would, again, be logical to expect that these internal bonding interactions should be governed by a distribution of energies.

VI. 4. REFERENCES

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Table VI-1-Lignites Studied, Their Drying Kinetics, and Solvent Swelling Behaviors

<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>k (hr⁻¹)</u>	<u>E(kJ/mol)</u>	<u>N_s^w</u>	<u>N_s^p</u>	<u>N_s^b</u>
Beulah	65.6	3.6	1.1	0.8	11.0	17.9	26.0	0.54	101	10.5	11.2	12.5
Freedom	63.5	3.8	0.9	1.4	6.1	24.3	27.9	0.60	159	8.8	10.1	13.1
Glenn Harold	61.1	4.4	0.8	0.4	7.4	25.9	28.9	0.35	180	7.7	12.3	15.1
Gascoyne	60.9	4.2	0.6	1.4	8.2	24.7	30.7	0.26	29	7.7	9.9	18.0

•All analyses on a dry weight percent basis, except moisture which is ASTM value on an as-received, bed moist basis. Oxygen by difference. N_s values in (mmol/cc); w- water, p- pyridine, and b- n-butylamine.

Figure VI-1. Rate of drying of Beulah lignite at 303 K, as a function of relative humidity. Each point represents an average rate for drying a sample from the next higher relative humidity.

Figure VI-2. Sorption isotherms for water on four N.D. lignites. Open symbols-desorption; closed-adsorption. Solid curves with circles-303 K, dashed curves 323 K (∇) and 333 K ($\blacktriangle, \triangle$).

Figure VI-3. Differential Scanning Calorimetric curves for drying of Beulah lignite. The sample lost approximately 8% by mass of water during the preparation for the experiment, and an additional 21.25% during drying to 100°C. The mass loss in going to 150°C from 100°C was an additional 2.09%. The mass loss in going from 150°C to 200°C was not determined. See text for description of the experiment.

Figure VI-4. DSC results as in Fig. 3, showing the reproducibility of the curves for several separate experiments, and involving an additional step of heating to 250°C. The step from 150°C to 250°C involved loss of an additional 1.5% of the mass of the sample.

Figure VI-5. The heat effects associated with removal of mass from the sample, during "drying" in various temperature intervals. Also shown for comparison are enthalpies of vaporization of pure saturated bulk water, as a function of temperature.

Figure VI-6. A DSC scan of water saturated Beulah lignite, showing the modest heat of fusion compared to the large heat of water vaporization. Note that the experiment in this case involved heating the sample isothermally at 125°C, once that temperature was achieved. The end of the "drying" process could not be easily discerned by such a procedure.

VII. HEATS OF MIXING OF COAL AND SOLVENTS

VII.1. INTRODUCTION

The heat of mixing of coals with solvents has been studied by a variety of means¹⁻²¹. Here the interest is in the heat of mixing as it affects the thermodynamics of coal swelling processes. Earlier, heats of mixing had been of interest as they revealed features concerning the surface areas of coals and surface groups on coals. Generally speaking, the literature is not very large, but it paints a fairly consistent qualitative picture. There are some significant quantitative differences between the results of different studies.

Heat of wetting of coals has been studied using classical immersion techniques, liquid flow calorimetry and inverse gas chromatography. If the solvent is in a vapor phase, prior to adsorption, the value that is obtained includes the enthalpy of condensation of the solvent. This must be kept in mind when comparing results obtained from immersion experiments (in which the solvent is already condensed) and the vapor adsorption experiments. Generally studies have been performed with relatively polar liquids, since these give the higher heats of mixing (or wetting).

Here we are interested in how the heat of mixing of coal and water depends upon moisture content. Figure VII-1 shows data from the literature on this topic. We already have an indication from the previous chapter that the heat of mixing of partially moist coal and water should not be very large, since it appeared as though the isosteric heat was very near the heat of condensation of pure water, except at very low moisture contents. The values exhibited in Fig. VII-1b are of the order of typical hydrogen bonding values, but it is important to recognize that these are *net* heats. This means that the values include the energy requirements for breaking hydrogen bonds that exist within the dry coal. Thus nothing can be inferred about the nature of the sites that hold water from values such as those in Fig. VII-1b, except to note that the values in the case of the Wyodak coal are much higher than the values for the Beulah-Zap lignite or the Blair-Athol bituminous coal. More discussion of this point will be

presented below.

There is also a small problem in interpreting the results of immersion experiments in terms of specific interactions. Non-specific interactions can also contribute a small amount to the measured heats. For example, immersion of Pocahontas No. 3 coal in alkanes results in a release of between 3 and 7 J/g⁸ and immersion of Bruceton coal in room temperature tetralin gives about 21 J/g¹⁹. For carbons, values over 100 J/g are not uncommon (e.g. ref. 22). Therefore, even non-specific interactions can give values comparable to those for specific interactions. Typical values for specifically interacting solvents are given in Table VII-1. Therefore it is necessary to be careful in interpretation of immersion results, and recognize that the enthalpy values are subject to several factors.

We did not have a suitably accurate immersion calorimeter for performing enthalpy of interaction measurements directly. Rather, we had a flow calorimeter which allowed exploring the heat effects in going from one concentration of specifically interacting solvent to another in a solution of two solvents. While this instrument (or another like it) has been used less than immersion calorimeters, there are still a number of reports concerning its use for coals^{10,13,16-18}.

The flow microcalorimeter provides measurements of the heat effects seen when mixing coal and solvents. We were particularly interested in how the swelling behavior of coals correlated with the heat of mixing, since this is a central issue in the present study. Our approach here was to use small amounts of a specifically interacting solvent in a weakly interacting solvent (here, n-heptane). The experiment consisted of creating a step change in concentration from pure heptane to the mixture, and following the heat effect of adsorption, and then reversing the step change and following the reverse process of desorption. Because of the obvious difficulty in creating heptane-water solutions, these experiments were not performed directly with water. Rather, the choice was made to explore the behavior of other specifically interacting solvents with coal, since we have already established the similarity of behavior of water and other specifically interacting solvents. Swelling measurements were separately conducted, using the same mixtures.

VII.2. EXPERIMENTAL

The flow microcalorimeter is a commercial device (Microscal, Ltd.) , used here in an unmodified form. Briefly, it consists of a tube maintained in a carefully controlled thermal environment, which is instrumented with calibrated thermistors, capable of showing very small heat effects within the tube. The tube is packed with a few tens of milligrams of coal, and a flow of solvent is introduced, at carefully controlled rate through the bed. Again, the experiments involved establishing a steady flow of non-specifically interacting solvent (e.g. heptane) through the coal sample bed, and then switching this flow to another strongly interacting solvent, and measuring the resultant heat release. Cycling back and forth between heptane and the strongly interacting solvent gives a measure of the reversibility of the sorption process involving the strongly interacting solvent. For a fully reversible sorption process, the integrated heat release during adsorption should exactly balance the heat absorption during desorption.

The preparation of the coal has a significant effect on the results obtained. Here, all results will be reported on the Argonne National Laboratory Premium Coal Sample Beulah Zap lignite. The particular aspects of sample preparation will be discussed in connection with the results outlined below.

It should be noted that one of the main concerns in performing such tests is that coals will swell when exposed to specifically interacting solvents. This is, of course, precisely the effect that we are interested in studying. Significant swelling will be a major problem, since the sample cell in the flow microcalorimeter is of finite volume, and attached to very small tubes that carry the pure liquids into and out of the cell. Significant swelling will cause loss of void volume causing the pressure drop through the cell to increase to the point that a constant flowrate cannot be maintained by the syringe pumps feeding the liquids, and it can damage the filters at the exits of the cell. Therefore it was always necessary to pack the cell such that there would be at least 10% void volume within the cell, to allow for expansion during uptake of the specifically interacting solvent.

It should also be kept in mind that the normal volumetric swelling ratio of this coal in

water is approximately 1.3 (i.e. 30% increase in volume) and in alcohols a comparable value is obtained. In even stronger solvents such as pyridine, a swelling ratio of over 2 (i.e. >100% swelling) is seen. Thus the experiments that we are performing here cannot be safely carried out by switching between a weak solvent and a pure specifically interacting solvent. The use of "inert" fillers mixed with the coal, so as to keep the percentage swelling low, is also problematic; no material that we have thus far tested gives a low enough heat of adsorption so as to not raise questions about the accuracy of the results for the coal. Therefore we work with "neat" coal samples, and keep the swelling low by keeping concentration jumps small. It is possible to measure heat effects at high concentrations of specifically interacting solvent, by first preswelling the sample outside of the cell in a slightly lower concentration mixture.

VII.3. RESULTS

The results of a series of experiments using heptane and 1% propanol-in-heptane solutions are shown in Table VII-2. The effects of different temperatures of measurement and different sample preparation methods are summarized in this table. Typical raw data are illustrated in Figure VII-2.

The reproducibility of the flow microcalorimetric technique is illustrated in the first two lines of Table VII-2, in which identical samples were examined under identical conditions. The values of adsorption and desorption enthalpies from several sequences are seen to be in good agreement. The variation in the run-to-run values represents the inherent precision of the method, which, generally speaking, is in the range of about 10% (in this range of values or higher).

A main source of uncertainty comes from the integration of peaks which have a significant tail (particularly in the desorption experiments), or involve a significant shift in the baseline. Such shifts in baseline were not uncommon, when changing from the pure heptane solvent to 1% propanol in heptane. It is not believed that the shift was a consequence of a difference in the temperatures of the solvents, but rather a consequence of a change in the heat transfer

situation in the cell, either as a result of swelling of the sample, or the change in thermal properties of the solvent. It is believed that the failure to recognize these aspects of the measurements led us to earlier erroneously conclude that there was a spurious heat effect due to mixing .

We have noted the importance of sample history in determining the values we obtained. It appeared as though samples tended to exhibit higher heats, the more cycles to which they had been exposed. This may in part be due to oxidation of the samples. The fourth and fifth lines of Table VII-2 show samples dried at identical temperatures, but one with air exposure after (and possibly during) drying, and the other without such exposure. The sample dried in the calorimeter (thus avoiding air exposure) gave consistently lower values of the heat of adsorption and desorption. Further to this point, the experiments performed at 297 K (experimental sequences 23 and 29) were performed with the same sample, with experiment 29 being conducted a week later than experiment 23. Again, the sample shows higher values at later times, after it had had an opportunity to oxidize at higher temperatures (329 K). Note that drying alone does not seem to result in unusually large values of the heat of adsorption, since the room temperature dried sample examined at 299 K gave values comparable to the undried samples (experiments 4 and 18) and the freshly dried sample (experiment 23).

Another factor that determines the magnitude of the heating effect is the residual moisture content of the lignite. It is the severity of drying that determines how much water is left in the sample, and thus how many hydrogen bonding sites are available for the propanol to interact with. Since water does not readily partition into pure heptane, water that is initially present (or picked up as a result of handling, during filling the sample cell) might not be readily removed in room temperature experiments. This is supported by a comparison of the results for samples that are undried (first two lines of Table VII-2) with the results for the sample dried in-situ (the fifth line of the table). There is also evidence of a trend with number of cycles in the case of experiment 23, as might result from progressive loss of water, during cycling. Comparison of the results for experiment 4, in which an undried sample is immediately measured, with the results of experiment 18, in which the undried sample had been exposed to measurements at 329 K, also support this viewpoint, as does a comparison of the results of

experiment 15 and experiment 6.

We have thus far seen no consistent trend resulting from extraction of the samples with pyridine, prior to testing. This agrees with another study⁶. We believe that moisture and oxidation effects are probably more important. The effects of these variables also agree with another study¹¹.

Thus in reporting results of this kind, it is crucial to specify the conditions of sample preparation. It is for this reason that the results of Table VII-2, when combined as they are, appear to be widely scattered. In fact, there are clear trends apparent. Using the mean adsorption heats for the undried, unextracted samples, a clear trend of heat of adsorption with temperature is visible, in Figure VII-3. It is clear that the higher temperature experiments exhibit greater exothermicity than does room temperature. Adding the data from the dried, but unextracted coals, Figure VII-4, does not alter the conclusion, although there is again more scatter introduced, presumably because of the greater oxidation of some of the dried samples.

Simple thermodynamic reasoning requires that an exothermic process should be driven in a direction of lesser exothermicity with increase in temperature. Thus an increase in heat of mixing with increase of temperature would initially appear unreasonable. A similarly counterintuitive trend has been reported earlier for triethylamine vapor interacting with bituminous coal¹⁰, in precisely the same experimental system as gave the more expected trends with acetonitrile and water. We can offer a hypothesis for these trends, related to creation of more specific interaction sites by thermal processes. If the sites are created by heating of the coal, the possibly endothermic nature of the site creation would not be visible in the adsorption experiments. How the sites are created is not entirely clear, but there are some relevant observations that can be offered.

One possible explanation for the increased availability of specific interaction sites at higher temperatures is that diffusional processes are faster at elevated temperatures. Diffusion of solvents into coals (including Beulah lignite) is an activated process²³. Thus it might be argued that the sample shown in Fig. VII-2 had, in fact, not reached true equilibrium, but rather the rate of diffusion into the sample had slowed to a point so as to make it appear so. Apart from the fact that the data of Fig. VII-2 do not really support this, we have separately

measured the kinetics of propanol swelling, and find characteristic timescales that are consistent with full equilibration being reached during the thermal measurements. Thus we rule out a mass transfer explanation.

The other possible explanation for site creation is the dissociation of interactions that initially bind the specifically interacting sites in coal. Two possibilities suggest themselves. The first is that moisture is present on the surface. If upon heating to a higher temperature the coal is dried to a greater degree, then there might be more unoccupied sites for the specifically interacting propanol to interact with. The other possibility is that the sites are initially bound up by specific coal-coal interactions, and are created by thermal dissociation. Regarding both these hypotheses, we have earlier noted that the extent of swelling of Beulah lignite is not a strong function of temperature in the range of temperatures in question here²³. The samples for which we found this to be true were, however, extensively dried prior to swelling. We have also reported that the extent of swelling is significantly influenced by the degree of pre-drying of the samples²⁴.

As noted above, the role of drying in determining thermal effects is somewhat supported by the data of Table VII-2. It appears that generally, the more severely dried samples do give larger heats than do the more gently dried. We recall also the possibility that more severe drying led to oxidation, and thus creation of more sites. It also appears that extraction of the samples leads to greater heat effects in most cases.

The order in which the experiments were performed on any sample had no influence. For example, the same sample was used for experiment 12 at 329 K before it was used for experiment 18 at 298 K, and this sample gave low temperature results not much different from many fresh samples. Thus the process of site creation is clearly reversible, and this is an important aspect of its nature.

In summary, we believe that the temperature dependence of the heat of sorption most likely arises from creation of more specific interaction sites with increasing temperature. The process is somewhat reversible, but appears to be somewhat influenced by how the samples are prepared. This is not an effect that is easily assigned to only one factor. Drying, oxidation,

and dissociation of coal-coal interactions may all play some role, but the reversibility of the effect seems to argue most strongly for a reversible creation of sites with increase in temperature. The apparent inconsistency with the swelling results, which showed little temperature dependence, suggests that the measured heat effects do not correlate directly with extent of swelling.

The magnitude of the heat of adsorption of the propanol on the lignite is thus about 10 to 50 J/g. The values are not a strong function of concentration of propanol, as was noted in Figure II-15. These values are also comparable to values reported by other workers for the heat of immersion of low rank coals in pure alcohols and water (e.g. Wyodak subbituminous gives 110 J/g in methanol, 95 J/g in propanol and 23 J/g in dodecanol⁶). Pre-extraction had no effect on the values reported in that study, in agreement with our results. Water immersion gives values of about 80 J/g^{7,10} to 130 J/g¹². The same coal as is of interest here, the Beulah-Zap lignite, has been reported to give a heat of immersion of 63.6 J/g in methanol¹¹. Thus the fact that higher values than ours were obtained using propanol on Wyodak may well be attributable to the difference in coals, since the above methanol value for Beulah lignite was lower than that reported for Wyodak. Table VII-1 also supports this conclusion, since the higher rank coals all exhibit lower propanol immersion heats. It is thus inappropriate to attach too much significance to the exact enthalpy value obtained for a particular coal-solvent combination. Instead the rough magnitude of the values serves to indicate the degree to which there is specific interaction between the coal and solvent, as discussed in Chapter II.

The heats of mixing can be put into perspective by considering the amount of swelling that accompanied the release of the heat. These extents of swelling were measured in separate experiments, as described in Chapter II (see Figure II-12). The volumetric swelling ratio, $Q = 1.07$, is given by $V_{\text{final}}/V_{\text{initial}}$. Assuming for the moment linear additivity of coal and propanol volumes $Q = (V_p + V_c)/V_c$, where p and c refer to pure propanol and coal, respectively. Then it is possible to say that $(m_p/m_c) = (Q-1)(\rho_p/\rho_c)$. Taking into account the density difference between the coal (1.3 g/cc) and propanol (0.8 g/cc), this means that the mass of propanol imbibed is of order 4%, meaning that the heat effect is quite large, on a per mol of propanol basis. For example, if we take the heat effect to be 28 J/g coal, then the heat

effect would be crudely 700 J/g propanol, or 31 kJ/mol of propanol.

The large magnitude of the heat of mixing, expressed on a per mol of propanol basis, is typical of what others have also reported^{10,13,18}. It is difficult to assign a high degree of accuracy to the absolute value that we have obtained because the measurement of swelling ratio, at such low extents of swelling, is quite difficult and subject to large uncertainties (these could alone make a factor of two difference). Furthermore, there is no reason to believe that the the volumes of coal and alcohol would necessarily be additive at low uptakes, as assumed here for calculational purposes. Still, the heat effect is undoubtedly large, meaning that there are energetically quite favorable interaction sites for the propanol in the coal. In addition, these are reversible sites. The magnitude of these heat effects suggest that these can be simple hydrogen-bonding sites, as is quite often assumed.

From these data, we can conclude that the heat effects measured at low extents of swelling are associated with the filling of very strong specific interaction sites. These interaction sites probably exist in an unfilled state within the dry or heptane-immersed coal. As the first sites are filled, the heat effect drops to near zero values. In terms of equation II.23 of Chapter II, this means that the swelling must be entropically driven to completion, because the enthalpy is small after the empty sites are filled.

What came as a surprise was the fact that the heat effect does not similarly drop off to much lower values as these few initial sites are filled in the water immersion experiments (see Figure VII-1b). The near-linearity of the heat release curves with initial moisture content suggests an almost constant heat release per mole of water sorbed. The linear regressions are shown in Fig. VII-1b. From the slopes of the lines, the partial molar enthalpy of mixing is easily estimated, and found to be about 11.9 kJ/mole of water for the Wyodak coal and roughly 3.3 kJ/mole for the Beulah lignite and Blair Athol bituminous coals. Considering equation (II.23), the ratio of the partial molar entropy change to partial molar enthalpy change can be calculated. It is assumed for the purposes of this calculation that the correlation for coal shrinkage upon moisture loss, developed in Chapter V, applies. This leads to the following estimate for the partial molar entropy term:

$$R[\ln(a + bm) + 1 - (a + bm)]$$

where m is the moisture content in percent, and a and b here are .00803 and 0.009, respectively. (This comes from the fact that the *fractional* shrinkage = $[1 - 1/Q]$).

The ratio of the partial molar entropy contribution to partial molar enthalpy is shown in Figure VII-5. It is clear that entropy drives the process forward in the early stages, but it is actually the enthalpy that drives it to completion. This was an unexpected result, which means that the uptake of water ceases upon exhaustion of enthalpically favorable sites in the coal.

VII.4. CONCLUSIONS

The picture that emerges is that there are quite large heat effects associated with low uptakes of solvents by the coal. The fact that the heat of wetting decreases dramatically with uptake has been illustrated many times, and is seen here with propanol. The final equilibrium uptake of propanol in a swollen coal probably takes place at near zero partial molar enthalpy of mixing, as we have argued earlier.

The surprising trends observed with water as a swelling agent suggests that enthalpy, rather than entropy, drives the swelling to completion, and thus dictates moisture capacity.

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Table VII-1

Typical Heats of Immersion of Coals in Solvents (J/g)

<u>Coal</u>	<u>Methanol</u>	<u>Ethanol</u>	<u>Propanol</u>	<u>Butanol</u>	<u>Water</u>	<u>Pyridine</u>
Beulah Lignite	63.6 [11]	-	-	-	57.3 [11]	104.6 [13]
Illinois No. 6 Bituminous	36.4 [11]	7.8 [10]	5.1 [10]	3.9 [10]	15.1 [11] 24 [10] 30 [12]	127.6 [13]
Wyodak Subbituminous	110 [6]	-	95 [6]	91 [6]	125 [12] 83 [7]	150.5 [13]
Virginia Bit.	24 [9]	-	19 [9]	15 [9]	2.5 [9]	-
Pocahontas No. 3 Bituminous	15 [5]	15 [5]	14 [5]	-	5.4 [5]	30.5 [13] 15 [5]

Values in braces are references from which the data were obtained.

Table VII-2

Summary of Heats of Adsorption and Desorption on Beulah Lignite of 1-propanol from 1%

Solution in n-heptane

<u>Sample</u>	<u>Temp.(K)</u>	<u>ΔH_a(J/g)¹</u>	<u>ΔH_d(J/g)¹</u>	<u>ΔH_a(J/g)²</u>	<u>ΔH_d(J/g)²</u>	<u>ΔH_a(J/g)^m</u>
Undried, unextracted (-400/9) ^a	325	-26.3	26.3	-25.0	27.9	-26.4
Dried ^e , unextracted (-400/12)	329	-24.2	26.2	-29.0	28.4	-27.0
Dried ^b , unextracted (-200/27)	329	-44.0	39.3	-44.6	38.1	-41.5
Dried ^b , extracted (-400/r7)	330	-52.8	40.1	-51.2	40.0	-46.0
Dried ^c , extracted (-400/v1)	333	-35.1	32.5	-35.3	33.5	-34.8
Dried ^e , unextracted (-400/15)	313	-29.5	35.2	-33.2	29.4	-31.8
Undried, unextracted (-400/6)	311	-29.4	23.2	-20.7	29.9	-25.8
Dried ^b , unextracted (-200/25)	312	-24.3	27.9	-30.3	30.8	-28.3
Dried ^b , extracted (-400/r4)	318	-44.4	47.4	-54.9	45.5	-48.1
Undried, unextracted (-400/4)	300	-13.7	11.8	-13.0	10.5	-12.3
Dried ^e , unextracted (-400/18)	298	-17.8	15.4	-18.1	17.6	-17.2
Dried ^d , unextracted (-400/21)	299	-16.7	17.0	-11.1	15.8	-15.2
Dried ^b , unextracted (-200/23)	297	-10.3	12.4	-14.2	15.9	-13.2
Dried ^b , unextracted (-200/29)	297	-22.8	24.3	-22.4	21.4	-22.7
Dried ^b , extracted (-400/r1)	297	-13.9	26.8	-19.4	25.0	-21.2

1. Refers to first cycle of adsorption (ΔH_a) and desorption (ΔH_d), 2. refers to second cycle.m. Refers to average heats of adsorption of the alcohol from the alkane carrier.

a. First values in parentheses refer to mesh size of particles, second to experiment numbers.

b. Vacuum oven-dried at 345 K.

c. Vacuum dried, in-situ in the flow microcalorimeter, at 343 K.

d. Vacuum oven-dried, at room temperature.

e. Vacuum dried, in-situ in the flow microcalorimeter, at 323 K.

Figure VII-1a. Heats of immersion of coals in water, as a function of initial moisture content.
 Triangles- Wyodak⁷; Squares-Beulah lignite¹¹; Diamonds-Blair Athol bituminous⁴.
 Values on graph give the oxygen contents of the coals.

Figure VII-1b. The data of Figure VII-1a replotted on a dry coal basis. The slopes of the regression lines are: Wyodak - 0.660; Beulah -0.187; Blair Athol -0.180 kJ/g water.

Figure VII-2. Sample output from an experiment in the flow microcalorimeter, showing a typical adsorptio/desorption cycle. (Beulah Lignite, 1% propanol in heptane at 325 K)

figure VII-3. Heat of 1-propanol adsorption on Beulah Lignite, from 1% propanol in n-heptane. Samples were undried, unextracted.

Figure VII-4. Heat of 1-propanol sorption on Beulah Lignite. Squares are data from undried, unextracted samples of Fig. 2. Triangles are for predried samples.

Figure VII-5. Ratio of partial molar entropy of mixing to partial molar enthalpy of swelling, from (II.23).
The top two curves are for Beulah and Blair Athol coals, the lower curve for Wyodak (see Fig. VII-1).

VIII. IMPLICATIONS FOR THERMAL DEWATERING PROCESSES

This project was begun on the premise that water retention in coals involves a solvent swelling type of process. This hypothesis has received strong support from all of the measurements and analyses performed during the course of the study. In Chapter II, it was seen that significant swelling of coals requires some minimum electron donor strength in a solvent. Solvents that are not effective electron donors do not swell unmodified coals to any significant degree. Water is an electron donor, although there is some considerable uncertainty as to its strength. Nevertheless, in the range of donor strengths that water is believed to exhibit, there is the potential for significant swelling to occur.

Chapter II also presented evidence in support of the notion that there are definite specific interaction sites in coal, and that the number that can be filled is a function of electron donor strength. There is, moreover, a correlation between the heat of immersion of coal in solvents and the molar uptake of solvents. In the cases studied in Chapter II, it appears as though the swelling equilibrium can be achieved at near zero enthalpy of mixing, implying that the swelling can be driven to completion by entropy. It was seen in Chapter VII that the same appears to not hold for water.

In Chapter III, it was noted that the coal behaves as a fairly rigid, glassy solid. The results of Chapter IV showed that water has a plasticizing effect on the coal, a result which is made even clearer in an attached paper describing the effect of water on swelling and transport of solvents in the coal. While there was some difficulty in obtaining accurate tensile modulus values by DMA, the order of magnitude of the values that were obtained corroborated the results of Chapter III, in suggesting that even when extensively water swollen, the structure of low rank coals is glassy.

The results of Chapter V left little doubt that the structure of coal can be extensively swollen by water. In fact, a single correlation of extent of swelling with moisture content appears to apply across all ranks from lignite up to high volatile bituminous. Thus it is clear that water swells coal just as do many other electron donor solvents, and is undoubtedly interacting with specific interaction sites in so doing. The swelling of the coal by water does not change the fundamentally

glassy nature of the network structure.

Chapter VI showed that most of the moisture in lignites is held in interactions with strength not much different than those that exist in bulk water itself, even though there is certainly evidence for different strength specific interaction sites in the lignites. Chapter VII re-examined the issue of heats of mixing of solvents with coal. It was seen that the number of stable interaction sites appears to be a weak function of temperature, up to a certain point, presumably due to dissociation of coal-coal interactions that allow more coal-solvent interactions. The heat of immersion of coals in water was seen to be subject to remarkably constant partial molar enthalpy of mixing. The heats of interaction per mole are not large (3.3 to 11.9 kJ/mole), consistent with the fact that the heat of vaporization of water from coal is not much different than the heat of evaporation of pure bulk water (Chapter VI). These heat effects are presumably net heat effects, reflecting the net heat of interaction including dissociation of coal-coal non-covalent interactions. A model of the process was presented in Chapter II. The fact that the coal remains in a glassy state, even when fully swollen, implies that many such interactions cannot be dissociated by water.

It appears from the results of Chapter VII that the final extent of swelling of coal in water is determined by exhaustion of enthalpically favorable sites. It is clear from Chapter II that other stronger electron donor solvents are able to interact with more sites.

In terms of the proposal that moisture retention be controlled by changes in the crosslink density of the coal, it now appears that this strategy is not as promising as originally believed. For one thing, it is clear that the structure of the coal remains highly crosslinked, even when it is fully swollen with respect to water. The benefit of addition of more covalent crosslinks is unclear. In Chapter II, it was noted that the elastic properties of the coal can be significantly affected by dissociation of non-covalent crosslinks during swelling. When the dissociation of crosslinks ceases, the process of expanding the structure becomes abruptly more difficult. Addition of crosslinks will not change the character of the process, but only the magnitude of the values of the different free energy terms. The reason for the pessimism concerning a proposal to add crosslinks in order to prevent moisture regain may be illustrated by a sample calculation.

If it is supposed that the partial molar entropy of mixing is given by II.22,

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

then it is clear that at low extents of swelling, the entropic contribution to the partial molar free energy of mixing is very large (see Figure VII-5). We will assume that the uptake of moisture is to be no more than 5% by mass, which implies that the structure will swell by about 4%, or $Q=1.04$. From this, it can be noted that the entropic contribution to the partial molar free energy change is about - 5.7 kJ/mole as a minimum. Since the enthalpy of mixing was seen to be about -3.3 kJ/mole at the very least, the partial molar free energy of mixing driving force is about -9 kJ/mole. From II.14, the value of M_c that is needed to assure that swelling equilibrium will not exceed the 5% value is absurdly low ($M_c=2.1$ daltons).

Thus we believe that the more usual course of dewatering, involving removal of oxygen functional groups by low temperature pyrolysis, offers a more realistic (and of course demonstrated) hope of dewatering lignites to a significant degree.

PUBLICATIONS BASED UPON THIS PROJECT

Solvent Swelling of Macromolecular Networks by Specifically Interacting Solvents - Applications to Coal

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Introduction

This study has been motivated by a basic scientific question concerning the properties of coal— to what extent is the ability of coal to hold moisture a manifestation of the well-known ability of coal to swell, when exposed to good solvents? The question implies that the long-held belief that coal holds a significant portion of its moisture by classical capillary condensation processes, is in error. This seems to be a very real possibility for low rank coals- i.e. lignites. To explore this hypothesis further requires an examination of the basic phenomena governing the swelling of coals in good solvents. The thermodynamics of moisture retention has probably never been correctly accounted for, in that moisture retention is not a simple surface adsorption process. This paper explores the ramifications of solvent swelling theories in these systems. It should be remembered at the outset that coal contains an enormous range of functional groups, capable of a broad range of hydrogen bonding or acid-base interactions.

Solvent Swelling Theory as it Applies to Coals

The theory of solvent swelling in polymers (here used as models for coals) has been well described elsewhere¹⁻⁴. The starting point for all solvent swelling models is substantially the same, a statement that at swelling equilibrium, the Gibbs free energy of the system must be at a minimum. It is assumed that the change in the Gibbs free energy of the solvent-network system during swelling is made up of two separable contributions --one due to elastic deformation of the network, and the other due to mixing of the components. Thus

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

Since the overall pressure-volume product does not change significantly during the swelling process, the above Gibbs free energies are roughly equivalent to Helmholtz free energies (ΔA_{mix} and ΔA_{el})³. Equilibrium is determined by the minimization of the free energy:

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

where n_s is the number of moles of solvent imbibed into the network structure. It is in the details of calculating the individual contributions of elastic deformation that the well-known models of swelling differ from one another. If the chains of the network are assumed to follow Gaussian statistics, the elastic free energy term for swelling a so-called "phantom network" (one in which the chains are free to move through one another) is given by²:

$$\Delta A_{\text{el}} = (3\xi RT/2)[(1/v_c)^{2/3} - 1] \quad (3)$$

where v_c is a measure of the network deformation, equal to both the volume fraction of coal in the swollen network, and thus, the inverse of the volumetric swelling ratio of the coal. If the network deforms in an affine manner (meaning that the motion of the crosslink junctions is suppressed by the existence of neighboring chains), the comparable expression is^{3,4}:

$$\Delta A_{el} = (3vRT/2)[(1/v_c)^{2/3} - 1] - \mu kT \ln v_c \quad (4)$$

Real networks behave closest to the affine limit at low deformations, and the phantom limit at high. In both cases, the enthalpy change due to deformation of the network is assumed to be negligible. The expression (4) contains the controversial logarithmic term that Flory maintained should be present², but which many authors do not include⁴.

The parameters ξ , μ , and v are used to characterize the network structure. ξ is the cycle rank of the network, the number of independent circuits in the network or the number of "cuts" that would have to be made to reduce the network to a tree structure with no closed cycles. The quantity ξ , on a molar basis, may be determined for a perfect network from³:

$$\xi = (V_0 \rho_c / M_c)(1 - 2/\phi) \quad (5)$$

A perfect network is defined as one with no dangling chain ends. It is probably a fair approximation for coals, which have a highly crosslinked structure and few long sidechains. The parameter ϕ is the number of chains meeting at a junction. For crosslinking in a network, $\phi > 2$. As compared to the case of ordinary polymers, in which ϕ is often known, in the case of coals, the quantity is unknown. It is thought that the structure of coals probably involves chains of aromatic units, joined by aliphatic carbon, ether, or heteroatomic linkages. The crosslinks may then involve aromatic units that are simultaneously linked to two or more other such units, or from secondary or tertiary aliphatic carbons.

The parameter v is the number of moles of network chains, and is related to ξ through:

$$v = \xi / (1 - 2/\phi) = V_0 \rho_c / M_c \quad (6)$$

and μ is the number of moles of junctions in the network, and is given by:

$$\mu = 2v/\phi \quad (7)$$

The assumption of Gaussian chain statistics is likely to be poor in the case of a highly crosslinked network of fairly short chains. The Gaussian chain must have an end-to-end distance which is small, compared to its fully extended length. This will not be possible in rigidly crosslinked networks such as that of coal. Modifications to the Gaussian statistics have been suggested by both Kovac⁶ and by Lucht and Peppas⁵. Kovac developed a modification of Gaussian statistics for freely-jointed short chains, using the three chain model and obtained:

$$\Delta A_{el} = -(3RT\rho_c V_0 N / 2M_c)[\ln(1 - v_c^{2/3}/N) - \ln(1 - 1/N)] \quad (8)$$

The parameter N introduced here is the number of repeat units in the chain between crosslinks:

$$N = M_c / M_{cluster} \quad (9)$$

where $M_{cluster}$ is the size of a basic repeat unit in the structure, and usually assumed to be constituted mainly of a fused aromatic ring cluster. The value of $M_{cluster}$ is difficult to determine, and has been estimated from molecular weights to be characterized by values between 100 and 500 daltons.

Regardless of the elasticity model chosen, the criterion of swelling equilibrium is that given in (2), except that as noted above, it is assumed that $\Delta A_{el} = \Delta G_{el}$. This then gives for the phantom network model, (3):

$$[\partial(\Delta G_{\text{mix}}/RT)/\partial n_s]_{T,p} = - [(1-2/\phi)\rho_c V_s v_c^{1/3}] / M_c \quad (10)$$

For the affine model, (4):

$$[\partial(\Delta G_{\text{mix}}/RT)/\partial n_s]_{T,p} = \rho_c V_s v_c^{1/3} [(2v_c^{2/3}/\phi) - 1] / M_c \quad (11)$$

For the modified Gaussian model, (8):

$$[\partial(\Delta G_{\text{mix}}/RT)/\partial n_s]_{T,p} = - \rho_c V_s v_c^{1/3} / [1 - N^{-1} v_c^{-2/3}] M_c \quad (12a)$$

$$[\partial(\Delta G_{\text{mix}}/RT)/\partial n_s]_{T,p} = - \rho_c V_s v_c^{1/3} [1 + N^{-1} v_c^{-2/3}] / M_c \quad (12b)$$

(the latter approximation was suggested by the author⁶, and the former derived by us from (8)).

The question of which elasticity model is correct remains a matter of some debate, but our feeling is that all are deficient in at least one important respect. None includes a contribution from the dissociation of non-covalent crosslinks in the coal. This is the topic of the present paper.

The calculation of the free energy of mixing normally follows the analysis by Flory², based upon the liquid lattice theory. The free energy of mixing is modeled as being determined by two separate contributions, one due to the enthalpy of mixing, and the other due to the entropy of mixing. The overall expression for the free energy of mixing is:

$$\begin{aligned} \Delta G_{\text{mix}} &= RT (n_s \ln v_s + \chi n_s v_c) \\ &= RT(n_s \ln[1-v_c] + \chi n_s v_c) \end{aligned} \quad (13)$$

where the entropic contribution is embodied in the first term in parentheses, and the enthalpic in the second term. The coal-solvent interactions are assumed to be non-specific pairwise interactions (involving dispersion forces). The enthalpy of mixing ($RT\chi n_s v_c$) would be positive (endothermic) for such 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. The use of (13), unmodified, in the evaluation of the partial molar free energy of mixing yields:

$$[\partial(\Delta G_{\text{mix}}/RT)/\partial n_s]_{T,p} = \ln(1-v_c) + v_c + \chi v_c^2 \quad (14)$$

Substitution of (14) into an appropriate model derived from the elasticity equations will yield an expression in which M_c is generally the only "unknown", since v_c is normally obtained from solvent swelling data. It is for the purpose of estimating M_c that this type of analysis has been routinely applied. Still, it must be noted that there are significant difficulties inherent in applying the theories because χ is generally not known (and not really meaningful in the case of specifically interacting solvents, which include virtually all good solvents for coal). Also, as noted above, the elasticity models are probably inadequate.

In an effort to obtain a better expression for the mixing term than that implied by equations (13) and (14), we assume that the calculation of mixing entropy is correctly handled by the Flory theory. To improve upon the mixing enthalpy contribution, particularly for specifically interacting solvents (including water), we look to actual experimental results for guidance. These measurements are underway in our laboratory.

Modifications to Classical Solvent Swelling Theory

A difficulty in using the existing theories of solvent swelling is that they all assume that there are only two kinds of interactions possible in the coal network - covalent interactions (i.e. the covalent linkages between chain elements that are counted either as main chain linkages or crosslinks) and non-specific interactions between chain segments (i.e. van der Waals interactions). In the classical model, the solvent molecules substitute for the van der Waals interactions on a

random (i.e. non-specific) basis, and the mixing enthalpy calculations effectively involve estimating the difference between solvent-solvent and solvent-polymer pairwise interactions (quantitatively characterized by the parameter χ in equation 13 above).

This viewpoint is inadequate for several reasons. First, the nature of specific interactions is such that exothermic mixing processes do occur. Also, specific mixing interactions involve, as the name implies, a non-random interaction of solvent with the macromolecular matrix. This in turn implies that there is a saturable limit to the number of such interactions possible, determined by the number of specifically interacting groups in the network. We have seen this to be the case in coals swollen with a series of linear alkyl amines.

There are yet further complications in application of the classical theory to coal networks. The first arises from the fact that, unlike the situation in polymer networks, there are many different types of interaction sites in coal, ranging from strongly acidic to strongly basic, in the general sense of Lewis acids and bases, i.e. electron acceptors and donors, respectively. In actuality, the broad spectrum of donor-acceptor interactions, as outlined by Gutmann⁷, is of relevance in this case. This spans the range of charge transfer processes, and includes the very important subset of hydrogen bonding interactions.

It is not the existence of a wide variety of possible acceptor-donor interactions between coals and solvents that presents the problem. Rather, there is a strong probability that many internal charge transfer processes occur within the coal network, resulting in non-covalent crosslinks. In a solvent that is unable to dissociate some or all of such non-covalent crosslinks, the network behaves as though it were much more highly crosslinked than what would be the case if only its covalent crosslinks were involved. This is presumably the origin of the unusually high values of crosslink density obtained from elastic properties of dry coal⁸, and is consistent with coal's assuming rubbery properties at or below room temperature, if swollen in an appropriate solvent⁹.

Good solvents for coal are those that can disrupt the non-covalent interactions by substituting for one of the coal functional groups involved in the non-covalent bonding interaction. Generally speaking, strong nitrogen bases (i.e. good electron donors) have been the most effective swelling solvents, and there is thus a suggestion that there are strong electron donors present in the coal (there are known to be many nitrogen functional groups). The variation of coal swellability with electron donor strength has been well demonstrated in a classic study, which also showed that the ordinary solubility parameter was wholly inadequate for correlating the data¹⁰.

The above leads to the conclusion that the possibility of non-covalent crosslink dissociation should be included in an analysis of solvent swelling of coals. To not include this feature is to rule out any possibility of explaining the swelling behavior of coals with the full range of specifically interacting solvents. That is to say, the effective crosslink density in a strong electron donor solvent such as pyridine is lower than the effective crosslink density in a weaker donor solvent, such as propanol. The former swells coals significantly more than the latter, and this is quite possibly a manifestation of the inability of the propanol to dissociate non-covalent crosslinks as well as does the pyridine. The alternative explanation has historically involved invoking differences in solubility parameter between coal and solvent (which would be felt through its effect on χ), but this is clearly inadequate in this case, since the two solvents named have similar solubility parameters. The importance of including (or excluding) specific interaction effects in analysis of the swelling behavior of coals was recognized by Larsen and coworkers¹¹.

A straightforward, albeit crude, approach for including non-covalent crosslink dissociation

in swelling models is as follows, using the modified Gaussian model of elasticity (8) as the starting point. Differentiation with respect to n_s yields:

$$[\partial(\Delta G_{el}/RT)/\partial n_s]_{T,p} = \rho_c [1 - v_c^{-2/3} N^{-1}]^{-1} [(V_s v_c^{1/3}/M_c) - (3V_0 v_c^{-2/3}/2M_c^2)(dM_c/dn_s)] \quad (15)$$

The variation of M_c with solvent uptake is related to the number of crosslinks broken:

$$\begin{aligned} (dM_c/dn_s) &= (dM_c/d\mu) (d\mu/dn_s) = - (2V_0 \rho_c / 3\mu^2) (d\mu/dn_s) \\ &= - (3M_c^2 / 2V_0 \rho_c) (d\mu/dn_s) \end{aligned} \quad (16)$$

Note that in this model, $\phi=3$ has been assumed. The term $(d\mu/dn_s)$ is related to the efficiency of crosslink disruption by solvent. Presumably, not every imbibed solvent molecule will dissociate a non-covalent crosslink. It is therefore assumed that $(d\mu/dn_s) = -f$, where $0 \leq f \leq 1$. The quantity f may in fact be a function of n_s . This then leads to:

$$\begin{aligned} [\partial(\Delta G_{el}/RT)/\partial n_s]_{T,p} &= v_c^{1/3} [1 - v_c^{-2/3} N^{-1}]^{-1} (V_s \rho_c / M_c) \\ &\quad + (9fN/4) [(N-1)^{-1} - (Nv_c^{2/3} - 1)^{-1}] \end{aligned} \quad (17)$$

The case of $f=0$ (i.e. no bond dissociation) is identical with the result expressed in (12a), in which $[\partial(\Delta G_{el}/RT)/\partial n_s]_{T,p} = -[\partial(\Delta G_{mix}/RT)/\partial n_s]_{T,p}$ has been assumed.

It has now been assumed that initially the coal contains covalent and non-covalent crosslinks. If μ is the total number of crosslinks at any time, μ_c is the total number of covalent crosslinks (a constant), and μ_{nc} is the number of non-covalent crosslinks at any time (a function of n_s), then

$$\mu = \mu_c + \mu_{nc} = 2V_0 \rho_c / 3M_c \quad (18)$$

given the assumption of $\phi=3$, as is consistent with the Kovac three-chain model. This may be rearranged to give:

$$(2\rho_c / 3M_c) = (\mu_c + \mu_{nc}) / V_0 \quad (19)$$

The right hand side of (19) represents the total number of crosslinks per unit volume. Let the ratio of non-covalent crosslinks initially present to covalent crosslinks be r :

$$r = \mu_{nc,0} / \mu_c \quad (20)$$

Then it may be seen that:

$$(2\rho_c / 3M_{c0}) = (1 + r) \mu_c / V_0 \quad (21)$$

where M_{c0} is the initial molecular weight between effective crosslinks, both covalent and non-covalent. As solvent is added, crosslinks are dissociated and M_c continually increases as dictated by $(d\mu/dn_s) = -f$. Making the assumption that f is constant, (19) may be rewritten as :

$$\begin{aligned} (2\rho_c V_s / 3M_c) &= (\mu_c + \mu_{nc,0} - fn_s) V_s / V_0 = (\mu_0 - fn_s) V_s / V_0 \\ &= (2\rho_c V_s / 3M_{c0}) - f / (v_c^{-1} - 1) \\ &= (1 + r) V_s \mu_c / V_0 - f / (v_c^{-1} - 1) \\ &= (1 + r) V_s (2\rho_c / 3M_{c,max}) - f / (v_c^{-1} - 1) \end{aligned} \quad (22)$$

The initial value of M_{c0} and the value $M_{c,max}$ (the molecular weight between crosslinks when all non-covalent crosslinks are broken) are unknown. The value M_{c0} is likely to be quite low, as supported by the calculations of M_c from mechanical properties that give very low values⁸. The expression (22) can be rewritten as:

$$M_c = M_{c,max} / [1 + r - \alpha f (v_c^{-1} - 1)] \quad (23)$$

where $\alpha = 3 M_{c,max} / 2 \rho_c V_s$. The quantity α is a constant for any coal/solvent pair. Finally, this expression may be used to obtain N , as a function of extent of swelling, since $N = M_c / M_{cluster}$:

$$N = [(1+r)/N_{max} - (\alpha/N_{max}) f (v_c^{-1} - 1)]^{-1} \quad (24)$$

defining $(1+r)/N_{max} = \gamma$ and $(\alpha/N_{max}) = \beta$, then the expression for N may be rewritten as:

$$N = [\gamma - \beta f (v_c^{-1} - 1)]^{-1} \quad (25)$$

The expression (17) may also be rewritten in terms of the same variable set:

$$\begin{aligned} [\partial(\Delta G_{el}/RT)/\partial n_s]_{T,p} = & (3/2\beta)[N v_c^{-1/3} - v_c^{-1}]^{-1} \\ & + (9fN/4)[(N-1)^{-1} - (N v_c^{2/3-1})^{-1}] \end{aligned} \quad (26)$$

Note that there are effectively four variables (β , γ , f , and v_c) needed to evaluate (26). Note too that the term $[(N-1)^{-1} - (N v_c^{2/3-1})^{-1}] < 0$, for all realistic values of v_c (≤ 1). This means that the effect of dissociation of crosslinks is to always decrease the partial molar free energy of elastic deformation, relative to the case of no dissociation.

There is a useful constraint on the choice of the variables in (26). In particular, N can never exceed N_{max} . This implies from (24) that:

$$1 \geq [(1+r) - \alpha f (v_c^{-1} - 1)]^{-1} \quad (27)$$

Rearranging:

$$(Q-1) = (v_c^{-1} - 1) \leq (\gamma - N_{max}^{-1})/\beta f \quad (28)$$

where $Q (= v_c^{-1})$ is the actually measured swelling ratio of the coal in a solvent. This means that beyond a certain predicted swelling ratio, all crosslinks have been dissociated, and the expression (26) must give way to one in which $f = 0$.

Other bounds on the variables also suggest themselves. Since r can be no less than zero, the lower limit of γ is $1/N_{max}$. The upper limit on γ comes from the recognition that N cannot be meaningfully less than unity, so that γ itself will never be more than unity. In the case of β , if the density of coal is taken as 1.3 g/cc, then $\beta = 1.15 (M_{cluster}/V_s)$. Aromatic cluster molecular weights cannot be less than one benzene ring (72 daltons), and solvents of interest typically do not have molar volumes in excess of about 130 cc/mol. Thus β will have a minimum value of order 0.6. Clusters have been claimed to be as large as 500 daltons, and solvents as small as water ($V_s = 18$ cc/mol) are of interest, so the maximum value of β could be as large as about 32. Finally, f can probably assume values only between zero and unity, assuming that one solvent molecule cannot dissociate more than one non-covalent crosslink.

It can also be noted that (28) implies certain values of the swelling number $(Q-1)/V_s$, if it is assumed in this case that the swelling equilibrium happens to correspond to the situation in which all crosslinks are just dissociated, and the swelling thus becomes more difficult. This condition is given by rearrangement of (28):

$$\begin{aligned} N_s = (Q-1)/V_s = & (\gamma - N_{max}^{-1})/\beta f V_s = 3rf/2\rho_c M_{cluster} \\ = & 1.15 rf/M_{cluster} \end{aligned} \quad (29)$$

If $M_{cluster}$ is of order 10^2 , then the product (rf) must be near order unity, in order for swelling

numbers to be of order 10^{-2} as we have observed. This seems quite reasonable, as noted below.

An initial result of the theory is seen in Figure 1. In this figure are shown the calculations using (25), (26), and (28), as well as (14) for the free energy of mixing. In the case of the free energy of mixing calculation, the value of χ was taken to be zero, in line with our earlier estimates of the heat effects during swelling. These heat effects are thought to be quite small.

The figure shows the much lower free energy of elastic deformation that result when crosslink dissociation is included. The figure also shows the abrupt jump upward to the non-dissociative elastic deformation curve when the criterion of (28) is reached. In this case, this jump immediately takes one to the equilibrium swelling criterion, at a reasonable value of about $Q=1.8$. Note that this behavior is predicted for a value of $\gamma=0.45$, before the completion of all dissociative processes, and requires a $\gamma=0.25$, when they are complete (since $r=0$ at the end, whereas it was 0.78 to start). The value of $N_{\max}$ implied by the fully dissociated case is 3.8. The parameter f was taken to be 0.1 (i.e. one in ten solvents molecules imbibed breaks a crosslink) and $\beta=2.08$ is a reasonable value for propylamine.

Clearly much work needs to be done in the way of testing this model against many other data, but these initial results appear encouraging in terms of offering a model structure that at least presently seems much more reasonable for predicting the behavior of strongly interacting solvents, than have earlier theories.

Discussion

The fact that coals have a swelling/shrinking colloidal behavior in response to moisture gain has been well established, and we have recently shown that the behavior extends well into the bituminous range of ranks (see Figure 2)¹². Thus there is little doubt about the swelling of coals being an important aspect of establishing moisture retention equilibrium. We have also performed coal swellability with a series of linear alkyl amines, following earlier work¹³. These results are shown in Figure 3. The linear relationship between the swellability of coal and the molar volume of the alkyl amines shows clearly the inadequacy of any of the existing swelling theories (such as eqs. 10-12, combined with 14) to describe the process. These data clearly suggest that there is essentially a titratable population of sites within the coal, that will strongly interact with this class of solvents. This forces one to explore modifications to the theories, such as proposed here.

As noted in passing above, the measurements that have been performed in this laboratory also strongly suggest that the actual partial molar enthalpy of mixing is quite near zero, close to swelling equilibrium (it can be quite far from zero at low solvent uptakes, but this is not the region of interest). This means that the process is essentially entropically driven to final swelling equilibrium.

In summary, it appears that the uptake of good swelling solvents is essentially completely governed by specific coal-solvent interactions, but these interactions do not exhibit particularly strong net enthalpies of mixing. We postulate that the latter is a result of the fact that the net enthalpy of mixing involves breaking essentially as strong intra-coal interactions as are formed in the interaction with the solvent. This must be accompanied by a loosening of the network structure, by virtue of the removal of strong non-covalent crosslinks. Hence the model proposed above appears to be consistent with the known swelling behavior of coals, in specifically interacting solvents.

Conclusions

Swelling of coal network structure is not adequately described by any existing theories derived from Flory-Rehner theory. The main difficulty is that the swelling of coal in any sort of good swelling solvent (e.g. water, nitrogen bases) involves specific interactions that are not properly accounted for. The theories can be modified to take into account the disruption of non-covalent interactions that are set up when coal is put into a dry state. This paper has summarized some of the considerations in this direction.

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Figure 1. Partial Molar free energies for mixing and elastic deformation, propylamine solvent.
 This case used $f=0.1$, and $r=0.78$, $N_{\max}=3.8$.

$$\beta=2.08, \gamma=0.45$$

Figure 2. Shrinkage of coals of different rank upon drying.

Figure 3. Swelling of coals in linear alkyl amines at 298 K.

THE ROLE OF MOISTURE IN THE MACROMOLECULAR STRUCTURE OF COALS

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1. INTRODUCTION

Coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain is well established [1-4]. The fact that water can be held by polar groups within the structure of coal also is well documented [5]. There is considerable experimental evidence that there are at least two mechanisms by which water is held in coals. Differential scanning calorimetry (DSC) has suggested that water is held in a tightly bound "unfreezable" form as well as in a bulk "freezable" form [6,7]. Another study, based on proton NMR examination of the water associated with a brown coal, reached similar conclusions [8]. The water is present in a free phase and a bound phase, the latter water molecules having some "mobility" and an ability to exchange with one another on a timescale of a typical experiment (order of fractions of a millisecond). The apparent freezing temperature of the bulk water is a bit below 273K (consistent with other results [6,7,9]), and decreases with heat treatment of the coal [8].

There has also been indirect evidence from dehydration experiments to support the view that water exists in several forms in coal. Variations in the extent of shrinkage brown coal per unit of moisture removed have been interpreted in terms of the role of different types of moisture in coal [1]. The isosteric heat of moisture sorption on coals has been observed to be a function of amount of water in the coal [10]. The fact that hysteresis in coal moisture sorption isotherms must be determined by shrinkage and swelling effects [11] complicates interpretation of such data, however. Perhaps one of the simplest illustrations of the multifaceted nature of water in coals has been provided by the observation that the dehydration behavior as a function of time is not particularly simple [12- 14]. There is a suggestion from recent data that the process of moisture loss may be second order [13] or of apparent order between 1.3 and 2.4 relative to remaining water in the case of bound water [14].

It thus appears that water is retained tightly and in several forms in coals and that coal behaves like a swellable colloid in the presence of water. These two facts have not yet been merged into a unified theory of water retention in coals. This communication explores these observations in terms of interactions of coals with specifically interacting solvents.

2.0 RESULTS

In our earlier work, we reported on the kinetics of shrinkage of large block samples of lignites [4]. We have observed the kinetics of drying of bed-moist samples of four North Dakota lignites, shown in Table 1. The samples were ground to less than 74 μm particle size, and mass loss rates were measured in zero relative humidity environment at a constant 333 K or 323 K. The results of sample mass (M) with time (t) were seen to follow a first order mass loss law: $dM/dt = -k M$, which implies that a plot of $\ln (M/M_0)$ vs. t is linear with slope $(-k)$. The values of k are given in Table 1, together with apparent activation energies (E) for the

drying. No evidence of multistep drying kinetics were seen in these experiments, which only followed moisture loss to 85% of original levels. The drying rates are much higher than those reported for a similar Beulah-Zap sample in one study [13], and much lower than those reported in another [14]. The origin of the discrepancy is unclear, except that in ref. 14, the rate was not modeled as first order in remaining moisture. The value of activation energies are quite variable, and their interpretation is uncertain to say the least. The higher values are very surprising. We believe that the interpretation of drying kinetics in terms of a simple first order model may be inappropriate in any case, as will be discussed further below.

Table 1-Lignites Studied Their Drying Kinetics, and Solvent Swelling Behaviors

<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>k (hr⁻¹)</u>	<u>E(kJ/mol)</u>	<u>N_s^w</u>	<u>N_s^p</u>	<u>N_s^b</u>
Beulah	65.6	3.6	1.1	0.8	11.0	17.9	26.0	0.54	101	10.5	11.2	12.5
Freedom	63.5	3.8	0.9	1.4	6.1	24.3	27.9	0.60	159	8.8	10.1	13.1
Glenn Harold	61.1	4.4	0.8	0.4	7.4	25.9	28.9	0.35	180	7.7	12.3	15.1
Gascoyne	60.9	4.2	0.6	1.4	8.2	24.7	30.7	0.26	29	7.7	9.9	18.0

•All analyses on a dry weight percent basis, except moisture which is ASTM value on an as-received, bed moist basis. Oxygen by difference. N_s values in (mmol/cc); w- water, p- pyridine, and b- n-butylamine.

More precise measurement of drying rates of the same Beulah sample of Table 1 were performed in a thermogravimetric (TGA) device operated at 303 K. These measurements were performed by introducing controlled relative humidity conditions into the chamber, then following mass loss to constant (apparent equilibrium) values, before introducing the next lower humidity conditions. The results are shown in Fig. 1. They shown distinctly two-stage drying behavior. Below about 75% relative humidity, the rates are much lower than above that value. This apparently supports the multistep behavior suggested by others [14], but the rate is first order in remaining moisture in the low humidity regime. The low humidity rates are not well predicted extrapolation of the drying rate from the values in Table 1; much lower values would be predicted. This suggests that it is highly dangerous to attempt to fit simple models to such drying rate data. The drying of coals probably involves the removal of moisture from a wide range of sites, characterized by a distribution of activation energies.

It has been noted [e.g.15] that the moisture loss from coal increases with drying temperature, even above 373 K. This supports the idea that there is a distribution of energies associated with water retention and that some water is held more strongly in coal than in pure bulk water. Just how much more strongly is revealed by other types of experiments. Sorption isotherms were measured as earlier described [4] for the lignites of Table 1 and results are given in Fig. 2. The fact that the isotherms do not shift at all (Beulah) or very little with temperature means that the isosteric heat of moisture vapor sorption is close to the heat of condensation of pure water (i.e. 42.7 kJ/mol). Even when there is a shift between 303 K and 323 K the results imply isosteric heats of order 70 kJ/mol or less. In fact, there is reason to believe that the apparent shift in the isotherms could be an artifact of thermally induced crosslinking even at these low temperatures; the solvent swellability of these coals is significantly reduced by drying at 373 K for one hour [16], and we have noted significant decreases in both pyridine and DMSO swellability of the coals upon 333 K drying (though the isotherm determinations at 303 K have not been performed following heating, to verify this hypothesis). The low values

of isosteric heats agree well with earlier studies [10,11]. They also agree well with the low heats of immersion measured on a subbituminous coal (order 10^{-2} kJ/mol [17]), since such measurements would be net of the heat of condensation of water.

The broad range of sites involved in holding moisture is also suggested by DSC scans of undried coals. Typically, there is a broad endotherm centered at temperatures above 373 K and often not completed until about 473 K [e.g. 18]. Great care must be exercised to not create a diffusional resistance within a typical sample holder, which would create the impression of high temperature water loss, but mass loss clearly does occur at temperature above 373 K [15]. Such DSC data showing a broad temperature range for moisture loss have recently been interpreted in terms of a diffusion controlled release of moisture [13]. We propose that a distribution of activation energies for moisture loss may fit such data as well, and would be consistent with the picture of different types of water-coal interactions, as suggested by the other data above.

The fact that water is a good swelling agent for low rank coals cannot be overlooked. Recently, we have proposed [19] that the swelling of coals in good solvents is governed by a process that was earlier suggested to effectively involve a titration of specific interaction sites [20]. The swelling of coals in specifically interacting solvents is better examined in terms of the swelling number (N_s) than the volumetric swelling ratio (Q) itself; $N_s = (Q-1)/V_s$, where V_s is the molar volume of the solvent, and thus N_s represents the number of titratable sites per unit volume of coal [19]. The values of N_s are shown for three solvents in Table 1 (the solvent swelling ratios were measured as described elsewhere [21]). Not shown are data on ethanol, toluene and hexane, which are ineffective in these lignites (all give $N_s=0$, except ethanol, for which $0 < N_s < 3.9$). It appears on the basis of such data that the stronger the electron donor, the higher N_s , and that different coals react differently to electron donor strength. This is understood in terms of a distribution of different sorption site strengths within the coal, if there is a competition for sites with inherent electron donors in the coal. From classical swelling theory, it is possible to estimate that the net partial molar enthalpy of mixing of the good solvents with coal would be fractions of a kJ/mol [19]. This is again consistent with the observations of isosteric heats as being close to heats of condensation.

It is hypothesized that the retention of moisture in lignites involves a solvent swelling type of behavior, governed by the nature of different specific interaction sites within the lignites. The net enthalpy of interaction of liquid water with the coals is not large, whereas the interactions are comparable in strength to intermolecular interactions in bulk water, as suggested by the high temperatures needed to dry coals. This means that during wetting of a dry coal, the exothermic wetting process must be counterbalanced by endothermic processes involving the dissociation of strong non-covalent bonding interactions in the dry coal. It would, again, be logical to expect that these internal bonding interactions should be governed by a distribution of energies.

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Figure 1. Rate of drying of Beulah lignite at 303 K, as a function of relative humidity. Each point represents an average rate for drying a sample from the next higher relative humidity.

Figure 2. Sorption isotherms for water on four N.D. lignites. Open symbols-desorption; closed-adsorption. Solid curves with circles-303 K, dashed curves 323 K (V) and 333 K (▲,△).