STUDY OF HYDROCARBON-SHALE INTERACTION

Progress Report #1

MASTER

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ABSTRACT

This report summarizes work on Hydrocarbon-Shale Interaction at Juniata College from June 1, 1976 through September 30, 1976. Funds for the work were obtained from the National Science Foundation Undergraduate Research Participation Program, and from ERDA contract #E(40-1) 5197. The three faculty involved were Dr. Paul Schettler, Dr. Dale Wampler, and Dr. Donald Mitchell. The four students were Eric Jensen, Sharon Steckbeck, Craig Zychal and Linda Hoeflich. These people worked full-time from June 7 through August 13. Paul Schettler has worked part-time on the contract from September 1 to October 1.

Work was accomplished in the following areas: Constrictive and Geometric Effects Associated with Gas Production from Shale Wells, Diffusion Constants, Hydrocarbon Gas Analysis, Adsorption Isotherms and Powder X-ray Diffraction. In addition, one of the students spent three weeks preparing a Bibliography on Adsorption and Diffusion in Shale which is included. Finally we have included a detailed description of the procedures used in construction and calibration of the apparatus used for sorption measurements.

All experimental work was done on cores from Well #20403 in Lincoln County, West Virginia.

It is anticipated that the first part (Constrictive and Geometric Effects) will be submitted for journal publication in its present form. The other reports should be considered preliminary in form,

GAS PRODUCTION IN SHALE WELLS:

CONSTRUCTIVE AND GEOMETRIC EFFECTS

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INTRODUCTION

Recent attention has been focused upon the possible inclusion of Devonian and other shales in the eastern U.S. as a natural gas reserve. The total hydrocarbon content of these shales is large and in addition is present in large fraction as natural gas. Gas is currently obtained from a number of wells in West Virginia, Ohio, and Pennsylvania. Characteristically the wells behave as might be expected from wells drilled into tight (low permeability) formations in that the gas production rates are relatively low, but wells continue to produce over 30 and more years. Wells in shale would be more economically feasible if the rate of production could be accelerated.

There seems to be general agreement that the reservoir is the shale itself and that gas diffuses through the microporous structure of the bulk shale to a macroscopic fracture system which is intersected by the well bore. Recently, Schettler⁽¹⁾ constructed a simple mathematical model consistent with this view that resulted in semi-quantitative fits to well productivity data published by Columbia Gas⁽²⁾. The purpose of this paper is to survey some of the existing mathematical solutions to diffusion problems of a similar vein for relevance to the problem of gas production from fractured tight formations.

We believe that mathematical models will play a crucial role in the process of pinpointing and evaluating those parameters important to well production. Efficient well location and stimulation efforts depend upon the intelligent optimization of these parameters.

THEORETICAL

The diffusive flow of gas through shale can be expected to follow Fick's first law

$$(1) \quad J = -D \nabla C(x, t)$$

where J is the flux, $C(x, t)$ is the concentration at point x and time t , ∇ is the gradient operator, and D is the diffusion constant.

Thus for any given concentration profile fluxes (or flow rates) can be calculated as a function of position in the rock. These fluxes in turn determine a new concentration profile which can be calculated by substitution of the equation of continuity into (1), resulting in Fick's second law

$$(2) \quad \frac{\partial C(x, t)}{\partial t} = D \nabla^2 C(x, t)$$

Solutions to (2) are available for a variety of boundary conditions corresponding to different physical situations, and work in this field has been well summarized by Crank⁽³⁾.

The simplest relevant model⁽¹⁾ assumes that diffusion through the bulk rock is the "rate-limiting step" in well production and that the well bore is intersected by a single plane fracture which serves as a high permeability drain of rock near the fracture to the well bore. It is further assumed that the pressure at the wellhead is kept constant at p_o . The result of this model is that well production can be expected to be given by

$$(3) \quad \frac{dM_T}{dt} = A(C_2 - C_0) D^{\frac{1}{2}} \pi^{-\frac{1}{2}} t^{-\frac{1}{2}}$$

where

$$\frac{dM_T}{dt} = \text{rate of gas production}$$

$$D = \text{diffusion constant of gas through bulk rock}$$

$$t = \text{time}$$

- A = total area of exposed rock facing fractures that contribute to production
- C_2 = initial concentration of the gas in the rock before start of degassing
- C_0 = concentration of gas in the rock which would be at equilibrium with gas at pressure p_0 . During degassing the concentration of gas in the rock decreases from C_2 toward C_0 as a lower bound

Although fits can be made to the anticipated $t^{-\frac{1}{2}}$ law with sufficient accuracy to support the basic validity of the equation, nevertheless, it seems clear that individual wells differ from each other in ways that cannot be described by a simple one-parameter equation. Investigation of four main categories of elaborations will be made here: the effect of adsorption, the effect of an ensemble of fractures each with separate degassing rates, the effect of constrictions associated with fractures, and finally fracture geometries other than planar. The effects of each of these will be taken up in turn.

In respect to the first point, the diffusion constant is generally decreased by adsorption because the adsorbed molecules are (relatively) immobile. If there is an equilibrium between adsorbed and mobile molecules such that each molecule spends a fraction of its time sorbed and the remaining time mobile, then the diffusion constant is simply attenuated (relative to an unadsorbed constant) by the fraction of time the average molecule is in the desorbed state. As this fraction is $\frac{1}{1+K}$ where K is the equilibrium constant between stationary and mobile states, $\frac{1}{1+K}$ becomes the appropriate attenuation factor. In the simplest case where K is a constant independent of concentration, this is the only correction needed, and with this understanding, Fick's laws are unchanged. Only in the case of a concentration-dependent K must specific account be taken of the corresponding change of D with concentration. This possible complication is not further considered here.

The second complication is to assess effects arising from the expectation that different parts of the fracture system may contain different amounts of gas, C_2 , and furthermore, that various sections may have different diffusion constants. In this case, the total well production is the sum of the production of each section, i.e.,

$$(4) \quad \frac{dM_T}{dt} = \sum_i A_i (C_{2i} - C_0) D_i^{\frac{1}{2}} \pi^{-\frac{1}{2}} t^{-\frac{1}{2}}$$

In the case of continuous changes of properties the summation would be replaced by an integration. In any event, (4) reduces to

$$(5) \quad \frac{dM_T}{dt} = A (C_2 - C_0) D^{\frac{1}{2}} \pi^{-\frac{1}{2}} t^{-\frac{1}{2}}$$

i.e., the same as equation (3) but with the use of averaged parameters. In particular, consideration of variations does not result in deviations from the $t^{-\frac{1}{2}}$ law. Hence observed deviations must result from causes other than the variation of diffusion constants and gas concentrations from point to point in the well.

As a general rule, flat curves will be caused by a reservoir which is tapped by a highly constrictive outlet. The fact that some productivity curves are flatter than that predicted by the $t^{-\frac{1}{2}}$ law implies then that diffusion from the rock is not the rate-limiting process but rather that this is supplemented by some other constrictive effect. It seems natural to associate this with the fracture, and the simplest boundary condition to describe a constrictive effect thus arising is

$$(6) \quad D \left(\frac{\partial C}{\partial x} \right)_{x=0} = \frac{D}{g} (C(0,t) - C_0)$$

where g is a measure of the magnitude of the constrictive effect scaled appropriately by the diffusion constant of the bulk rock, and $C = C(x,t)$ is the concentration of the gas at point x (as measured into the bulk rock from the fracture surface) at time t . Physical examples as to when Equation (6) is applicable include the case

wherein the diffusion constant changes magnitude near a fracture, in which case g can be interpreted as a skin thickness, δ , multiplied by the ratio of the diffusion constant of bulk rock to that of the skin, D_S (D_S is small in comparison with D). Another possibility is that finely divided material plugs the fractures in which case g can be interpreted as $\frac{\delta D}{D_F \beta}$, where D_F is the diffusion constant of the material plugging the fracture, δ is the length associated with the plug, and β is the ratio of fracture cross-sectional area to bulk rock area.

Equation (6) in conjunction with Equation (2) results in

$$(7) \quad \frac{C(x,t) - C_2}{C_0 - C_2} = \operatorname{erfc} \frac{x}{2\sqrt{Dt}} - \exp\left(\frac{x}{g} + h^2 \frac{Dt}{g^2}\right) \operatorname{erfc}\left[\frac{x}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{g}\right]$$

Applying Equation (1) at $x = 0$

$$(8) \quad \frac{dM_T}{dt} = E \exp(z^2) \operatorname{erfc}(z)$$

where $E = \frac{D}{g} (C_2 - C_0) A$, $z = Bt^{\frac{1}{2}}$, $B = \frac{D^{\frac{1}{2}}}{g}$, and $\operatorname{erfc}(z) = \frac{2}{\pi^{\frac{1}{2}}} \int_0^z \exp(-z^2) dz$.

For large $Bt^{\frac{1}{2}}$, Equation (8) can be rewritten as

$$(9) \quad \frac{dM_T}{dt} = \frac{d_0 M_T}{dt} \left(1 - \frac{g^2}{2Dt}\right), \text{ i.e., } \left(1 - \frac{g^2}{2Dt}\right)$$

where $\frac{d_0 M_T}{dt}$ is the flow rate of a similar, unconfined well. It can be seen from this latter equation that the effect of the constriction is to decrease the rate of production, particularly at short times, thus resulting in curves that are flatter than those expected from a simple $t^{-\frac{1}{2}}$ model.

Whereas constrictive effects flatten production curves, consideration of fracture geometries other than flat planar can be expected to result in production curves that are steeper than the $t^{-\frac{1}{2}}$ law.

In many cases, the relevant rock surfaces will not be a single fracture but a network of interconnected joints or other fractures which divide the rock mass into a number of finite reservoirs each degassing into fractures on all sides. Initially, the depletion zones will be small and the net effect can be expected to be similar to the case resulting in Equation (3). However, at longer times the depletion zones moving into the reservoir from the fracture surfaces will begin to overlap, the entire reservoir will start to become depleted, and the unmodified $t^{-\frac{1}{2}}$ law will overestimate the gas produced at long times. For example, an ensemble of spherical reservoirs gives

$$(10) \quad \frac{dM_T}{dt} = \frac{3M_\infty}{\pi^{\frac{1}{2}}} \frac{D^{\frac{1}{2}}}{a} t^{-\frac{1}{2}} - \frac{3DM_\infty}{a^2} + \text{higher terms}$$

where M_∞ is the total amount of gas finally evolved, $\left((C_2 - C_0)\frac{4}{3}\pi a^3\right) N$, a is the sphere radius, and N is the number of spheres involved.

The lead term is identical to Equation (3) as soon as the substitution for M_∞ is made. The second (and higher) terms are due to the encroachment of the depletion zones on each other and their effect is opposite to Equation (7), i.e., the effect of the correction becomes greater as t increases. The corresponding solution for a cylinder is similar.

$$(11) \quad \frac{dM_T}{dt} = \frac{4M_\infty}{\pi^{\frac{1}{2}}} \frac{D^{\frac{1}{2}}}{a} t^{-\frac{1}{2}} - \frac{DM_\infty}{a^2}$$

RESULTS

Figure I shows a reproduction of the data of Bagnall and Ryan⁽²⁾ and the fits obtained from the constrictive model. More specifically, best values of the parameters E and β in Equation (8) were determined by a computer program utilizing Marquardt's algorithm for non-linear least squares⁽⁴⁾. The parameters E and β are related to "well size" $(C_2 - C_0)A$ and g by $\frac{Eg}{D}$ and $\frac{D^{1/2}}{\beta}$ respectively. (If concentration units are cu.ft. gas/cu.ft. rock then the dimension of well size is area.) Thus production data combined with rock diffusiveness data, D, from independent measurements* results in estimates of well size (i.e., total fracture area times gas concentration) and the degree of constriction g. The fits obtained are quite quantitative with the exception of the most highly productive wells.

In contrast to the low productivity group, the highly productive wells have somewhat steeper production rate curves than can be fitted by the constrictive model even in the limit of no constriction (i.e., a $t^{-1/2}$ law). This suggests that in these highly productive wells some other effect is manifest. This group of wells is accurately fit by the equation

$$(12) \quad \frac{dM_t}{dt} = \mathcal{A} t^{-1/2} - \beta$$

where $\mathcal{A} = 7164 \text{ MCF/day}^{1/2}$ (corresponding to a well size of $1.73 \times 10^{11} \text{ m}^2$) and $\beta = 4.5 \text{ MCF/day}$. As shown in Fig. II, utilizing Equation (10) $\mathcal{A}$ and β can be combined to give M_∞ and a "lump size" a.

$$(13) \quad M_\infty = \frac{\mathcal{A}^2}{\beta} \frac{\pi}{3}$$

$$(14) \quad a = \frac{\mathcal{A}}{\beta} \pi^{1/2} D^{1/2}$$

and hence $M_\infty \sim 1.3 \times 10^{12} \text{ cu.ft.}$ and $a = 65 \text{ cm}$ (assuming $D = 5 \times 10^{-7} \text{ cm}^2/\text{sec}$).

* We have used the value of $D = 5 \times 10^{-7} \text{ cm}^2/\text{sec}$ as a rough estimate, based on preliminary measurements made in our laboratory on representative shales.

(These results are fairly insensitive to the details of geometry. Assuming cylinders the corresponding values are $.95 \times 10^{12}$ cu.ft. and 32 cm.)

Figures III and IV show concentration profiles for the case of constriction, (i.e., Equation (7)) both as a function of the magnitude of the constriction and time. The outstanding feature of Fig. III is the degree to which a constrictive effect alters the whole nature of the concentration profile; in particular, it markedly decreases the depth of the depletion zone and the steepness of the concentration profile. As Fig. IV illustrates, as time increases the process associated with diffusion through the bulk rock becomes more important and the constrictive effects of less relative importance. This correlates with Equation (8) and Fig. I which illustrate that increased constrictive effects flatten primarily the low-time part of the production-time curves.

CONCLUSION

It would appear from the calculations presented here that a successful well results from the simultaneous optimization of several parameters. First, the well bore must intersect a network of fractures or be otherwise stimulates so that a large surface area of rock is connected to the bore by means of "macroscopic" fractures. (The relevant area is simply the area associated with the faces of these fractures; it has no connection with the surface area of bulk rock obtained by BET measurements.) Second, the bulk rock must be at least somewhat permeable to hydrocarbon gases, as well as having hydrocarbon gases present within it. Well productivity is a function of the simultaneous attainment of these two criteria in the bulk rock containing a fracture system connected to the well bore. In particular, for a given fracture system well productivity is maximized when

$$\int_{\text{all fractures}} (C_2 - C_0) D^{\frac{1}{2}} dA = \overline{(C_2 - C_0) D^{\frac{1}{2}}} A$$

is maximized. Thus it would appear that $C_2 D^{\frac{1}{2}}$ is the bulk rock parameter that is most closely related to well productivity (for a given fracture system).

The effect of these bulk rock parameters (A and $\overline{C_2 D^{\frac{1}{2}}}$) can be extensively modified by the detailed structure of the fracture system itself. The case of primary importance is the presence of constrictions which attenuate production. These effects may be localized in the fractures themselves either by virtue of attenuated dimensions or by virtue of mud or other filling which acts as a plug. However, other possibilities not confined to the fracture itself cannot be ruled out. For example, it is conceived that some sort of restrictive skin effect should be considered for the bulk rock on the fracture surfaces. Thus, the surface may have properties different from the bulk rock due to mineral deposition or other plugging of the mini/micro pore system of the shale itself as a result of fluid flow throught the fracture. The constrictive skin thus resulting would produce effects similar to those resulting from plugging of the primary fracture.

In any event a characteristic of any constriction is that it is localized, and hence can be removed by small scale processes, at least in theory. In other word, while it is probably not feasible to attempt to modify bulk rock parameters such as $C_2 D^{\frac{1}{2}}$ on a massive scale, the constrictive parameter may be relatively sensitive to the type of well stimulation employed.

A second influence of the detailed nature of the fracture system on well production is shown in reservoir depletion effect associated with non-planar geometries in general and closed "networks" of fractures which isolate finite reservoirs in particular. The depletion zones associated with such lumps move in from the fracture surfaces eventually interfering with each other; the net effect is a drop off in productivity with increasing time as compared to that predicted by a $t^{-\frac{1}{2}}$ law. The magnitude of the depletion zone is given by $\sqrt{Dt}$. Geometric network effects should become important on a time scale of $\frac{a^2}{D}$ and greater, where a is a length parameter associated with the network (sphere or cylinder radius for the specific models dealt with here). On this time scale, $\overline{C_2}$ is a more useful bulk rock parameter than $C_2 D^{\frac{1}{2}}$. However, for the wells considered by Bagnall and Ryan, only a few (the most productive) wells are in this category even though the time scale is a quarter century.

Unfortunately, for both the simple model and the constrictive models, M_∞ can not be defined because the depletion zone can expand from the fracture structure without limit and, though the rate of production, $\frac{dM_T}{dt}$, decreases monotonically with time, nevertheless its integral over time (the total gas evolved) can be made to be any arbitrarily large value simply by letting the time span of production extend long enough. Likewise the volume of rock drained of gas is arbitrarily large, although over reasonable time periods, this volume is all within a few centimeters from the surface of a fracture connected in turn to the bore.

Only in the case of significant network effects will production data directly yield M_{∞} and hence a total volume of rock drained.

It is reasonable to suppose that the fracture geometry of most wells is such that network (depletion zone interference) effects are observable on some time scale. However, it would appear from the data presented by Bagnall and Ryan that for a high percentage of shale wells this time scale is large in comparison to a quarter century. Thus, it would appear that well production data alone cannot normally be used to determine M_{∞} as a practical matter, but rather that production data must be combined with some understanding of the natural and induced fracture system and the bulk rock parameters $C_2 D^{\frac{1}{2}}$ as a function of depth (assuming it remains constant along bedding planes) as well as C_2 (if the rock is known to be highly fractured) in order to estimate reserves, optimum well spacings and productivity.

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CAPTIONS

Figure I

Flow rate (million cu.ft./day) is plotted against time (years). The points are averaged values from four categories of wells. The lines are fits obtained as described in the text. Values of the parameters are as follows from upper to lower curves:

size (meters ²)	g(cm)
1.216×10^{11}	.00897
$.845 \times 10^{11}$	4.79
$.506 \times 10^{11}$	6.016
$.254 \times 10^{11}$	6.318

Figure II

Flow rate (MCF) is plotted against time (years). The points are experimental data and the curve is the fit obtained.

Figure III

Concentration is plotted against distance (cm) into the rock for different amounts of constrictive effects, as measured by g. The values of this parameter are 8.62, 4.80, and .00897 cm from top to bottom. The profiles were compiled with $t = 4$ years. The surface of the rock is at $x = 0$ and the constriction is represented by δ .

Figure IV

Concentration is plotted against distance (cm) into the rock for times of 1, 4, and 20 years; $g = 4.80$ cm for all curves.

Fig. I

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Fig. III

Fig. IV

DIFFUSION CONSTANTS IN DEVONIAN SHALE

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DIFFUSION CONSTANTS IN DEVONIAN SHALE

INTRODUCTION

Diffusion constants can be measured by determination of the fluxes and concentration gradients associated with Fick's first law.

$$(1) \quad J = -D \text{ grad } C$$

where J is the flow of material, C is the concentration and D is the diffusion constant.

Insofar as Equation (1) is a general equation covering all diffusive flow phenomena, it can be applied in particular to problems of desorption, wherein the rate of outgassing from the rock into a vacuum (or region of chemical potential) is determined in essence by the geometry of the rock and the diffusion constant. Specific calculations for a variety of geometries have been accomplished over a number of years. These solutions have been compiled by Crank⁽¹⁾ among others. Carman and Haul⁽²⁾, Nandi and Walker⁽³⁾, Stoessel and Honor⁽⁴⁾, have utilized sorption rates to study diffusion constants of porous substances. Apparently of wide applicability these methods have not been applied to shale in a systematic manner although some scattered results have been reported⁽⁵⁾.

The approach used here is to subject a ground sample of sorbent (initially at equilibrium with some partial pressure of nitrogen or other gas) to a step function change in pressure and the rate of degassing (or sorption) followed by noting the (small) changes in pressure within the closed vessel in which the sample is enclosed.

The exact mathematical solution (for an ensemble of spherical particles) is:

$$(2) \quad \frac{P_0 - P_T}{P_0 - P_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6 \alpha (\alpha+1) \exp(-D q_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2}$$

wherein the q_n 's are the non-zero roots of

$$(3) \quad \tan q_n = \frac{3 q_n}{3 + \alpha q_n^2}$$

P_0 = pressure at time 0+ (just after the step first)

P_∞ = pressure at $t = \infty$

P_T = pressure at time t

a = particle radius (sphere assumed)

$\alpha = \frac{\text{Volume system}}{\text{Volume shale}} \cdot \frac{1}{K}$ where K is the partition coefficient

Equation (2) does not converge readily at low times, the time domain of greatest practical interest. In this latter region Equation (2) can be expanded in a power series resulting in

$$(4) \quad \frac{P_0 - P_T}{P_0 - P_\infty} = \frac{1+\alpha}{\alpha} \frac{6}{\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}} - \frac{1+\alpha}{\alpha^2} \frac{9(\gamma_1^3 + \gamma_2^3)}{\gamma_1 + \gamma_2} \frac{Dt}{a^2}$$

where $\gamma_1 = \frac{1}{2} [(1 + \frac{4}{3} \alpha)^{\frac{1}{2}} + 1]$ and $\gamma_2 = \gamma_1 - 1$. α , a parameter depending on the experimental arrangement and the sorptive capacity of the sorbing material, can be obtained in terms of the pressures. Thus Equation (4) becomes the basis of a method for obtaining diffusion coefficients. More specifically

$$(5) \quad \alpha = \frac{P_\infty - P_2}{P_0 - P_\infty}$$

A determination of the pressure after equilibrium is reestablished, P_∞ , allows determination of α .

P_0 can be found from the lead term of a 2nd degree (or higher) polynomial fit to pressure versus square root of time data.

The next term determines $6 \pi^{-\frac{1}{2}} (\alpha + 1) \alpha^{-1} (P_0 - P_\infty) D^{\frac{1}{2}} a^{-1}$.

By using sieved samples the particle radius, a , is known, hence D can be calculated.

EXPERIMENTAL

Ground, weighed (5.60 g), dust-free samples from core that had only recently been removed from the can were obtained in two sieve sizes, 500-700 microns and 175-350 microns. We desired to get as large a fraction as possible of the rock in one of the two sieve sizes. The actual procedure was to grind a shaker mill for 15-30 sec., sieve, and then to regrind the oversized particles, resieve, and so forth. The purpose of this procedure was to submit particles of the right size to as little additional punishment as possible, and to make the process as efficient as possible so that a large fraction of rock ended up in the correct mesh size. Dust affects the diffusion measurements and by providing a large surface from which sorbtion/desorbtion will occur. It was found necessary to further eliminate this by placing the sieved sample between two small mesh sieves and blowing the dust off with a hand blower.

The sieved samples were then placed in a pyrex cell which was then attached to the system shown in Figure I by glassblowing. The system was carefully calibrated as has been described elsewhere (in the BET section). The system and sample was next carefully evacuated for a few minutes, then placed under an atmosphere of prepurified nitrogen and the cell immersed in liquid nitrogen. After waiting for equilibrium (about 15 min. depending on mesh size) a run was commenced as follows. First a measurement of the pressure was made (P_2). Then V_1 was closed, V_2 was opened and gas added to (or removed from) that part of the system containing the gas buret (set at Mark #8). A computer program was then started that automatically collected up to 1000 pressure readings spaced 0.2 sec apart.

The equipment used was a NOVA 1220 computer with a 5 volt (12 bit) analog/digital converter which collected readings from a Datametrics 1173 electronic manometer and type 570D barocell. On the 1000 torr range the precision of pressure measurements was ± 0.5 torr; on the 0-100 torr scale the precision was ± 0.05 torr. With the computer running V_1 was opened. The computer program subsequently found $t = 0$ by a search for the applied step function. The least square polynomial fits were made over the interval from 2 sec to 180 sec using a weighted least squares routine that corrected for the overweights of long times that results from the unequal spacing of data points on a $t^{1/2}$ scale. (The collected data points are equally space on a scale linear in time (.2 sec) hence unequally spaced on a scale that is non-linear.) The program then continues to collect (but not save) pressure data until the pressure becomes constant. This pressure is then taken as the equilibrium pressure P_∞ . The length of time required to obtain it varies but is typically about 15 minutes over our range of mesh sizes. The program then calculates P_0 , α , and D , and allows for a number of output options. For example, it allows a visual comparison of the data, the polynomial fit, and the exact function (Equation 2) with each other on a CRT.

As a part of initial checkout of the system "runs" were made using an empty cell. A variety of effects were uncovered attributable to attainment of pressure equilibrium upon opening V_1 and temperature equilibrium of gas flowing into or out of the cell at liquid N_2 temperature. However, these effects were of no consequence after the first second or two. Thus for the time period after 2 seconds pressure changes are entirely the result of sorbtion/desorbtion.

RESULTS

After a rather extensive period involving measurements under a variety of conditions, the following set of conditions was chosen for a set of six core samples from the Lincoln County Well #20403. Each of these core samples was run under three different pressure conditions, and two different mesh sizes, 51 individual measurements in all. In the tables that follow Medium refers to 175-350 μ mesh size and Large refers to 500-700 μ mesh size. The three different pressure conditions were as follows: Condition 1) P_2 was 100 torr and P_0 was about 640 torr obtained by setting the pressure in the buret at 700 torr. Condition 2) corresponds to $P_2 \approx 600$ torr and an initial buret pressure of 700 torr. For condition 3) the numbers are 10 torr and 100 torr respectively. The depths are those shown on the cans furnished to us⁽⁶⁾.

3221 Large

Pressure type	P_2	P_0	P_∞	Coef $\times 10^{-7}$	Alpha
1	87.9	637.1	613.8	7.3	22.6
2	613.3	700.6	694.8	7.2	14.2
3	12.7	87.0	83.3	7.9	18.8

3221 Medium

1	120.1	646.7	641.1	3.2	94.0
3	11.0	86.7	86.3	2.4×10^{-4}	200.0
2	606.4	690.1	688.0	2.4	39.1
4	94.7	583.4	554.2	1.8	15.7

3281 Large

Pressure Type	P_2	P_0	P_∞	Coef $\times 10^{-7}$	Alpha
1A	93.3	634.1	626.0	14.8	65.4
1D	627.0	86.7	88.4	8.0	317.4
3A	13.0	84.9	77.3	7.9	8.5
1A	99.6	634.3	598.6	6.6	14.0
1A	114.7	647.9	612.8	6.3	14.2
1D	610.8	87.4	116.7	7.8	16.8
2A	574.7	675.7	660.6	5.5	5.7
*	279.1	94.2	117.8	7.8	6.9
3D	117.9	41.2	52.9	8.8	5.6
3D	52.9	20.0	26.7	7.3	4.0
1A	98.6	512.7	454.6	7.1	6.1
1A	139.6	544.6	489.3	7.1	6.3
3A	12.7	66.0	53.5	7.5	3.2

3281 Medium

1	90.3	610.9	590.3	2.2	3.2
2	589.4	672.4	666.5	0.20	13.1
3	14.4	82.3	79.5	6.0	23.4

* This run was non-standard.

3716 Large

1	99.1	625.6	604.5	15.1	23.9
2	605.0	708.9	700.7	10.6	11.6
3	9.1	84.4	80.8	19.3	20.0

3716 Medium

1	138.7	656.0	617.7	2.7	12.5
2	618.2	751.8	733.4	2.0	6.3
3	9.2	73.2	70.6	4.5	24.0

Pressure Type	P_2	P_0	P_∞	Coef $\times 10^{-7}$	Alpha
<u>3736 Large</u>					
1	120.6	656.4	626.8	14.4	17.1
2	661.6	757.8	745.1	8.9	6.6
3	21.9	86.5	81.1	36.2	11.0
4	113.3	657.7	614.3	15.6	11.5
<u>3736 Medium</u>					
1	105.0	641.3	620.1	3.0	24.3
2	620.6	725.0	717.3	2.7	12.5
3	7.6	76.4	74.6	5.6	37.2
4	122.1	634.2	595.7	2.6	12.3
<u>3886 Large</u>					
1	94.2	642.4	592.8	15.4	10.0
2	593.8	688.1	673.8	11.4	5.6
3	10.4	84.0	76.2	7.5	8.5
<u>3886 Medium</u>					
1	121.1	634.8	597.2	2.5	12.6
2	597.7	702.9	689.0	2.0	6.5
3	9.5	76.0	73.9	4.7	30.1
<u>4026 Large</u>					
1	148.4	687.1	684.6	6.6	206.7
2	685.1	790.1	788.6	24.7	66.2
1	88.4	694.6	691.4	19.1	190.8
1	88.4	653.3	650.9	12.6	234.5
<u>4026 Medium</u>					
1	112.3	672.3	669.4	2.5	191.0
1	92.3	652.4	649.4	3.2	186.2
3	10.6	86.8	86.3	5.7×10^{-3}	177.2
4	86.4	648.1	646.0	6.9	266.3

DISCUSSION

The purpose of the data array chosen was to delimit the important variables associated with rates of desorption from the shales considered. In particular, it would appear from the data collected to dates that variations of diffusion constant occur as a function of mesh size. The diffusion constant measured for the six samples was on an average 340% ($\pm 148\%$ standard deviation) greater for the larger mesh size (500-700 μ) than for the smaller (175-350 μ) material. We believe that this result is compatible with existing S.E.M. photographs of shale which suggest that there are a number of small cavities and cracks in the shale which serve as high permeability conduits from the interior of the particle to the particle surface. Larger particles may be expected to have relatively more such conduits and hence faster sorption/desorption diffusion rates relative to the results expected of a model that assumes homogeneous particles.

The second correlation was that the diffusion constants apparently increased by about 39% as the pressure was increased from 100 - 700 torr. This result is less certain because of the very small pressure changes involved during a run using pressure options 2 and 3, less than 10 torr but explainable in terms of a concentration dependent partition coefficient between the gaseous and sorbed material*. Nevertheless we feel that there are good reasons for expecting this trend. It should be noted that in the case of adsorption larger diffusion constants might be expected to occur as one moves out of the steep low pressure region of an isotherm. The highly active adsorption sites are occupied and hence existing gas phase molecules within the pore spaces are less apt to be trapped and held immobile by these sites. **.

* This dependence on concentration is discussed in more detail in another part of this report.

** See also "Gas Production in Shale Wells: Constrictive and Geometric Effects" elsewhere in this report.

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Figure I. The system used to make sorption studies.

The system is connected to a standard high vacuum system (capable of 10^{-6} torr) at valve V_2 . Included in that vacuum system is a precision manometer, McCleod gauge, Toepler pump for bringing samples of gas to atmospheric pressure for gas analysis, and connections to nitrogen and other gas supplies.

Fig. I

ANALYSIS OF HYDROCARBON GASES FROM CORES OF WELL #20403

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ANALYSIS OF HYDROCARBON GASES FROM CORES OF WELL #20403
LINCOLN COUNTY, WEST VIRGINIA

INTRODUCTION

An analysis was made of the gases evolved from core samples taken from Well #20403, Lincoln County, West Virginia. The samples were two-inch thick, three-inch diameter sections taken at 10-foot intervals for 1300 feet, from 2726' to 4026' level. The samples had been sealed in metal cans at the site over an approximately two-week period beginning January 14, 1976; thus, any gases evolved from the time of sealing to the time of measurement were contained in the cans.

EXPERIMENTAL

The pressure inside the cans was measured before starting the gas analysis. This was accomplished by making a septum on the lid of each can with silicone rubber aquarium sealer. Once the rubber had cured, a small hole was punched in the can through the septum. The pressure was immediately read using a 23-gauge needle connected by a piece of copper tubing to a pressure gauge. In this manner, the pressure could be read and a gas sample later removed without contaminating the gas. The pressure readings were taken on June 18, 1976, 142-156 days after the cans were sealed.

The gases in the cans were analyzed by GC analysis June 24-30, 1976. Two chromatographic separations were necessary for complete analysis of all gases.

	Separation I	Separation II
Column Material	5A Molecular Sieve (120-170 Mesh)	20% Dow Corning Silicone Grease/Chromosorb W. (60-80 Mesh)
Column Length	1.5 m	1.5 m
Column Diameter	1/4 "	1/4 "
Column Temperature	100° C	ambient - - - 25° C
Carrier Gas	Argon	Helium
Flow Rate	110 ml/min	300 ml/min
Detector	Thermal Conductivity	Thermal Conductivity
Retention Time		
H ₂	0.7 min	0.18 min
O ₂	1.1 min	0.18 min
N ₂	1.3 min	0.18 min
CH ₄	2.1 min	0.18 min
CO ₂	retained	0.20 min
C ₂ H ₆	retained	0.22 min
H ₂ S	retained	0.25 min
C ₃ H ₈	retained	0.30 min

As indicated, the molecular sieve column resolves nitrogen, oxygen, hydrogen, and methane while retaining all other gases. The silicone grease column elutes oxygen, nitrogen, hydrogen, and methane as a single "air" peak while separating the other gases.

Response factors for the gases were checked and recalibrated against those previously used for this analysis. From earlier work, it was known that sensitivity to flow rate was high, thus making determination of absolute detector response difficult. Relative retention times, with respect to nitrogen for Column I and with respect to air for Column II, were used to determine peak identity.

The detector of each GC was interfaced into a NOVA 1220 computer. The computer was programmed to accept data at a predetermined rate depending upon which GC was being used. Due to the nature of the analysis it was necessary to calibrate the detector responses by first injecting a known amount of air into each column at the beginning of each series of runs, i.e., once in the morning and once in the afternoon. The air and nitrogen peaks recorded were used to calibrate the detector response. It was found that this response varied slightly from day to day. After the standards had been run, the program went into the analysis routine. A known amount of each gas sample was injected into each GC and the data was collected. The data was displayed on a CRT as it was collected. A peak-finding routine processed the data in real time to obtain retention times and peak areas. From the retention times it can be seen that overlap occurs in several cases. The perpendicular drop method (A. W. Westerberg, Anal.Chem., 41, 1770 (1969)) was used to assign areas for overlapping peaks.

Once the data had been collected from both GC's, it was immediately processed by a computer routine. Using programmed relative response factors, each of the peaks was automatically identified. The routine then used the data from Separation I to apportion the area of the "air peak" in Separation II among the gases hydrogen, oxygen, nitrogen and methane. The total amount

of gas found per ml injected as well as percent composition were calculated by the computer and printed out. Once the standards had been run, a typical analysis of the gas content of one can took 8-10 minutes.

The reproducibility of the GC results were checked by running an analysis of a core gas sample five times in succession. The mean standard and relative percentage were calculated for each component. It was found that for peaks from the molecular sieve column there was a relative precision of about 4%, with about 2% for those from the silicone grease column. We estimate the relative accuracy of the analysis to be within 10% of the actual value.

The calculation for the amount of gas evolved by each sample was carried out as follows. The can containing the top core sample was opened and the shale removed. The can was weighed and its volume was measured in order to obtain "standard" values for weight and volume of a can. Each other sample can was then weighed, and the weight of the shale sample and the dead volume which gas could occupy within the can were calculated. Assuming that each can was sealed at one atmosphere pressure in air, the pressure measurements were used to calculate the number of moles of gas which had been given off by the shale. The value for number of moles of hydrocarbon given off per gram of shale was calculated by adding the total percent hydrocarbon composition from the GC analysis and multiplying by the total number of moles present at the time of the pressure reading and dividing by the weight of the shale.

RESULTS

The results of the gas analysis for each of the core samples are included in the accompanying chart, along with the value for micromoles of hydrocarbon per gram of shale for each sample. Several generalizations can be made from these data.

First, the samples do not appear to be equally productive at all levels. There are two highly productive bands, one running from approximately 3300' to 3600', and the other from 3800' to the last sample at 4026'. The samples within these two sections had evolved significantly more hydrocarbons than had the other samples as shown by the figures for methane composition and number of micromoles of hydrocarbon evolved per gram of shale. Other sections of the core were productive, but not to the extent of these two sections.

Second, there was an expected absence of hydrogen and hydrogen sulfide in all samples. These gases had previously been observed in degassed samples, but at elevated temperatures. It has been noted that low-temperature degassing of shales produced little or no H_2S as compared to the previous high temperature degassing. These results lend support to the theory that the appearance of H_2S and H_2 is the result of pyrolysis.

Third, CO_2 tended to appear only in samples from the upper portion of the core. It was observed only three times below 3416' and not at all below 3806'. There is a correlation in that CO_2 appeared only when methane was also present. This was the case in all but one sample containing CO_2 . However, the converse is not true, i.e., the presence of methane did not guarantee that CO_2 was also present. The largest amount of CO_2 which appeared was 7.9%. Beyond this there did not seem to be a correlation between the amount of CO_2 degassed and the amount of methane degassed.

There was no observable correlation between the value of the methane/ethane ratio to the depth of the sample. In most cases where significant quantities of methane were present, the ratio ranged from 2 to 4.

One very notable trend which appeared was reduction of the oxygen/nitrogen ratio in the cans. In air this ratio is normally .268 by volume. In all but four samples this ratio had been reduced below the expected error in the analysis routine. The four "normal" values ranged from .258 to .268, while the ratios for all other samples were below .258, ranging as low as 0.0 in five cases. There was no detectable amount of other gases in the cans with the "normal" O_2/N_2 ratio, and there was no measurable pressure above atmospheric. Although some rusting of the interior of the cans occurred where the sample had scraped the side of the can, absorption of oxygen from this source can account at most for only 20% of the oxygen depletion observed as determined by quantitative analysis of the rust in some of the cans.

There are a number of explanations for the unexpected size of the O_2/N_2 ratio. One is that the core samples contain some metal, probably iron (II) which can be oxidized to iron(III) by the oxygen. A second possibility is the oxidation of some organic compound in the shale. Finally, oxygen may be displacing methane on active absorption sites on the shale. There is some evidence for the latter possibility in that some samples contained high methane (47%), 0% oxygen, depleted nitrogen, but no overall pressure suggesting a mole for mole replacement reaction in the shale. (Cans were checked for leaks by immersion in warm water but no leaks were found, thus reinforcing the replacement reaction hypothesis.) The effects observed could be expected to depend sensitively upon the structure of the particular shale being sampled so that the variability of these results from can to can is not surprising. We are continuing work in this area.

A phenomenon observed in several samples may in part explain the depletion of the O_2/N_2 ratio. There were a few samples which showed no measurable pressure, but upon gas analysis showed extremely high methane content (47%), total loss of oxygen and depletion of nitrogen. A random check of some of the cans showed that none were leaking gas, so this idea was discarded as an explanation for the pressure decrease. What appears to have happened is a nearly one to one exchange of gas molecules. If this is the case, these particular samples could well show a high rate of diffusivity.

GAS ANALYSIS AS A FUNCTION OF DEPTH, WELL #20403

Depth of Sample	Weight of Shale (g)	P (lb/in ²)	mm HC per g shale	% CH ₄	% C ₂ H ₆	% C ₃ H ₈	% CO ₂	% O ₂	% N ₂
2726'2"	1154.6	0	-----	-----	-----	-----	-----	-----	-----
2736'2"	1215.6	0.4	0.44	1.3	0	0	0	17.7	81.0
2746'2"	1079.7	0	0	0	0	0	0	15.5	84.5
2756'2"	1166.1	0	1.37	2.7	1.1	0	3.5	6.2	86.4
2766'2"	896.3	0	0	0	0	0	3.4	10.5	86.2
2776'2"	1112.6	0	0.69	1.8	0	0	3.6	8.4	86.2
2786'2"	843.7	0.68	0	0	0	0	0	18.0	82.0
2796'2"	1023.1	0	0	0	0	0	0	19.1	80.9
2806'2"	703.1	0	0	0	0	0	0	19.3	80.7
2816'2"	1196.5	0	0.26	0.8	0	0	7.1	8.1	84.0
2826'2"	1034.1	0	0	0	0	0	0	17.9	82.1
2836'2"	1205.1	0	1.48	3.4	1.0	0	0	14.0	81.7
2846'2"	719.1	0	0	0	0	0	0	16.7	83.3
2856'2"	1052.4	0	0.34	0	0.8	0	0	11.0	88.2
2866'2"	935.8	0	0	0	0	0	5.2	8.9	85.9
2876'2"	1219.2	0.56	1.09	3.1	0	0	0	17.2	79.7
2886'2"	1429.1	0	3.49	11.1	2.3	0	2.9	10.8	72.9
2896'2"	1187.9	0	7.61	17.8	3.2	1.0	7.9	2.1	67.9
2906'2"	1463.3	0.75	0	0	0	0	0	19.8	80.2
2916'2"	1133.7	0	4.0	6.6	3.0	1.2	4.6	4.5	80.0
2926'2"	1107.2	0	5.27	10.6	3.2	0	4.8	1.8	79.7
2936'2"	1096.6	0.44	6.68	11.2	3.8	1.7	5.7	0	77.5
2946'2"	1068.0	0	6.51	12.0	3.0	1.2	7.3	1.3	75.2
2956'2"	938.9	0	0.94	2.0	0	0	0	17.0	81.1

2966'2"	895.6	1.56	2.87	3.2	1.8	0	0	17.4	77.5
2976'2"	1172.5	0	2.78	6.0	1.9	0	3.7	9.8	78.6
2986'2"	984.9	0	4.68	7.6	2.2	0.6	3.1	10.6	75.8
2996'2"	845.6	0	6.71	9.9	2.3	0	0	14.8	73.0
3006'2"	1046.7	1.12	2.32	3.6	1.6	0	0	17.1	79.7
3016'2"	1219.8	0	3.33	5.8	2.2	0	2.9	10.5	78.6
3026'2"	1352.0	0.93	1.96	4.1	2.4	0	0	15.4	78.1
3036'2"	1405.3	0.56	2.76	7.9	2.0	0	0	12.3	77.8
3046'2"	1183.5	1.03	3.28	6.3	2.5	0	0	13.9	79.3
3056'2"	1082.3	1.25	3.19	5.4	2.0	0	0	16.4	76.2
3066'2"	1090.9	0.96	2.46	4.4	1.5	0	0	15.0	79.1
3076'2"	988.8	1.43	0.24	0.5	0	0	0	16.9	82.6
3086'2"	961.9	0	4.43	7.1	2.4	0	2.7	13.1	74.7
3096'2"	951.6	0	3.07	4.9	1.6	0	0	15.8	77.7
3106'2"	841.3	1.37	4.27	5.3	1.8	0	0	15.9	77.0
3116'2"	711.4	0.75	4.49	4.5	1.7	0	0	15.3	78.4
3126'2"	818.6	0.37	0.71	0	1.2	0	0	18.2	80.6
3136'2"	1583.5	0.62	1.92	6.2	2.2	0	0	13.7	77.9
3146'2"	707.9	0	0	0	0	0	0	20.9	79.1
3156'2"	1066.5	0	2.0	3.4	1.6	0	0	16.4	78.7
3166'2"	1263.9	0.94	3.23	7.4	2.2	0	0	12.1	78.3
3176'2"	1463.0	0	0	0	0	0	0	20.5	79.5
3186'2"	1346.2	1.80	5.48	12.4	3.7	1.0	0	12.4	70.6
3191'2"	1279.5	0.87	4.02	8.7	2.7	0.9	0	10.0	77.7
3201'2"	1321.9	0.37	2.61	6.5	2.1	0	0	11.8	79.6
3211'2"	1027.4	0	4.69	7.0	2.9	1.1	0	4.0	78.5
3221'2"	1497.7	0	4.14	12.5	3.5	1.1	0	6.0	73.7

3231'2"	1385.8	0	1.49	3.9	1.5	0	0	16.0	78.6
3241'2"	1811.6	0.87	2.01	8.3	2.7	0	0	11.4	77.6
3251'2"	1592.7	0	4.12	13.4	4.1	1.5	0	4.5	76.6
3261'2"	1203.0	0	0.56	0	1.6	0	0	17.0	81.4
3271'2"	990.1	0.87	2.88	4.4	1.7	0	0	15.6	78.3
3281'2"	1763.5	1.00	1.24	4.6	1.9	0	0	15.4	78.2
3291'2"	1988.6	0	1.56	8.5	2.4	0	0	10.5	78.7
3301'2"	1227.8	0	2.11	4.5	1.8	0	0	14.9	78.7
3311'2"	918.6	0	10.40	16.2	3.9	1.0	0	7.4	71.5
3321'2"	1663.8	0	2.52	8.5	3.1	0.9	3.7	10.3	73.5
3331'2"	1547.5	3.50	10.60	29.7	5.9	1.7	5.4	4.8	52.6
3341'2"	1968.9	1.50	2.82	13.9	2.8	0.8	0	13.3	69.1
3351'2"	1708.1	0	2.66	10.3	2.8	0.7	0	12.8	73.4
3366'2"	1886.7	0	11.22	49.6	14.1	6.9	0	0	29.4
3376'2"	1505.8	0	3.46	9.9	3.3	1.2	0	10.4	75.2
3386'2"	1173.0	0	1.72	3.5	1.4	0	0	18.1	77.0
3396'2"	1440.8	0	4.49	12.8	3.5	1.2	0	10.9	71.7
3406'2"	925.0	4.37	17.30	18.3	5.9	2.9	3.3	9.1	60.4
3416'2"	872.3	1.37	19.20	21.6	7.2	4.5	4.6	5.4	56.7
3426'2"	1452.8	0	18.60	44.9	17.1	11.1	0	0	26.9
3436'2"	1749.3	6.25	19.2	47.5	16.2	9.2	0	0	27.0
3446'2"	1272.3	2.45	20.8	36.3	12.5	8.2	0	3.1	39.8
3456'2"	1775.5	1.50	6.9	24.0	7.0	3.6	0	6.6	58.7
3466'2"	1599.1	0	10.10	33.7	8.5	4.5	0	5.2	48.0
3476'2"	1276.8	0	9.60	22.4	5.9	2.6	0	10.3	58.8
3486'2"	1410.0	0.56	2.37	6.1	2.4	0	0	15.4	76.0
3496'2"	1343.1	0	3.60	8.1	3.2	1.1	0	16.1	71.4

3766'2"	1167.0	0.28	0	0	0	0	0	18.5	81.5
3776'2"	879.9	0	0	0	0	0	0	19.0	81.0
3786'2"	907.1	0	0	0	0	0	0	17.9	82.1
3796'2"	1268.5	0	0	0	0	0	0	17.6	82.4
3806'2"	882.5	1.50	9.6	11.2	4.6	0.9	5.6	7.6	70.2
3816'2"	912.8	0	0	0	0	0	0	18.6	81.4
3826'2"	867.1	0.37	0	0	0	0	0	18.7	81.3
3836'2"	926.1	0	0	0	0	0	0	21.2	78.8
3846'2"	1041.4	0	0.50	0	1.1	0	0	14.8	84.1
3856'2"	912.8	0.75	0.90	0	1.7	0	0	16.9	81.4
3866'2"	1267.8	0.60	0.50	0.4	1.2	0	0	18.9	79.5
3876'2"	1001.0	0.44	9.4	14.6	4.6	1.5	0	10.1	69.1
3886'2"	908.7	0.56	2.9	3.7	1.9	0	0	18.3	76.2
3896'2"	1337.1	2.00	5.9	13.3	3.7	1.0	0	12.4	69.6
3906'2"	1024.4	6.25	25.3	29.1	9.4	3.1	0	7.5	50.9
3916'2"	918.6	4.78	28.2	29.4	9.0	4.6	0	6.5	50.5
3926'2"	849.5	0	6.2	7.9	2.8	0.5	0	16.7	72.0
3936'2"	M I S S I N G								
3946'2"	950.1	4.81	27.3	29.1	10.2	4.1	0	6.5	50.0
3956'2"	941.9	4.37	16.2	16.8	6.8	2.5	0	13.2	60.7
3966'2"	760.3	5.37	25.5	18.6	7.8	3.2	0	12.9	57.5
3976'2"	770.8	2.50	25.7	25.6	7.2	2.6	0	9.5	55.0
3986'2"	844.1	1.60	18.1	19.9	6.9	2.7	0	11.2	59.3
3996'2"	1010.3	0	7.6	10.5	5.1	2.0	0	13.3	69.1
4006'2"	923.0	1.31	8.6	11.6	3.7	0.8	0	11.7	72.1
4016'2"	910.3	0	24.1	33.6	10.7	3.9	0	6.7	45.1
4026'	768.5	7.31	40.3	28.1	10.7	4.9	0	7.8	49.0

ISOTHERMS OF DEVONIAN SHALES

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ISOTHERMS OF DEVONIAN SHALES

INTRODUCTION

We believe that the determination of gas-shale isotherms will provide a very effective tool in the estimation of hydrocarbon reserves as these measurements relate the amount of gas held within a sample of rock to the (equilibrium partial) pressure of the gas outside the rock. With the aid of an understanding of the structure of the fracture system associated with a well, it may be possible to estimate reserves from a knowledge of static well head pressure alone, given isotherm data or estimates.

In this study we have concentrated upon isotherms attained at low (liquid N_2) temperature wherein adsorption on the surface of pores can be expected to be the dominant mechanism by which nitrogen is held within the rock. In this region nitrogen can be expected to sorb onto exposed surface area within the rock (perhaps between the layers forming the clay particles) in mono layers at low applied partial pressure increasing through higher multilayers as pressure increases. This understanding has been quantified by Brunauer, Emmet and Teller⁽¹⁾.

This theory predicts that pressure and amount of gas adsorbed will be related by

$$(1) \quad n_s = \frac{c n_m x}{(1-x)(1 + (c-1)x)}$$

where

n_s = # moles of gas adsorbed

n_m = # moles of gas required for a monolayer

c = a parameter

x = p/p_o

p = pressure of the gas

p_o = condensation pressure of the gas at the temperature considered

Whereas p_0 is a parameter associated with the gas used, n_m and c are basically parameters associated with the sorption process itself. The interpretation of n_m as the number of moles of gas associated with a monolayer, allows its reinterpretation in terms of the surface area of sorbent available for adsorption since the approximate value of the area of a molecule is available independently. The area so calculated usually remains approximately constant as one changes gases.

Hill⁽²⁾ has rederived Equation (1) in a manner that allows molecular interpretation of c in terms of the partition functions of the first vs. the higher multilayers of the sorption process which in turn is interpretable in terms of a difference of free energies. Specifically

$$(2) \quad c = \exp \left(- \frac{\overline{\Delta G}}{RT} \right)$$

where $\overline{\Delta G}$ is the difference in molar free energy of the monolayer and the multilayer sorption process. Thus the model, when applicable, gives information not only about the extent of surface area available for sorption but also about the basic thermodynamics of the sorption process.

A second model for the mechanism of entrapment of gas in the rock has been proposed by Smith⁽³⁾. In this model, gas is entrapped in the empty pores within the rock and the "sorption isotherm" is given by

$$(3) \quad n_g = \kappa \rho$$

where κ is interpreted as $\kappa/\rho RT$ where κ is the porosity and ρ is the density. At low pressures (i.e., x small) the BET equation also becomes linear and the corresponding coefficient of proportionality is interpreted as $\kappa' = c n_m / p_0$.

It should be stressed that both Equations (1) and (3) are approximations in the sense that it is most probable that gas is present both in pores and on the

available surface. The quantity of primary interest is the total moles of gas per gram, $n_T (= n_s + n_g)$, and this quantity is given by

$$(4) \quad n_T = \frac{RT\alpha}{\rho} + \frac{c n_m x}{(1-x)(1 + (c-1)x)}$$

The relative predominance of the two terms depends on the relative values of the parameters for the core at hand.

EXPERIMENTAL

The apparatus used is shown in Figure I, and was calibrated as is described elsewhere*. The procedure of sample preparation is the same as that utilized for diffusion constant measurements, and the BET measurements were made immediately after the diffusion constant measurement on the same sample. The density of the shale was taken as 2.59 g/ml and the net volume of the cell was calculated using this value in conjunction with the empty cell volume and weight of shale used. Before the run the sample was evacuated at room temperature on the apparatus for one half hour. Then Valve #1 was closed, the sample cooled to liquid nitrogen temperature (with a covered dewar filled with liquid N_2 through which a slow stream of gaseous nitrogen was passed) and the gas buret filled to a prescribed (initially low) pressure, then Valve #2 was closed. The amount of gas in the buret can be calculated by PV relationship. Upon opening V_1 , the amount of gas in the apparatus can be recalculated and the difference attributed to sorption. The process can either be repeated, or (more simply) the volume of the system can be changed simply by changing the volume in the gas buret. The pressure sensor was a Datametrics Barocell used in conjunction with a NOVA 1220 laboratory computer which permits rapid data analysis. The computer read the pressure once every 2.5 minutes; the pressure was taken as at equilibrium when consecutive readings were within 1 bit

* See the section of this report entitled "Calibration".

(about .1%). Typical times to reach equilibrium thus defined were about 30 minutes but varied from sample to sample.

The parameters c and n_m were determined by doing a linear regression of $\frac{x}{n(1-x)}$ against x .

$$(5) \quad n_m = \frac{1}{m + I}$$
$$c = 1 + \frac{m}{I}$$

where m and I are the slope and intercept of the resulting line.

The room temperature runs were made in an identical manner except that the gases used were helium and methane, the liquid N_2 thermostat was omitted, and the pretreatment consisted of heating to $200^\circ C$ under vacuum for one half hour.

RESULTS

Measurements were made on 10 samples corresponding to five different depths, each with two different mesh sizes, large and medium corresponding to mesh sizes of 500-700 μ and 175-350 μ respectively. The results are shown in Table I in terms of the parameters n_m and c . The areas reported are based on assuming an area of a nitrogen molecule of $16 \text{ \AA}^2$, and the ΔG 's are calculated from Equation (2).

In addition, Figures II - XI show the individual isotherms. The points are experimental while the lines correspond to the theoretical isotherm of Equation (1) for the parameters given in Table I. The surface area of the smaller meshed material is about 32% greater corresponding presumably to a greater percentage of pores open to the exterior. The values we found (average $5.62 \text{ m}^2/\text{g}$) are small in comparison to that found for pure illite ($92.2 \text{ m}^2/\text{g}$)⁽⁴⁾.

Figure XII shows the He and CH_4 isotherms on a shale sample (the same sample that resulted in the isotherm of Fig. XI). Markedly less material was sorbed; further there was no significant curvature of either isotherm.

DISCUSSION

These results raise several interesting problems. First, the low surface areas exhibited suggest that some of the available passages and pores are blocked. As a general rule we are finding pronounced illite peaks based on x-ray analysis, but only 5% of the surface area of pure illite. The suggestion that some of the adsorptive areas are unavailable is strengthened by the observation that smaller mesh samples in general have larger surface areas/gram. This does not preclude the possibility that in addition kerogen or some other substance is occupying sites that would be available in samples of illite that are not laden with organic material.

The room temperature results, though very preliminary, have several interesting features. In contrast to the low temperature results it is possible to interpret the mechanism of sorption in terms of an open porosity model although the porosities thus calculated seem large, 13% and 46% for CH_4 and He respectively. In fact, these percentages are so large as to suggest that adsorption plays at least a partial role. The wide difference between the CH_4 and He porosities is noteworthy from three points of view.

First, the adsorption model alone is hard pressed to explain why He (the gas with the lower polarizability, the lower boiling points, and the lower heat of vaporization) should be preferentially adsorbed. Second, the porosity model alone permits explanation of the order of the result in terms of some pores being too small to admit CH_4 ; however, the open pore model is hard pressed to explain 46% porosity. Third, the combination model of Equation (4) may provide explanation in terms of adsorption surfaces that are accessible only through narrow pores. In any event we hope to supplement this lone pair of room temperature isotherms with more complete data in the near future.

REFERENCES

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TABLE I

BET Parameters from nitrogen isotherms at 77° K.

Sample Depth (uncorrected)	Particle Size	c	ΔG^0 (kilcal)	moles for a monolayer/g $\times 10^{-5}$	specific surface area (m^2/g)
3221' 2"-4"	large	265	.85	4.39	4.18
3716' 2"-4"	medium	229	.82	8.73	8.31
3716' 2"-4"	large	138	.75	6.82	6.49
3886' 2"-4"	medium	212	.82	8.37	7.96
3736' 2"-4"	medium	343	.89	8.53	8.12
3736' 2"-4"	medium	194	.80	8.38	7.98
3736' 2"-4"	large	314	.88	7.60	7.23
4026'	medium	46	.58	1.01	.96
4026'	large	201	.80	5.37	.51

Figure I. The system used to make sorption studies.

The system is connected to a standard high vacuum system (capable of 10^{-6} torr) at valve V_2 . Included in that vacuum system is a precision manometer, McCleod gauge, Toepler pump for bringing samples of gas to atmospheric pressure for gas analysis, and connections to nitrogen and other gas supplies.

Fig. 1

CAPTIONS

Isotherms at 77° K. Moles sorbed/gram is plotted as a function of pressure (torr).

Depths are those printed on cans.

Fig. II	3221' 2-4"	large mesh
Fig. III	4026' 2-4"	large mesh
Fig. IV	4026' 2-4"	medium mesh
Fig. V	3736' 2-4"	large mesh
Fig. VI	3736' 2-4"	medium mesh
Fig. VII	3886' 2-4"	large mesh
Fig. VIII	3886' 2-4"	medium mesh
Fig. IX	3716' 2-4"	large mesh
Fig. X	3716' 2-4"	medium mesh
Fig. XI	3221' 2-4"	large mesh (second of two runs)

Isotherms at room temperature. Moles sorbed/gram is plotted as a function of pressure (torr) for two gases CH₄ and He.

Fig. XII	3221' 2-4"	large mesh
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Fig. II

Fig. III

Fig. IV

Fig. V

Fig. VI

Fig. VII

Fig. VIII

Fig. X

Fig. XI

Fig. XII

X-RAY DIFFRACTION OF DEVONIAN SHALE

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X-RAY DIFFRACTION OF DEVONIAN SHALE

INTRODUCTION

A number of powdered shale samples were analyzed by x-ray diffraction methods in order to determine their composition and structure. The purpose of these studies was to find relationships between x-ray patterns, mineral composition, permeability, BET parameters, and gas content for the same samples on which we were making these other measurements.

PROCEDURE

In order for all x-ray diffractions of shale samples to be as precise as possible it was necessary to prepare all the mounts in an identical fashion. First, a small piece of shale rock was pulverized on a metal plate with a hammer until no section was larger than a few millimeters in length. Then all the fragments were placed into the ball mill for about 15 minutes. After this time the crushed rock was sifted through a 250 mesh sieve. This sifted material was then used to prepare two types of mounts; the acetone smear (used at low angles of an x-ray run) and the cavity fill mount (used at high angles).

In the acetone smear mount a small amount (about two small scoopfuls) of sifted shale sample was put in an agate mortar and pestle with three or four drops of acetone added. The sample and acetone were mixed until a thick soupy consistency was obtained. A Pasteur pipette was then used to draw up the acetone suspension and transfer it to a clean glass slide. After the smear on the slide was of uniform thickness it was placed on a warm hot plate to evaporate the acetone. The dried sample mount was then placed onto the x-ray diffraction instrument and run at slow scan (low-high) from 5 to 30 degrees (20).

The cavity fill mount was prepared by adding the sifted shale to a plastic washer with an inner diameter of 0.5 inches, an outer diameter of 0.25 inches, and 0.06 inches thick. The sample powder was added into a slightly heaped mound in the center of the washer. The mound was then spread as evenly as possible while adding more powder in order to keep a mound slightly raised above the washer. Taking another glass slide the shale sample mount was pressed down so an evenly exposed surface was made. The sample mount was then placed onto the x-ray diffraction instrument and run at slow scan (low-high) from 30 to 70 degrees (2θ).

The best results were obtained using the following settings on our GE XRD6 x-ray diffractometer:

Scan rate	0.4 deg/min
detector slit	0.1 deg
time constant	10 sec.

The diffractometer scan for each sample was analyzed by first recording the peak position (2θ) for each peak significantly above background (determined from blank sample runs). The 2θ values were then converted to d spacings. Probable mineral composition was then determined by comparison of the observed d spacings with the most intense d spacings reported for minerals commonly found in shales in the Inorganic Section of the ASTM X-Ray Powder Data File. The primary evidence for the presence of feldspar in the samples is the appearance of a peak near a 2θ ($K\alpha$) value of 27.8° , corresponding to an intense peak for feldspar. Other feldspar peaks were not noted for most samples.

RESULTS

The minerals found included quartz, illite, chlorite, feldspar, and iron pyrite. Table I details the actual x-ray diffraction data, Table II summarizes the internal pressure of the can, the micromoles of hydrocarbon per gram of shale, the percent hydrocarbon gas, the odor and appearance of the sample, and the mineral composition for each core sample. The hydrocarbon gas data was compiled from that gathered from the gas chromatography analysis as detailed elsewhere in this report.

KEY TO TABLE

HC--hydrocarbon

Q--quartz (alpha)

I--illites

F--feldspar

C--chlorite

C_{Fe}--iron rich chlorite

P--iron pyrite (FeS₂)

(r)--significant amount of rust present on core or in can

TABLE I

Shale Core X-ray Diffractometer Data

Sample 1. Shale (3281.2-3281.4)

acetone smear 5° - 21° cavity fill 21° - 75° range 10^3

time const.(sec) 10

slit $1/10^{\circ}$

Sample 2. Shale (2736.2-2736.4)

acetone smear 5° - 43° cavity fill 43° - 72° range 10^3

time const.(sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.22	14.209	11
6.16	14.347	8
8.76	10.094	67
12.42	7.1265	38
17.71	5.0079	27
18.67	4.7525	12
19.79	4.4860	11
20.79	4.2724	18
25.37	3.5106	7
26.710	3.374	100
27.92	3.1955	8
29.82	2.9961	7
30.41	2.9393	3
31.25	2.8621	6
31.82	2.8122	16
34.98	2.5650	18
36.59	2.4558	12
37.59	2.3927	4
39.53	2.2796	9
42.10	2.1462	6
42.45	2.1293	9
45.35	1.9997	10
45.82	1.9803	9
50.18	1.8180	13
54.86	1.6734	7
55.39	1.6587	4
55.82	1.6469	3
58.63	1.5745	2
59.98	1.5422	11
61.71	1.5031	7
67.65	1.3849	7
68.22	1.3747	10

2θ (CuK α)	d	I/I ₁
8.76	10.096	29
12.41	7.1322	17
17.73	5.0073	12
18.73	4.7374	3
19.80	4.4838	6
20.84	4.2623	13
25.25	3.5270	13
26.67	3.3423	100
27.88	3.2000	11
28.94	3.0851	3
29.86	2.9921	5
31.24	2.8630	6
31.90	2.8053	12
34.92	2.5693	8
36.63	2.4532	7
39.47	2.2830	7
40.37	2.2341	4
42.45	2.1293	8
45.90	1.9770	7
50.16	1.8186	12
52.59	1.7402	5
54.88	1.6729	5
59.92	1.5436	8
67.76	1.3829	5
68.24	1.3743	9

TABLE I (cont.)

Sample 3. Shale (3221.2 - 3221.4)

acetone smear 5° - 38°
 cavity fill 38° - 75°
 range 10^3
 time const (sec) 10
 slit $1/10^{\circ}$

2 θ (CuK α)	d	I/I ₁
8.88	9.9579	31
9.75	9.0712	small
12.51	7.0754	18
17.00	5.2154	5
17.80	4.9828	14
18.29	4.8504	7
18.75	4.7324	7
19.86	4.4704	9
20.20	4.3959	6
20.88	4.2542	17
25.24	3.5284	15
26.69	3.3399	100
27.96	3.1910	plateau
28.59	3.1221	6
29.90	2.9882	5
31.31	2.8568	6
32.00	2.7968	5
33.12	2.7047	6
34.88	2.5721	8
35.96	2.4947	3
36.57	2.4571	9
37.12	2.4219	4
38.76	2.3231	4
39.45	2.2841	10
40.27	2.2394	8
40.76	2.2136	6
42.43	2.1303	10
45.33	2.0005	7
45.78	1.9819	5
47.37	1.9190	4
50.10	1.8207	14
54.90	1.6723	5
55.69	1.6504	4
56.25	1.6353	7
59.90	1.5441	10
61.67	1.5040	6
64.14	1.45.9	3
67.75	1.3831	6
68.70	1.3750	8

Sample 4. Shale (3406.2-3406.4)

acetone smear 5° - 30°
 cavity fill 38° - 72°
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2 θ (CuK α)	d	I/I ₁
8.80	10.048	11
12.45	7.1094	6
17.69	5.0135	4
19.80	4.4838	6
20.80	4.2704	18
22.06	4.0293	2
22.71	3.9154	2
23.92	3.7200	3
25.14	3.5422	5
25.80	3.4530	3
26.61	3.3497	100
27.67	3.2238	5
27.82	3.2067	5
28.43	3.1393	3
29.80	2.9980	2
32.98	2.7159	7
34.63	2.5901	4
34.88	2.5721	7
36.47	2.4636	8
37.00	2.4295	5
37.69	2.3866	3
39.41	2.2863	7
40.22	2.2421	3
40.71	2.2162	5
42.37	2.1322	6
45.71	1.9848	3
47.37	1.9190	3
50.08	1.8214	11
54.82	1.6746	4
56.22	1.6361	5
59.57	1.5519	2
59.88	1.5446	8
61.71	1.5031	4
64.12	1.4523	2
67.67	1.3845	4
68.18	1.3754	6

TABLE I (cont.)

Sample 5. Shale (3736.2-3736.4)

acetone smear 5° - 32° cavity fill 32° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

Sample 6. Shale (4026.2-4026.4)

acetone smear 5° - 34° cavity fill 34° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
8.84	10.003	13
12.51	7.0754	9
17.76	4.9939	6
18.80	4.7199	4
19.82	4.4793	3
20.86	4.2583	12
24.08	3.6956	3
25.18	3.5366	7
26.67	3.3423	100
27.86	3.2022	3
31.29	2.8586	2
34.61	2.5916	4
35.00	2.5636	7
36.02	2.4933	5
36.53	2.4597	8
37.69	2.3866	3
39.45	2.2841	8
40.31	2.2373	4
41.31	2.1854	2
42.43	2.1293	5
45.39	1.9980	3
45.80	1.9811	4
50.14	1.8193	10
54.92	1.6717	4
55.39	1.6587	3
55.86	1.6458	2
60.00	1.5418	7
61.76	1.5020	2
64.02	1.4543	3
67.75	1.3831	5
68.22	1.3747	7

2θ (CuK α)	d	I/I ₁
8.80	10.048	15
17.67	5.0192	5
19.80	4.4838	6
20.86	4.2583	19
22.96	3.8900	4
25.29	3.5215	5
21.61	3.3497	100
27.84	3.2045	5
28.47	3.1350	8
29.80	2.9980	4
30.80	2.9029	11
33.04	2.7111	18
34.92	2.5693	7
36.53	2.4597	8
37.08	2.4244	6
39.43	2.2852	10
40.20	2.2432	6
40.76	2.2136	9
42.43	2.1303	9
45.69	1.9856	5
45.57	1.9906	broad
47.41	1.9175	6
50.08	1.8214	15
54.88	1.6729	5
56.20	1.6367	13
58.96	1.5665	3
59.92	1.5436	11
61.67	1.5040	6
64.16	1.4515	4
67.67	1.3845	6
68.70	1.3750	9

TABLE I (cont.)

Sample 7. Shale (2836.2-2836.4)

acetone smear 5° - 32°
 cavity fill 32° - 70°
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
8.73	10.129	47
12.37	7.1552	21
17.69	5.0135	16
18.71	4.7424	5
19.71	4.5040	5
20.77	4.2765	12
22.79	3.9018	3
25.12	3.5449	16
26.59	3.3522	100
27.78	3.2113	4
29.80	2.9980	6
31.18	2.8684	4
35.04	2.5606	14
36.55	2.4584	12
37.63	2.3903	5
39.45	2.2841	12
40.27	2.2394	7
42.43	2.1303	11
45.41	1.9972	6
45.80	1.9811	7
50.14	1.8193	16
54.94	1.6712	5
59.98	1.5422	11
61.71	1.5031	4
67.73	1.3834	6
68.25	1.3741	10

Sample 8. Shale (2936.2-2936.4)

acetone smear 5° - 30°
 cavity fill 30° - 70°
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
8.73	10.129	26
12.35	7.1667	12
17.67	5.0192	9
19.75	4.4950	7
20.76	4.2785	14
25.08	4.2785	10
26.55	3.3572	100
27.78	3.2113	6
28.41	3.1415	3
32.94	2.7191	14
34.82	2.5764	12
35.92	2.5000	8
36.49	2.4623	10
37.02	2.4282	12
39.39	2.2874	12
40.69	2.2173	9
42.35	2.1341	9
45.78	1.9819	4
47.35	1.9198	7
50.04	1.8227	14
54.76	1.6762	6
56.20	1.6367	14
58.94	1.5670	4
59.90	1.5441	9
61.63	1.5049	7
64.20	1.4507	5
67.65	1.3849	6
68.16	1.3757	9

TABLE I (cont.)

Sample 9. Shale (2936.2-2936.4)

dark shale phase
 acetone smear 5° - 32°
 cavity fill 32° - 70°
 range 10^3
 time const. (sec) 10
 slit $1/10^0$

2 θ (CuK α)	d	I/I ₁
6.06	14.584	5
8.73	10.129	48
12.35	7.1667	16
17.67	5.0192	16
18.59	4.7728	7
19.75	4.4950	7
20.76	4.2785	20
25.08	3.5505	16
26.55	3.3572	100
27.35	3.2608	7
29.71	3.0069	9
31.04	2.8810	5
34.88	2.5721	15
35.96	2.4973	11
36.49	2.4623	13
37.61	2.3915	7
39.47	2.2830	15
40.25	2.2405	9
42.41	2.1313	12
45.29	2.0022	5
50.08	1.8214	15
54.80	1.6751	6
55.27	1.6670	6
59.88	1.5446	10
61.71	1.5031	6
64.12	1.4523	3
67.69	1.3841	6
68.20	1.3750	10

Sample 10. Shale (2936.2-2936.4)

silty layers
 acetone smear 5° - 70°
 range 10^3
 time const. (sec) 10
 slit $1/10^0$

2 θ (CuK α)	d	I/I ₁
6.19	14.278	small
8.76	10.094	40
12.39	7.1436	16
17.71	5.0079	15
18.67	4.7525	6
19.78	4.4883	7
20.82	4.2663	14
25.12	3.5449	14
26.61	3.3497	100
27.78	3.2113	9
29.82	2.9961	6
31.24	2.8630	4
34.84	2.5750	8
35.94	2.4897	6
36.49	2.4623	8
37.47	2.4001	3
39.41	2.2863	5
40.24	2.2410	4
42.39	2.1322	7
45.39	1.9980	15
50.10	1.8207	10
59.90	1.5441	8
67.67	1.3845	4
68.20	1.3750	5

TABLE I (cont.)

Sample 11. Shale (3036.2-3036.4)

acetone smear 5° - 43°
 cavity fill 43° - 70°
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.18	14.301	4
8.78	10.071	30
12.37	7.1552	18
17.71	5.0079	11
18.75	4.7324	6
19.75	4.4950	9
20.78	4.2745	17
25.08	3.5505	9
26.63	3.3473	100
27.61	3.2306	8
29.78	3.0000	5
30.57	2.9242	3
31.29	2.8586	3
33.00	2.7143	3
34.88	2.5721	9
35.88	2.5027	3
36.47	2.4636	9
37.00	2.4295	3
37.57	2.3939	3
39.39	2.2874	6
40.27	2.2394	4
40.73	2.2152	2
42.39	2.1322	8
45.49	1.9897	4
50.14	1.8193	14
54.86	1.6734	7
56.29	1.6343	6
59.98	1.5422	9
61.69	1.5035	4
67.75	1.3821	5
68.25	1.3741	9

Sample 12. Shale (3136.2-3136.4)

acetone smear 5° - 30°
 cavity fill 30° - 72°
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.18	14.301	5
8.73	10.129	47
12.39	7.1436	15
17.67	5.0192	12
19.69	4.5086	11
20.80	4.2704	19
25.14	3.5422	14
26.61	3.3497	100
27.76	3.2135	8
32.00	2.7968	11
32.94	2.7191	5
34.92	2.5693	17
36.49	2.4623	16
37.71	2.3854	6
39.43	2.2852	12
40.24	2.2410	7
42.39	2.1322	13
45.33	2.005	8
45.75	1.9831	9
50.08	1.8214	18
52.73	1.7359	6
54.88	1.6729	7
59.88	1.5446	14
61.55	1.5066	8
67.73	1.3834	6
68.18	1.3754	10

TABLE I (cont.)

Sample 13. Shale (4006.2-4006.4)

gray and green shale

acetone smear 5° - 30° cavity fill 30° - 75° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

Sample 14. Shale (3906.2-3906.4)

acetone smear 5° - 38° cavity fill 38° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2 θ (CuK α)	d	I/I ₁
8.78	10.071	42
12.43	7.1207	11
17.69	5.0135	14
19.76	4.4928	6
20.80	4.2704	17
25.16	3.5394	8
26.63	3.3473	100
27.82	3.2067	6
29.80	2.9980	4
30.71	2.9112	4
31.22	2.8648	4
34.96	2.5664	13
36.51	2.4610	10
37.61	2.3915	5
39.47	2.2830	11
40.31	2.2373	8
42.47	2.1284	10
43.71	2.0708	3
45.41	1.9972	5
45.82	1.9803	5
50.16	1.8186	11
59.96	1.5427	9
61.76	1.5020	6
67.71	1.3838	5
68.24	1.3743	8

2 θ (CuK α)	d	I/I ₁
6.18	14.301	2
8.76	10.094	14
12.45	7.1094	8
17.75	4.9967	6
18.75	4.7324	5
19.75	4.4950	9
20.78	4.2745	19
25.14	3.5422	6
26.61	3.3497	100
27.84	3.2045	6
29.78	3.0000	5
31.20	2.8666	4
31.94	2.8019	7
32.96	2.7175	5
34.88	2.5721	7
36.51	2.4610	8
39.47	2.2830	9
40.33	2.2362	6
40.78	2.2126	6
42.43	2.1303	9
45.51	1.9930	5
47.47	1.9152	1
50.10	1.8207	9
54.84	1.6740	5
56.25	1.6353	4
59.92	1.5436	7
61.67	1.5040	5
64.10	1.4527	3
67.69	1.3823	5
68.22	1.3747	8

TABLE I (cont.)

Sample 15. Shale (3806.2-3806.4)

acetone smear 5° - 31° cavity fill 31° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

Sample 16. Shale (3716.2-3716.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.10	14.488	4
8.82	10.025	23
12.49	7.0867	16
17.71	5.0079	10
18.78	4.7249	8
19.88	4.4659	7
20.82	4.2663	20
25.16	3.5394	15
26.63	3.3473	100
27.86	3.2022	8
28.49	3.1328	6
29.84	2.9941	4
31.22	2.8648	3
33.04	2.7111	11
34.94	2.5679	8
36.10	2.4880	5
36.51	2.4610	8
37.06	2.4257	7
39.45	2.2841	10
40.27	2.2394	5
40.76	2.2136	8
42.43	2.1303	9
43.88	2.0632	3
45.55	1.9914	3
46.61	1.9485	3
46.90	1.9372	1
47.12	1.9286	2
47.43	1.9167	4
50.14	1.8193	11
54.82	1.6746	4
55.35	1.6598	3
56.29	1.6343	9
59.90	1.5441	10
61.71	1.5031	6
64.29	1.4489	3
67.71	1.3838	5
68.29	1.3734	8

2θ (CuK α)	d	I/I ₁
6.16	14.347	4
8.78	10.071	33
12.45	7.1094	20
17.67	5.0192	11
18.75	4.7324	4
19.73	4.4995	4
20.78	4.2745	14
25.12	3.5449	14
26.63	3.3473	100
27.31	3.2654	2
27.82	3.2067	4
29.82	2.9961	4
31.18	2.8684	3
31.82	2.8122	3
34.92	2.5693	9
36.51	2.4610	8
37.63	2.3903	4
39.47	2.2830	10
40.27	2.2394	5
41.39	2.1814	3
42.39	2.1322	7
45.57	1.9906	5
50.14	1.8193	11
54.84	1.6740	4
59.92	1.5436	7
61.71	1.5031	4
64.06	1.4535	3
67.71	1.3838	4
68.24	1.3743	7

TABLE I (cont.)

Sample 17. Shale (3896.2-3896.4)

acetone smear 5° - 31° cavity fill 31° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
5.63	15.697	2
6.18	14.301	4
8.78	10.071	34
12.43	7.1207	19
12.69	5.0135	12
18.76	4.7299	5
19.76	4.4928	6
20.78	4.2745	15
22.88	3.8867	4
25.16	3.5394	15
26.61	3.3497	100
27.82	3.2067	5
29.63	3.0148	4
35.12	2.5551	10
36.24	2.4787	6
36.71	2.4480	8
37.82	2.3787	5
39.62	2.2747	8
40.48	2.2283	5
42.58	2.1231	6
45.75	1.9831	4
50.29	1.8142	8
60.15	1.5383	6
61.88	1.4994	3
67.85	1.3813	4
68.38	1.3718	6

Sample 18. Shale (3886.2-3886.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
5.59	15.809	2
6.16	14.347	2
8.78	10.071	26
12.45	7.1094	15
17.69	5.0135	11
18.76	4.7299	7
19.73	4.4995	7
20.78	4.2745	16
25.16	3.5394	13
26.61	3.3497	100
27.86	3.2022	6
29.73	3.0049	5
35.04	2.5608	9
36.00	2.4947	6
36.55	2.4584	9
37.61	2.3915	5
39.47	2.2830	10
40.25	2.2405	6
42.47	2.1284	7
45.35	1.9997	4
45.84	1.9795	4
50.14	1.8193	11
54.90	1.6723	3
59.96	1.5427	8
61.92	1.4985	4
67.71	1.3838	5
68.22	1.3747	6

TABLE I (cont.)

Sample 19. Shale (3946.2-3946.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

Sample 20. Shale (3926.2-3926.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.31	14.007	2
8.82	10.025	16
12.49	7.0878	7
17.73	5.0023	6
19.76	4.4928	9
20.82	4.2663	19
25.22	3.5311	5
26.63	3.3423	100
27.94	3.1932	3
28.49	3.1328	4
29.86	2.9921	3
31.37	2.8515	3
33.08	2.7079	7
35.02	2.5622	8
36.14	2.4853	7
36.61	2.4545	8
37.12	2.4219	7
37.75	2.3829	3
39.53	2.2796	11
40.43	2.2309	6
40.80	2.2116	8
42.51	2.1265	8
45.71	1.9848	5
47.47	1.9152	3
50.20	1.8173	10
52.08	1.7560	3
54.90	1.6723	3
55.37	1.6592	3
56.29	1.6343	7
60.04	1.5408	7
61.88	1.4994	6
64.29	1.4489	3
67.78	1.3825	5
68.27	1.3738	7

2θ (CuK α)	d	I/I ₁
6.20	14.255	4
8.75	10.106	27
12.39	7.1436	18
17.67	5.0192	9
18.65	4.7576	4
19.67	4.5131	5
20.73	4.2847	14
25.08	3.5505	14
26.55	3.3572	100
27.78	3.2113	6
29.75	3.0029	4
32.02	2.7951	3
34.96	2.5664	8
35.94	2.4987	4
36.53	2.4597	7
37.59	2.3927	2
39.45	2.2841	7
40.27	2.2394	3
42.43	2.1303	8
45.47	1.7947	4
50.12	1.8200	11
54.90	1.6723	4
55.39	1.6587	3
59.92	1.5436	7
61.73	1.5027	3
64.04	1.4539	2
67.73	1.3834	5
68.24	1.3743	7

TABLE I (cont.)

Sample 21. Shale (3386.2-3386.4)

Acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.16	14.347	2
8.78	10.071	31
12.43	7.1207	15
17.69	5.0135	11
18.73	4.7374	6
19.12	4.6417	4
19.76	4.4978	9
20.80	4.2704	14
22.96	3.8733	3
25.12	3.5449	12
26.63	3.3473	100
27.76	3.2135	7
29.78	3.000	3
31.20	2.8666	3
32.02	2.7079	2
34.88	2.5721	14
35.82	2.5008	6
36.51	2.4610	13
37.65	2.3890	5
39.41	2.2863	8
40.25	2.2405	5
42.39	2.1322	8
45.53	1.9922	4
50.12	1.8200	13
54.80	1.6751	5
56.20	1.6367	4
59.92	1.5436	10
61.75	1.5022	4
67.69	1.3841	5
68.22	1.3747	9

Sample 22. Shale (3456.2-3456.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.10	14.488	2
8.75	10.106	41
12.41	7.1322	18
17.69	5.0.35	18
18.69	4.7475	7
19.75	4.4950	7
20.18	4.4002	5
20.78	4.2745	13
25.08	3.5505	15
26.59	3.3522	100
27.78	3.2113	6
28.43	3.1393	4
29.75	3.0029	4
31.22	2.8648	6
33.10	2.7063	5
35.00	2.5636	15
36.00	2.4947	5
36.51	2.4610	11
37.10	2.4232	7
37.61	2.3915	7
39.43	2.2852	7
40.25	2.2405	4
40.71	2.2162	3
42.43	2.1303	8
45.39	1.9980	7
45.78	1.9819	6
47.49	1.9145	3
50.12	1.826	13
54.90	1.6723	7
56.29	1.6343	6
59.98	1.5422	9
61.76	1.5020	5
67.75	1.3831	5
68.27	1.3738	8

TABLE I (cont.)

Sample 23. Shale (3426.2-3426.4)

acetone smear 5° - 27° cavity fill 27° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

Sample 24. Shale (3416.2-3416.4)

acetone smear 5° - 30° cavity fill 30° - 70° range 10^3

time const. (sec) 10

slit $1/10^{\circ}$

2 θ (CuK α)	d	I/I ₁
6.18	14.301	2
8.78	10.071	11
10.41	8.4975	6
12.43	7.1207	5
17.73	5.0023	4
19.78	4.4883	6
20.82	4.2663	16
23.84	3.7323	3
24.82	3.5871	2
25.20	3.5339	3
26.61	3.3497	100
27.84	3.2045	4
29.90	2.9882	3
33.04	2.7111	5
34.86	2.5736	6
36.45	2.4649	9
37.08	2.4244	5
39.43	2.2852	10
40.73	2.2152	7
42.43	2.1303	6
45.84	1.9795	5
47.43	1.9167	2
50.12	1.8200	10
54.84	1.6740	5
56.24	1.6356	5
59.88	1.5446	7
61.71	1.5031	3
64.14	1.4519	2
67.73	1.3834	4
68.10	1.3768	6

2 θ (CuO α)	d	I/I ₁
6.24	14.164	2
8.76	10.094	16
12.37	7.1552	8
12.67	5.0192	5
18.61	4.7677	4
19.22	4.6177	5
19.75	4.4950	9
20.80	4.2704	21
22.96	3.8733	5
25.16	3.5394	6
26.59	3.3522	100
27.73	3.2169	4
28.47	3.1350	9
28.98	3.0810	3
29.84	2.9941	4
30.71	2.9112	3
33.02	2.7127	16
34.96	2.5664	11
35.92	2.5000	8
36.51	2.4610	11
37.06	2.4257	13
39.45	2.2841	10
40.27	2.2394	7
40.78	2.2126	11
42.23	2.1399	11
45.33	2.0005	5
45.75	1.9831	6
47.43	1.9167	8
50.12	1.8200	14
54.84	1.6740	5
56.25	1.6353	19
59.92	1.5436	11
61.67	1.5040	8
64.25	1.4497	6
67.75	1.3831	6
68.24	1.3741	9

TABLE I (cont.)

Sample 25. Shale (3396.2-3396.4)

acetone smear $5^{\circ} - 30^{\circ}$
 cavity fill $30^{\circ} - 70^{\circ}$
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
6.18	14.301	4
8.80	10.048	47
12.41	7.1322	21
17.67	5.0192	20
18.65	4.7576	5
19.71	4.5040	5
20.75	4.2806	12
25.08	3.5505	16
26.59	3.3522	100
27.76	3.2135	4
29.80	2.9980	6
31.10	2.8756	3
31.88	2.8070	4
34.86	2.5736	12
36.00	2.4947	7
36.43	2.4662	10
37.51	2.3976	5
39.31	2.2919	11
40.14	2.2464	7
41.80	2.1609	3
42.33	2.1351	8
45.29	2.0022	7
45.61	1.9889	6
50.04	1.8227	11
54.82	1.6746	4
59.86	1.5454	7
61.65	1.5044	5
67.65	1.3849	4
68.12	1.3764	7

Sample 26. Shale (3446.2-3446.4)

acetone smear $5^{\circ} - 30^{\circ}$
 cavity fill $30^{\circ} - 70^{\circ}$
 range 10^3
 time const. (sec) 10
 slit $1/10^{\circ}$

2θ (CuK α)	d	I/I ₁
8.78	10.071	9
12.43	7.1207	4
17.78	4.9884	3
19.76	4.4928	5
20.78	4.2745	17
25.29	3.5215	2
26.59	3.3522	100
27.80	3.2090	3
32.84	2.7271	5
34.71	2.5844	6
36.33	2.4727	7
36.92	2.4346	3
39.31	2.2919	7
40.10	2.2485	5
40.55	2.2246	4
42.29	2.1370	6
45.53	1.9922	4
47.27	1.9229	2
49.96	1.8254	12
54.67	1.6788	4
56.10	1.6373	5
59.76	1.5474	9
61.53	1.5071	3
67.57	1.3863	5
68.02	1.3782	9

TABLE I (cont.)

Listing of Shale Samples by Core Depth

2736	#2
2836	#7
2936	#8
dark shale phase	#9
silty layers	#10
3036	#11
3136	#12
3221	#3
3281	#1
3386	#21
3396	#25
3406	#4
3416	#24
3426	#23
3446	#26
3456	#22
3716	#16
3736	#5
3806	#15
3886	#18
3896	#17
3906	#14
3926	#20
3946	#19
4006	#13
4026	#6

TABLE II

SHALE SAMPLE	PRESSURE IN CAN (PSIA)	MICROMOLES HC/GRAM	GASES DETECTED (PERCENTAGE)	ODOR WHEN OPENED	APPEARANCE	MINERAL COMPOSITION
2736	0.40	0.44	O ₂ (17.7), N ₂ (81.0), CH ₄ (1.3)	no gas smell	medium gray- green laminated silty shale	Q, I, F, C _{Fe}
2836	0.25	1.48	O ₂ (14.0), N ₂ (81.7), CH ₄ (3.4), C ₂ H ₆ (1.0)	no gas smell	medium dark gray shale (silty)	Q, I, F, C _{Fe}
2936	0.44	6.68	O ₂ (0.0), N ₂ (77.5) CH ₄ (11.2), C ₂ H ₆ (3.8), CO ₂ (5.7), C ₃ H ₈ (1.7)	gas smell	dark gray shale with dispersed silty layers, fossils	Q, I, F, C _{Fe}
3036	0.56	2.76	O ₂ (12.3), N ₂ (77.8), no gas smell CH ₄ (7.9), C ₂ H ₆ (2.0)		dark gray shale with a vertical frac- ture healed with calcite	Q, I, F, C _{Fe} , P
3136	0.62	1.92	O ₂ (16.4), N ₂ (76.2), no gas smell CH ₄ (5.4), C ₂ H ₆ (2.0)		dark gray shale, layer of silty shale	Q, I, F, C
3221(r)	0.25	4.14	O ₂ (6.0), N ₂ (73.7), no gas smell CH ₄ (12.5), CO ₂ (3.2), C ₂ H ₆ (3.5), C ₃ H ₈ (1.1)		medium gray shale with numerous very dark gray bands	Q, I, F, C _{Fe} , P
3281	1.00	1.24	O ₂ (15.4), N ₂ (78.2), no gas smell CH ₄ (4.6), C ₂ H ₆ (1.9), C ₃ H ₈ (trace)		medium gray shale	Q, I, F, C

SHALE SAMPLE	PRESSURE IN CAN (PSIA)	MICROMOLES HC/GRAM	GASES DETECTED (PERCENTAGE)	ODOR WHEN OPENED	APPEARANCE	MINERAL COMPOSITION
3386	0.25	1.72	O ₂ (18.1), N ₂ (77.0), CH ₄ (3.5), C ₂ H ₆ (1.4)	no gas smell	medium gray shale with black bands of shale, silt- stone and pyrite found	Q, I, F, C _{Fe} , P
3396	0.25	4.49	O ₂ (10.9), N ₂ (71.7), CH ₄ (12.8), C ₂ H ₆ (3.5), C ₃ H ₈ (1.2)	slight gas smell	medium gray shale with black shale bands, occas. silt band	Q, I, F, C _{Fe} , P
3406	4.37	17.30	O ₂ (9.1), N ₂ (60.4), CH ₄ (18.3), CO (3.3), C ₂ H ₆ (5.9), C ₃ H ₈ (2.9)	no gas smell	dark shale with scorched appearance on horizontal	Q, I, F, C _{Fe} , P
3416	1.37	19.20	O ₂ (5.4), N ₂ (56.7), CH ₄ (21.6), CO ₂ (4.6), C ₂ H ₆ (7.2), C ₃ H ₈ (4.5), C ₄ H ₁₀ (trace)	strong gas smell	black shale, tarry leaf fossil?	Q, I, F, C _{Fe} , P
3426(r)	0.25	18.60	O ₂ (0.0), N ₂ (26.9), CH ₄ (44.9), C ₂ H ₆ (17.1), C ₃ H ₈ (11.1), C ₄ H ₁₀ (trace)	strong gas smell	black shale with silt bands, large pyrite crystals	Q, I, F, C _{Fe} , P
3446	2.45	20.80	O ₂ (3.1), N ₂ (39.8), CH ₄ (36.3), C ₂ H ₆ (12.5), C ₃ H ₈ (8.2)	strong gas smell	black shale	Q, I, F, C _{Fe} , P
3456	1.5	6.90	O ₂ (6.6), N ₂ (58.7), CH ₄ (24.0), C ₂ H ₆ (7.0), C ₃ H ₈ (3.6), C ₄ H ₁₀ (trace)	gas smell	medium gray shale with large black shale bands, silty bands	Q, I, F, C _{Fe} , P

SHALE SAMPLE	PRESSURE IN CAN (PSIA)	MICROMOLES HC/GRAM	GASES DETECTED (PERCENTAGE)	ODOR WHEN OPENED	APPEARANCE	MINERAL COMPOSITION
3716(r)	0.25	0.10	O ₂ (19.0), N ₂ (80.8), CH ₄ (0.2)	slight gas smell	blue gray and black laminated shale	Q, I, F, C
3736(r)	0.50	1.50	O ₂ (15.7), N ₂ (80.0), CH ₄ (2.5), C ₂ H ₆ (1.8)	slight gas smell	blue gray and black laminated shale	Q, I, F, C _{Fe}
3806(r)	1.50	9.60	O ₂ (7.6), N ₂ (70.2), CH ₄ (11.2), C ₂ CO ₂ (5.6), C ₂ H ₆ (4.6), C ₃ H ₈ (0.9)	strong gas smell	black and blue gray laminated shale	Q, I, F, C, P
3886	0.56	2.90	O ₂ (15.3), N ₂ (76.2), CH ₄ (3.7), C ₂ H ₆ (1.9), C ₃ H ₈ (trace)	no gas smell	dark gray and green laminated shale, some fossils	Q, I, F, C
3896	2.00	5.90	O ₂ (12.4), N ₂ (59.6), CH ₄ (13.3), C ₂ H ₆ (3.7), C ₃ H ₈ (1.0)	slight gas smell	dark gray and black laminated shale, fossils	Q, I, F, C
3906	6.25	25.30	O ₂ (7.5), N ₂ (50.9), CH ₄ (20.1), C ₂ H ₆ (9.4), C ₃ H ₈ (3.1)	strong gas smell	very dark black shale	Q, I, F, C, P
3926	0.25	6.20	O ₂ (16.7), N ₂ (72.0), CH ₄ (7.9), C ₂ H ₆ (2.8), C ₃ H ₈ (0.5)	little gas smell	medium gray and dark gray laminated shale, silty layer, fossils	Q, I, F, C _{Fe} , P

SHALE SAMPLE	PRESSURE IN CAN (PSIA)	MICROMOLES HC/GRAM	GASES DETECTED (PERCENTAGE)	ODOR WHEN OPENED	APPEARANCE	MINERAL COMPOSITION
3946(r)	4.81	27.30	O ₂ (6.5), N ₂ (50.0), CH ₄ (29.1), C ₂ H ₆ (10.2), C ₃ H ₈ (4.1), C ₄ H ₁₀ (trace)	strong gas smell	black and dark gray laminated shale with pyrite lam- inae	Q, I, F, C _{Fe} , P
4006	1.31	8.60	O ₂ (11.7), N ₂ (72.1), CH ₄ (11.6), C ₂ H ₆ (3.7), C ₃ H ₈ (6.8)	some gas smell	laminated dark gray shale and gray green shale, fossils	Q, I, F, C _{Fe}
4026	7.31	40.3	O ₂ (7.8), N ₂ (49.0), CH ₄ (28.1), C ₂ H ₆ (10.7), C ₃ H ₈ (4.5)	strong gas smell	black shale with pyrite crystals present	Q, I, F, P

DISCUSSION

When each can was opened, the odor of the contained gas and core sample was noted. These odors ranged from a slight scent to a strong smell of hydrocarbon gas, and were present when the can had internal pressure at the time of opening. The core samples with a strong odor were mostly those containing dark gray or black shale. In correlating the data from the gas analysis routine, however, it was observed that those cores with a high percentage of hydrocarbon gas (methane, ethane, and propane) did not necessarily have a strong odor. Therefore, the only conclusion that could be drawn from this observation was that the odor of gas indicated the presence of hydrocarbons and because of the pressure in the can, the probable release of them to the can's atmosphere.

After the core was removed from the can, the presence of any rust was noted, either on the can or on the shale itself. Since the cores were taken with a water-lubricated drill and there was water present in the well itself, the appearance of rust and mud was expected. The observation was made in an attempt to explain the reduced oxygen content of some of the samples. It was thought that the oxidation of the iron contained in the shale as iron pyrite and iron rich chlorite, and in the cans themselves, could explain this phenomenon. However, after a quantitative analysis by Eric Jensen was performed, it was discovered that the total amount of reduction could not be explained by even the maximum amount of oxidation.

When the core was split, the appearance of the shale was noted, including color, layering, and fossil content. In those samples that had been shown to have a high hydrocarbon gas content, iron pyrite was observed in bands and could be seen throughout the rest of the shale sample under an optical microscope. It appeared as black in the bands and as brassy crystals when rubbed. Also, elongate branchlike fossils were seen in several samples that had a high hydrocarbon content. In sample 3416 a shiny black substance was noted, looking much

like dried tar and reminiscent of either a leaf, or fish fossil.

In the dark shales, an oily film was noticed when an acetone smear was made. Grinding the sample in acetone took longer than usual, as the shale seemed to resist immersion below the surface of the suspension. When the preparation was completed, the surface appeared oily. Making a cavity fill mount was also more difficult, in that the darker shales seemed to pack into plate-like structure and complicated the smoothing process on the surface of the disk.

The samples that had shown a low hydrocarbon content were opened and were, almost without exception, light and medium gray shales. Many contained silty layers which are known to be more porous than the darker shales. Because of this, any gas that had been contained in these layers could have escaped much more rapidly and would not have been present at the time of analysis. Whether these silty layers contained hydrocarbons at one time or not remains undetermined.

After the twenty-four samples were completely analyzed, another phenomenon was noticed. It appeared that those samples which had high hydrocarbon contents showed broader, lower peaks in both the acetone smear and cavity fill areas. This broadening is distinctive of more disordered crystal structures, as shown by the overgrinding, and the subsequent peak broadening of minerals with more delicate crystal structures such as kaolinite. Those samples with lower hydrocarbon contents showed sharp, distinct peaks. The hypothesis was checked by picking samples at random, and in each case the theory held--those with high hydrocarbon contents showed broader peaks and those with low showed sharper peaks.

Assuming that all the samples were treated alike, it was then decided to see if the peaks on a particular sample could be changed after absorption of a hydrocarbon liquid onto a thin section. Using sample 3716, which had a low

hydrocarbon content, ethyl iodide was constantly dripped onto the surface during the scan of the 14.3 illite peak. However, the iodine atom tended to absorb too much x-ray radiation, so a hydrocarbon containing only carbon and hydrogen had to be chosen. Pentane and hexane evaporated too quickly, so ethyl benzene was used. An apparatus, consisting of a piece of tygon tubing, split the length of the sample, was attached to a reservoir. A piece of paper towel was wrapped around the tubing, thereby providing a method of keeping only a very thin film on the surface of the sample. The entire surface of the thin section was soaked and continued to be so throughout the procedure. No peak broadening was noticed during the subsequent analysis. The broadening effect observed must therefore be either an artifact of the grinding procedure, or must be correlated with gas in some way other than simple, immediate swelling in the presence of hydrocarbon.

CONCLUSION

The x-ray diffraction data collected indicated five major component minerals making up the shale samples. These consisted of quartz, illite, feldspar, chlorite, and iron pyrite. The first three occurred in every sample tested while the presence of chlorite and iron pyrite remained variable. It was observed, from the variation of the first four basal spacings of the chlorite peaks, that the iron to magnesium ratio of this mineral was quite versatile. This along with the presence of iron pyrite may explain the lack of oxygen in some of the core samples. The samples with little or no oxygen in their containers were seen to have a reddish-brown film on the outside of the core. This may be due to the oxidation of the iron in the core samples. The water used in drilling the cores would have contained some iron ions from the iron rich minerals and would have easily combined with the available oxygen sealed in the can.

Another relationship noticed was the presence of iron pyrite in most of the samples with a high hydrocarbon content. Since its grain size is larger than most of the other mineral grains in the samples it may accomodate the diffusion of hydrocarbons through the rock. This same relationship may be true with core samples containing siltstone except to a much larger degree. The quartz grains in the siltstone would facilitate diffusion of gases to such an extent that by the time the sample core was sealed in its container most or all the hydrocarbons once present would be gone. This may account for the low amount of gases found in the lighter colored siltstone-containing shales.

It was observed after all the x-ray diffraction data was completed that samples which contained a large amount of hydrocarbons gave broader peaks while those with very little had sharper peaks. On closer examination only two sets of peaks were affected this way, those for chlorite and illite. This indicates some type of interaction between these minerals and gas content. One explanation

may be that the presence of these hydrocarbons (or their carbonaceous source) cause a more complete breakdown of the crystals when the sample was ground for x-ray mounts. The relationship may be more direct, such as the organic material altering the structures of these two minerals enough so as to cause the broadening of the x-ray peaks. This explanation is not clearly the solution, since tests were run using a thin section of shale, which was soaked with ethyl benzene and then x-rayed with no effect on the peaks. This seemed to call more attention to the first explanation and also indicated that the source of the peak broadening may have been the carbonaceous matter in the samples, rather than the hydrocarbon gases.

CALIBRATION OF THE SORPTION STUDIES APPARATUS

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CALIBRATION OF THE SORPTION STUDIES APPARATUS

INTRODUCTION

The purpose of this section is to describe briefly the construction features and calibration procedures used in calibrating the apparatus used for sorption studies shown in Figure I.

The apparatus is constructed of pyrex glass and is connected to a standard pumping system, consisting of two-stage mechanical forepump, mercury diffusion pump, and liquid nitrogen trap. All joints are made by glass blowing and are leak tight as demonstrated by a Tesla leak tester. The ultimate attainable vacuum should be about 10^{-6} torr.

Both the cell and the gas buret are equipped with thermostats. The gas buret is surrounded by a tube with circulating water from a bath regulated within 0.02°C (0.01%) as measured by a standard calorimeter thermometer. The cell is temperature controlled by a variety of means depending on the application. For nitrogen sorption studies it is surrounded by a dewar filled with liquid nitrogen through which a slow stream of nitrogen is passed to minimize temperature changes due to O_2 sorption or other causes. The rest of the apparatus is at room temperature, which however is closely monitored during the progress of an experiment. The volume of the system thus not temperature controlled is minimized by using capillary tubing of 2.5 mm diameter i.d.

CALIBRATION

The calibration of the system is two fold: pressure and volume. Pressure measurements are made with a Datametrix 5700 barocell and associated electronics used in conjunction with the NOVA 1220 computer with a 12-bit analog to digital converter which corresponds to about .1% of full scale pressure on each of seven ranges (1000, 300, 100, 30, 10, 3, 1 torr). Provision

is made so that the upper ranges can be calibrated directly against a precision manometer; the lower ranges then can be calibrated against the upper ranges by measuring a high pressure, then decreasing the pressure by increasing the system volume by a known amount, then reading the pressure on a more sensitive scale. Proceeding in this way, ranges 1000, 300, 100 should be accurate to full scale corresponding to a maximum of .3% of reading if best use of scales is made. By adjusting volume changes on the buret so that maximum readings are obtained on both the high pressure ranges (1000, 300, 100) and the medium pressure ranges (30, 10) the error for these ranges should be about .14% of full scale; correspondingly the error for the low pressure ranges should be .17% of full scale. The average expected error of the mid ranges should be .33% at the low end when efficient use of the ranges is made; the corresponding number for the low ranges is .34%.

In addition to the pressure calibration careful volumetric calculations are made after each change or modification to the system. Initially the volumes associated with the gas buret were determined before construction of the system by temporarily glassblowing a buret valve at tip to the bottom of the buret, filling it with mercury, then progressively emptying and weighing the mercury collected at the various scribed levels indicated in Fig. I. Calibration temperature was 29.97°C corresponding to a mercury density of 13.5219 g/ml. Table I shows the average and standard deviation obtained as a result of two calibration runs.

Table I

Mark #	Volume	% error ($\frac{\text{std. dev.}}{\text{average}} \times 100$)
1	0.0	(defined)
2	5.491	.10
3	14.004	.12
4	26.004	.048
5	43.457	.008
6	65.764	.0055
7	92.197	.0011
8	123.707	.0044

After construction of the system these calibrated volumes can be used in conjunction with the ideal gas law to determine the volume of the rest of the system. This is accomplished by placing nitrogen (or dried air) in the system, closing Valve (2), and reading pressures at a variety of mark #'s. The volume of the system with Valve (1) closed, V_{D_1} , is $11.69 \pm .03$ ml (Jan. 25, 1976)

A volume V_D is defined as the volume obtained as above with the Valve (1) open, the system closed from the cell by glassblowing at M_3 , but subtracting the volume of the capillary between M_1 and M_3 . The volume of the cell is obtained by the weight of water required to fill it to M_2 and then to the top (corresponding approximately to M_3). The volume of the system to the left of Valve (1) is thus $V_D - V_{D_1} + V_{\text{cell}} - V_{\text{sample}} + hv$ where h is the distance between M_1 and M_2 , v is the volume of a cm of the capillary used (.051 ml/cm). This rather involved procedure has one great advantage. After initial calibration the cell can be sealed and resealed at M_3 and changes of the volume of the system kept track of simply by remeasuring h after each glassblowing operation. We estimate that errors resulting from this procedure are between .01 and .05 ml which is of the order of the uncertainty resulting from the basic PV volume calibration procedure.

The internal volume of the Barocell increases by .16 ml in an approximately linear fashion as the pressure is increased from zero to 1000 torr according to the manufacturer. This volume change is corrected for in our calibration and subsequent BET analyses. The apparatus is easily capable of discerning this variation of volume during calibration; but when the linear correction is concluded there appears to be no systematic variation in the remaining errors suggesting that the manufacturer's recommendation is sufficient.

These calibration procedures are to a large extent automated by a software package we have developed.

Figure I. The system used to make sorption studies.

The system is connected to a standard high vacuum system (capable of 10^{-6} torr) at valve V_2 . Included in that vacuum system is a precision manometer, McCleod gauge, Toepler pump for bringing samples of gas to atmospheric pressure for gas analysis, and connections to nitrogen and other gas supplies.

Fig. 1

GAS SHALE LITERATURE RESEARCH

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GAS SHALE LITERATURE RESEARCH

A literature search was necessary to gather background material on gas diffusion constants of shale and clays. It was discovered that little had been published in the literature concerning diffusion in shale, and only slightly more related to clay diffusion.

The search was begun with Chemical Abstracts Indexes, volumes 66 through 75 and 77 through 84. Key words that were considered included: absorption, adsorption, BET, clay minerals, clays, diffusion, gas, isotherms, shale, and surface area. The references were checked in Chemical Abstracts and, if relevant, were included in the journal search at Juniata and Penn State. Articles that were unavailable at those libraries were obtained through the interlibrary loan program. Science Citation Indexes were used when it seemed likely that an article would be used as a reference. In cases where an article was published in a foreign journal that was not translated the abstract was used.

Sources other than journals were also used. Adsorption isotherm theory, as well as BET theory, was found in Maron and Lando's Fundamentals of Physical Chemistry (1974) and in Shoemaker, Garland, and Steinfeld's Experiments in Physical Chemistry (1974). An article by Bruno J. Giletti, "Studies in Diffusion. I: Argon in Phlogopite Mica," in Geochemical Transport and Kinetics gave additional information on gas diffusion in a porous material.

However, most of the information useful to the research was gathered from the journal articles.

The BET theory, formulated in 1938 by Brunauer, Emmett, and Teller, uses the data of adsorption of gases by porous materials to determine their surface areas. It predicts a multilayer adsorption, as opposed to the Langmuir theory which is monolayer in nature. The gases used for the adsorption include nitrogen, argon, krypton, carbon dioxide, and xenon, and are kept at a temperature at or below their triple point. They adsorb onto the total surface area of the solid, including the spaces between layers and pore areas. Adsorption isotherms are plotted from the data gathered, giving the amount of gas adsorbed as a function of the equilibrium gas pressure at a constant temperature.

The effective diffusivity of a structure depends on the pore radius. The diffusion rate of the gas in the porous medium depends on tortuosity, porosity, the degree of pore saturation, and the presence of dead-end pore spaces. Tortuosity is defined as dm/dx , where m is the path itself, and x is the horizontal displacement. Because the actual path usually does not go in a straight horizontal direction, the ratio dm/dx is greater than one in typical cases. The way this value is applied to the definition of the rate of diffusion depends on the individual theory. It can be generally stated that as any of the above mentioned factors decrease, the diffusion constant increases. Typical values of diffusion constants in porous media can be found in the literature gathered.

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