

Not for Publication

Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Chicago, Illinois, Meeting, September 7-12, 1958

The Kinetics of the Sorption and Desorption of
Methanol on Coals of Various Ranks

George Ostapchenko and Paul Fugassi
Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh (13), Pa.

SUMMARY

The kinetics of the sorption and desorption of methanol were measured on eight American coals varying in rank from lignite to bituminous and were found to obey a second order rate equation. A mechanism for the sorption process is proposed which explains the variation of the experimental velocity constants with pressure and with the rank of the coal. An equilibrium sorption isotherm derived from the sorption mechanism permits the calculation of the moles of sorption sites per gram of coal, A . The value of A for the eight coals is found to be related to the oxygen content, O , in moles per gram of coal by the relationship, $A = 0.667(O)$. This relationship is consistent with the hypothesis that sorption occurs on hydroxyl groups, either unassociated or associated with carbonyl groups. From the evidence gathered from this relationship, it is concluded that sorption occurs on specific sites, probably hydroxyl groups, throughout the coal substance.

INTRODUCTION

There has been much discussion in the literature concerning the measurement of the surface area of coal and the interaction of polar molecules with the coal substance. A great deal of this discussion has been summarized recently(1) and it was concluded that the sorption of polar molecules is apparently complicated by swelling and imbibition, involving weak bonds between the sorbate and polar groups in the coal.

A kinetic study of the sorption of methanol on coal was made(2) and it was found to obey a second order rate equation. This rate equation was also found to be descriptive in cases of water and methanol sorption on such things as cellulose and proteins(3). In the case of methanol sorption on cellulose a mechanism was proposed which led to a new sorption isotherm equation that contains as one of the parameters, the moles of sorption sites per gram of sorbing material. This paper is concerned with the kinetics of the sorption of methanol on coals of various rank in order to obtain quantitative data concerning the interaction of methanol with coals as the rank changes from lignite to bituminous.

APPARATUS AND PROCEDURE

The apparatus and the procedures used in this kinetic study were the same as previously described(2) with the exception that three adsorption tubes connected in series were used instead of one. The spring constants were 1.92, 1.54 and 1.56 milligrams per millimeter extension.

ABSORBENTS AND ABSORBATES

The coal samples used in the sorption experiments are listed along with their ultimate analyses in Table I.

Table I
Ultimate Analyses of the Coal Samples

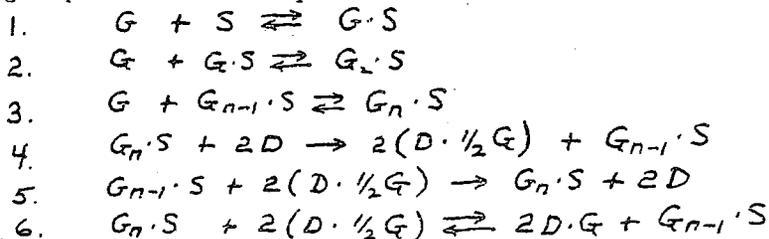
Coal Sample	Ultimate Analysis*					Ash
	C	H	N	O	S	
Upper Kittanning	80.6	3.8	1.1	3.7	1.3	9.5
Lower Kittanning	77.9	4.7	0.9	4.1	2.3	10.1
Upper Freeport	78.7	4.8	0.9	4.6	1.7	9.3
Wyoming	74.3	5.3	1.2	15.2	0.6	3.4
Kincaid Lignite	67.2	4.6	1.0	20.4	0.6	6.2
Illinois No. 6	65.2	4.9	1.2	10.4	4.0	14.3
Hendrix	81.8	5.5	1.7	6.8	1.1	3.1
Moundsville	74.5	5.2	1.4	5.7	4.2	9.0

*Moisture Free

All the coal samples were used in an unsieved, powdered form. The adsorbate, absolute methyl alcohol, analytical reagent, was obtained from the Fisher Scientific Company and was used without purification.

THE SORPTION MECHANISM

In setting up the mechanism for methanol sorption on coal, the mechanism has been made to conform to three requirements: (1) explanation of the second order rate equation, (2) explanation of the variance of the experimental velocity constant with pressure and (3) explanation of having one molecule on one site at equilibrium conditions. This third requirement is necessary since the equation for the equilibrium isotherm is a function of the pressure to the first power. The following sorption mechanism is postulated:



Reactions 1, 2 and 3 represent the adsorption of methanol vapor, G, on the surface sites, S, of the coal. All reactions involving surface adsorption of the physical type are known to be rapid both on theoretical and experimental grounds. The double arrow is used to indicate that these reactions are in equilibrium. Reaction 4 is the slow rate-determining step for the sorption process. A molecule from a site of the $G_n \cdot S$ type migrates into the interior and is held on two internal, D, sites, where n may be 1, 2, 3 , or combinations of 1, 2, 3 The exact value of n, or combination of n's, depends on the nature of the coal's surface and interior sites. The fraction of surface sites covered with n molecules is a function of the pressure and since these sites precede internal sorption, their concentration will enter into the experimental rate equation. Reaction 5 is the reverse of reaction 4 and is necessary to account for the reversibility of the reaction. Reaction 6 is a rapid equilibrium type reaction which accounts for the fact that one molecule is held on one site when equilibrium is reached.

THE RATE EQUATION

The rate equation derived from the above sequence of reactions is

$$k_4 \theta_n W_c t = \frac{f}{1-f}$$

In this equation k_4 is the true velocity constant, θ_n is the fraction of surface sites covered by n molecules, W_c is the moles of adsorbate per gram of sorbent at equilibrium, t is the time, and f is the fraction of the reaction completed at time t .

THE EQUILIBRIUM SORPTION EQUATION

The equilibrium sorption equation derived in a previous paper(3) is

$$W_c = \frac{AKK_1 p_0 c}{(1 + (K_1 - K_2) p_0 c)(1 - K_2 p_0 c) + K_1 K_1 p_0 c}$$

In this equation, A is the moles of sorption sites per gram of sorbent, K is the equilibrium constant for the distribution of methanol between the surface sites and the interior sites, K_1 is the equilibrium constant for the interaction of gas molecules and the surface sites containing one molecule, K_2 is the equilibrium constant for the interaction of gas molecules and the surface sites containing two molecules, p_0 is the vapor pressure of the adsorbate at the temperature of the experiment and c is the relative pressure.

RESULTS AND DISCUSSIONS

The experimental velocity constants, k_x , are derived from the experimental data by using equation 1. $f/(1-f)$ is plotted against t and a straight line is obtained whose slope is $k_x W_c$. Since W_c is known experimentally, the value of k_x is readily obtained. A typical plot of $f/(1-f)$ is shown in Figure 1 for methanol sorption at 45°C. on Wyoming coal at a relative pressure of 0.485. The kinetic data plotted in this way for the eight coal samples fell reasonably well on straight lines which covered 90% of the reaction.

The experimental velocity constant is given by the expression $k_x = k_4 \theta_n$. Since the k_4 is a constant k_x should vary with the relative pressure, c , in the same manner as θ_n . In the derivation of the equilibrium sorption equation θ_n is given by the following relationships:

$$\theta_n = (K_2 p_0 c)^{n-1} \theta_1$$

where

$$\theta_1 = \frac{K_1 p_0 c (1 - K_2 p_0 c)}{1 + (K_1 - K_2) p_0 c}$$

In Figure 2, θ_1 , θ_2 and θ_3 are plotted against c , using values of 1, 5 and 10 for $K_1 p_0$ and assuming $K_2 p_0 = 1$. In the region $K_1 p_0 = 5$ to $K_1 p_0 = 10$, the curve for θ_1 has a maximum at about $c = 0.3$, the curve for θ_2 has a maximum at about $c = 0.5$ and the curve for θ_3 has a maximum at about $c = 0.7$. The experimental curves of k_x versus c for Wyoming coal, Kincaid lignite and Illinois coal show a maximum at about 0.3, indicating that θ_1 contributes most in the kinetic mechanism. The curves for Hendrix and Moundsville coals show a maximum at about $c = 0.5$, indicating that θ_2 contributes most to the kinetic mechanism. The curves for Upper and Lower Kittanning coals show a maximum at about $c = 0.7$,

indicating that Θ_3 contributes most to the kinetic mechanism. The curve for Upper Freeport coal appears to be a straight line indicating that neither Θ_1 , Θ_2 , nor Θ_3 predominate but perhaps all three contribute in such a way as to give a straight line.

In Figures 3 to 6 are plotted the values of Θ_n for each of the coal samples studied. These curves were drawn using the experimental values for K_1 derived from the equilibrium sorption equation. Also plotted in these figures are the values of k_x/k_4 which should equal Θ_n at corresponding values of c . The agreement of these values is quite good. The values of k_4 used in the calculations are listed in Table 2.

Table 2
Values of the True Velocity Constants

Coal Sample	t, °C.	gms. coal
		k_4 , mole CH ₃ OH - hr
Upper Kittanning	45	100,000
	40	96,000
	35	92,000
Lower Kittanning	45	88,000
	40	72,000
	35	56,000
Wyoming	45	14,500
	35	12,600
	30	9,700
Kincaid Lignite	45	13,400
	35	11,100
	30	9,100
Illinois No. 6	45	21,500
	35	17,200
	30	14,000
Hendrix	45	78,000
	35	54,000
	30	50,000
Moundsville	45	65,000
	35	50,000
	30	45,000

In comparing this phenomena with the rank of the coal, it is seen that as the rank of the coal goes from lignite to bituminous the controlling factor in the sorption mechanism goes from Θ_1 through Θ_2 to Θ_3 . It can be postulated that this change is controlled by the relative attractive power of the surface sites and the interior sites for the methanol molecule. The surface of coal can be imagined as having many adsorption sites, each having a different affinity for the methanol molecule. The sites could be the same atom or group of atoms but having different affinities due to steric factors or interactions with other sites.

The sites having the lowest affinity would be capable of holding only one methanol molecule, Θ_1 , and those having a slightly greater affinity would be capable of holding two methanol molecules Θ_2 , etc. The internal sites would then attract the weakest held methanol molecule on the surface in greatest concentration. It is postulated that the methanol molecule most weakly held on the surface is the third molecule going on a site holding three molecules, the next would be the second molecule going on a site holding two molecules, the next would be the molecule going on a site capable of holding only one molecule. When the attractive power of the internal sites is high, the internal site will attract the methanol molecules on sites of most abundance. As the attractive power of the internal sites decreases the surface sites with one methanol molecule become stable and the interior sites attract the next most abundant and less weakly held methanol molecule or Θ_2 . This argument can be applied again for Θ_3 controlling the reaction mechanism. A measure of this attractive power would be the difference in free energy change for the methanol vapor going on the surface and the free energy change for the methanol vapor going into the interior. This information is available from the equilibrium sorption equation which will be discussed later and is shown in Table 3.

Table 3
Average Standard Free Energy Differences at 30°-45°C.

<u>Coal Sample</u>	<u>Free Energy Differences, cal./mole</u>
Lower Kittanning	+23
Upper Kittanning	- 6
Upper Freeport	-407
Moundsville	-708
Wyoming	-814
Hendrix	-918
Kincaid Lignite	-1117
Illinois No. 6	-1282

It can be seen from this Table and from Figures 3 to 6 that as the free energy difference goes from a high to a low negative value, the type of site controlling the kinetic mechanism changes from Θ_1 through Θ_2 to Θ_3 . The sites for methanol sorption on coal are probably the same type in the high rank coals as in the low rank coals. If it were assumed that all the properties of the coals were the same, except for the number of sites, then free energy changes would all be equal. However, there is evidence(4) that as the rank of the substance increases, the degree of compactness of the coal micelles increases. It is probable then, as the coal micelles become more compact the free energy change of the methanol molecule due to sorption will decrease.

The energies of activation, E_a , for the sorption process were calculated from the values in Table 2 by plotting $\ln k_s$ versus $1/T$ and measuring the slope. The values of E_a for the coal samples are shown in Table 4.

Table 4
Activation Energies for the Sorption Process

<u>Coal Sample</u>	<u>E_a, cal./mole</u>	<u>E_d, cal./mole</u>	<u>E_a - E_d, cal./mole</u>
Upper Kittanning	1625	7035	--5409
Lower Kittanning	8798	7191	1607
Upper Freeport	6614	4947	1640
Wyoming	5513	4795	358
Kincaid Lignite	5395	4850	545
Illinois No. 6	5826	2991	2835
Hendrix	5235	2162	3073
Moundsville	5501	2514	2987

The case of methanol sorption on Upper Freeport coal is similar to that reported earlier(2) for Pittsburgh Edenborn coal. The velocity constant for sorption did not vary with pressure, making it difficult to determine the degree of contribution of θ_1 , θ_2 , and θ_3 for the rate determining step. In this case the average value of k_x was used in determining the activation energy for sorption. These values are reported in Table 5.

Table 5
Experimental Velocity Constants for Upper Freeport Coal

<u>Coal Sample</u>	<u>t, °C.</u>	<u>k_x (av.)</u>	<u>$\frac{\text{gms. coal}}{\text{mole CH}_3\text{OH} - \text{hr.}}$</u>
Upper Freeport	45		2717
	40		2265
	35		2010

DESORPTION

The velocity constants for the desorption of methanol from coal were all independent of the pressure indicating that the experimental velocity constant is the true velocity constant. The velocity constants for the desorption of methanol for the eight coal samples are listed in Table 6.

Table 6
Velocity Constants for Desorption

<u>Coal Sample</u>	<u>t °C.</u>	<u>k_x, $\frac{\text{mas. coal}}{\text{mole CH}_3\text{OH} - \text{hr.}}$</u>
Upper Kittanning	45	4,000
	40	3,130
	35	2,790
Lower Kittanning	45	4,090
	40	3,270
	35	2,830
Upper Freeport	45	1,640
	40	1,470
	35	1,270
Wyoming	45	2,200
	35	1,780
	30	1,530
Kincaid Lignite	45	1,640
	35	1,370
	30	1,150
Illinois	45	3,360
	35	3,010
	30	2,710
Moundsville	45	3,930
	35	3,610
	30	3,110
Hendrix	45	3,870
	35	3,470
	30	3,270

The energies of activation of desorption calculated from these values are listed in Table 4, along with the differences in the activation energies. This difference is the heat of reaction for the rate-determining step (equation 4 of the sorption mechanism).

Considering the assumptions made and the experimental errors involved, it is difficult to draw any conclusions concerning the differences in energies for the different coal samples. However, it can be noted that the magnitude of the energies involved excludes compound formation of methanol with coal and indicates that the type of bonding is probably hydrogen bonding.

THE EQUILIBRIUM DATA

Equation 2, the equilibrium sorption equation contains 3 parameters A, K and K_1 which can be evaluated by solving a series of simultaneous equations. The values for A, K and K_1 for the eight coal samples are listed in Table 7.

Table 7
 Constants for the Equilibrium Sorption Equation

Coal Sample	t, °C.	moles of sites x 10 ⁴		K	K ₁
		A, gm. coal			
Upper Kittanning	45	16.4		2.66	6.82
	40	16.7		2.31	9.06
	35	16.4		2.41	10.33
Lower Kittanning	45	15.7		2.43	5.73
	40	15.6		2.09	8.11
	35	15.2		2.33	9.43
Upper Freeport	45	22.9		1.90	8.46
	40	23.2		1.62	11.69
	35	22.9		1.52	14.10
Wyoming	45	61.4		1.15	9.19
	35	66.0		1.06	15.71
	30	67.7		1.04	20.49
Kincaid Lignite	45	73.7		1.04	14.30
	35	82.7		0.84	25.34
	30	83.2		0.90	28.29
Illinois No. 6	45	53.0		0.79	14.48
	35	57.6		0.80	21.12
	30	61.0		0.69	32.29
Hendrix	45	25.9		1.60	14.48
	35	25.2		1.39	21.12
	30	23.9		1.21	32.29
Moundsville	45	22.8		1.64	12.00
	35	21.7		1.68	17.16
	30	20.4		1.35	26.10

It can be seen from Table 7 that the values for A, the moles of sites per gram of coal are independent of temperature and that the values decrease as the rank of the coal increases. It has been suggested(3) that the atom which forms the site for methanol sorption on coal is probably oxygen. In Figure 7 is plotted the moles of sites per gram of coal versus the moles of oxygen per gram of coal. The relationship obtained is linear with a slope of 2/3 which indicates 2/3 of the oxygen in coals from high rank to low rank, form sites for methanol sorption. Several workers(5)(6) have analyzed coals of varying rank in terms of OH, COOH, OCH₃, C=O, and non-reactive O groups in an effort to follow the changes occurring during the coalification process. Using the data of Blom et al.(6) and assuming various combinations of oxygen groups, it was found that the sum of OH and COOH groups gave the best agreement with the number of sorption sites in the coal. These data are plotted in Figure 7 and the agreement is quite good considering the experimental difficulties in determining the oxygen groups in coals. The fact that the sites responsible for sorption remain at a constant ratio with respect to the total oxygen during the coalification process indicates that the oxygen is lost in a very specific manner as coal ages. The exact manner in which the oxygen is lost is difficult to determine since little is known about the manner of the changes of the carbon and hydrogen during coalification.

Since the equilibrium constants K and K₁ are known at three temperatures, the values of ΔH, ΔF°, and ΔS could be determined. These values in cal/mole for ΔH and ΔF° and cal/degree for ΔS are shown in Table 8.

Table 8
Values of ΔH , ΔF° and ΔS for Equilibrium Sorption

Coal Sample	ΔH	K		ΔH	K_1	
		ΔF°	ΔS		ΔF°	ΔS
Upper Kittanning	1951	-620	8.1	-8111	-1215	-21.7
		-522	7.9		-1372	-21.5
		-540	8.1		-1430	-21.7
Lower Kittanning	843	-560	4.4	-9751	-1104	-27.2
		-459	4.2		-1303	-27.0
		-518	4.4		-1375	-27.2
Upper Freeport	4429	-408	12.6	-9980	-1351	-27.1
		-302	13.2		-1531	-27.0
		-256	13.5		-1621	-27.0
Wyoming	1131	- 67	3.8	-10,204	-1402	-27.7
		- 37	3.8		-1637	-27.7
		- 25	3.8		-1820	-27.7
Kincaid Lignite	1191	- 27	3.8	-7928	-1683	-19.6
		11	3.8		-1930	-19.3
		6	3.9		-2012	-19.5
Illinois No. 6	2331	151	6.9	-11,129	-1690	-29.7
		136	7.1		-1869	-30.0
		224	7.0		-2094	-29.8
Hendrix	3843	-297	13.0	-9508	-1628	-24.8
		-200	13.1		-2006	-24.4
		-113	13.1		-2045	-24.6
Moundsville	3440	-312	11.8	-10,827	-1572	-29.1
		-318	12.2		-1741	-29.5
		-179	11.9		-1966	-29.1

These values show that the energy associated with the sorption of methanol on coals is small compared to energies due to chemical reactions and, as pointed out in the discussion of the rate equation, are probably due to hydrogen bonding. There seems to be no correlation of these values with the rank of the coal.

CONCLUSIONS

The sorption of methanol on coal takes place in two steps. (1) The adsorption of methanol molecules on to the surface of the coal in a multilayer manner. (2) Migration of the molecules from the surface into the interior of the coal substance. The first step is rapid and the number of sites involved is small compared to the total number of sites responsible for sorption since the second order rate equation is obeyed during the entire sorption process.

The migration of the methanol molecules into the interior occurs primarily from only one type of surface site. This site may be holding either one, two or three methanol molecules, depending on the rank of the coal sample. As the rank of the coal increases from lignite to bituminous, the type of site determining changes from a surface site holding one methanol molecule to a surface site holding three methanol molecules. This change is related to the free energy changes for methanol sorption caused by the coalification process.

The moles of sites per gram of coal, A, responsible for methanol sorption can be calculated from the equilibrium sorption isotherm. The value of A

decreases as the rank of the coal increases and it was found that A varies directly with the oxygen content of the coal, O, in moles per gram according to the relationship $A = 0.667 (O)$. Since the oxygen content of coal cannot be obtained directly by analytical means, and is obtained by difference, the sorption of methanol on coal might be used as a means of determining oxygen directly.

The variation of the value of A with the rank of the coal is consistent with the hypothesis that the sites responsible for sorption are hydroxyl groups either isolated or in conjunction with a carbonyl group. This is corroborated by the energies derived from the sorption data which show that the type of bonding which occurs during methanol sorption is probably hydrogen bonding. The loss of oxygen in coal during the coalification process occurs in such a manner that for every two hydroxyl groups lost one other type of oxygen group is also lost. The loss of oxygen in this manner is quite specific and further investigations along these lines might provide quantitative data concerning the coalification process.

This communication has been abstracted from the thesis of George Ostapchenko submitted to the Graduate School, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree, Doctor of Philosophy. The authors wish to acknowledge and thank BCR, Inc. and the Coal Research Board, Commonwealth of Pennsylvania, for furnishing samples and analytical data for the Kittanning and Freeport coals. They also wish to thank Dr. Martin Neuworth, Pittsburgh-Consolidation Coal Co., for samples of Hendrix and Moundsville coals.

REFERENCES

1. Anderson, R. B., Hall, W. K., Lecky, J. A., and Stein, K. C., J. of Phys. Chem. 60, 1548 (1956)
2. Fugassi, J. P., Ostapchenko, G. and Trammell, R., Fuel, 37, 36 (1958)
3. Fugassi, J. P. and Ostapchenko, G., unpublished material
4. Bangham, D. H., Franklin, R. E., Hirst, W. and Maggs, F. A. P., Fuel, 28, 231 (1949)
5. Ihnatowicz, M., Prace Glownego Inst., Gornictwa (Katowice), Komm., 125 (1952)
6. Blom, L., Edelhausen, L. and van Krevelen, D. W., Fuel, 36 (1957)

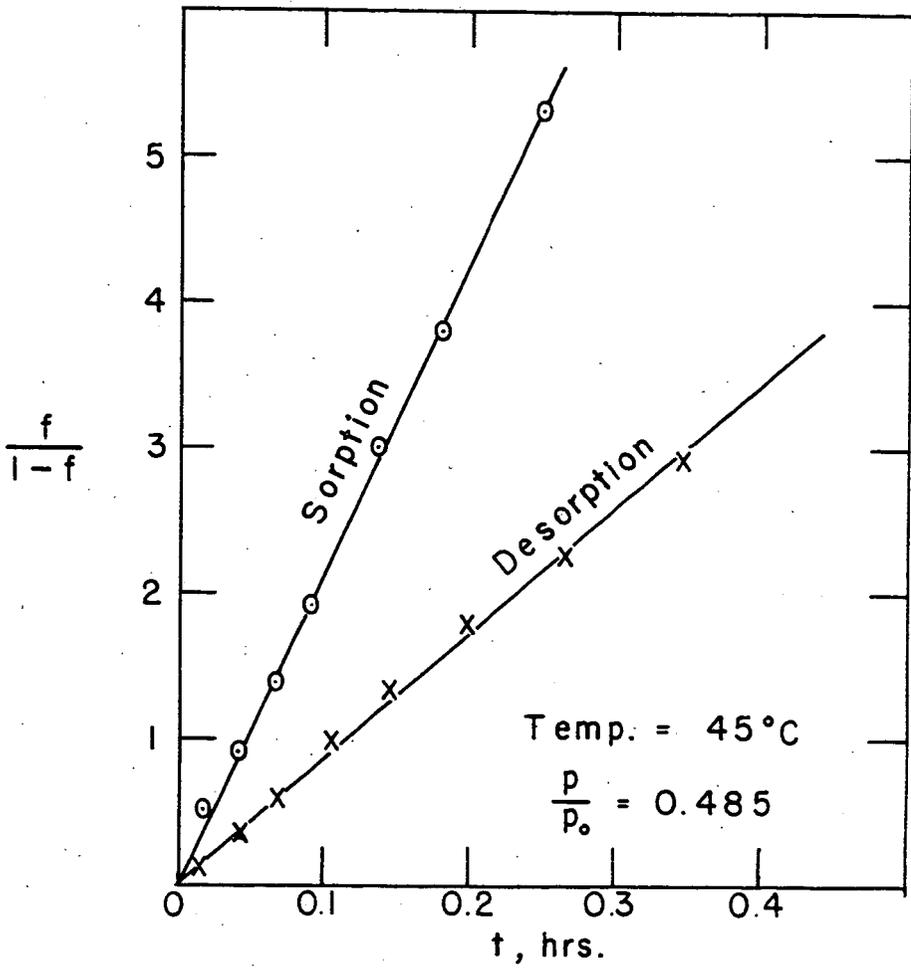


FIGURE 1 - RATE PLOTS

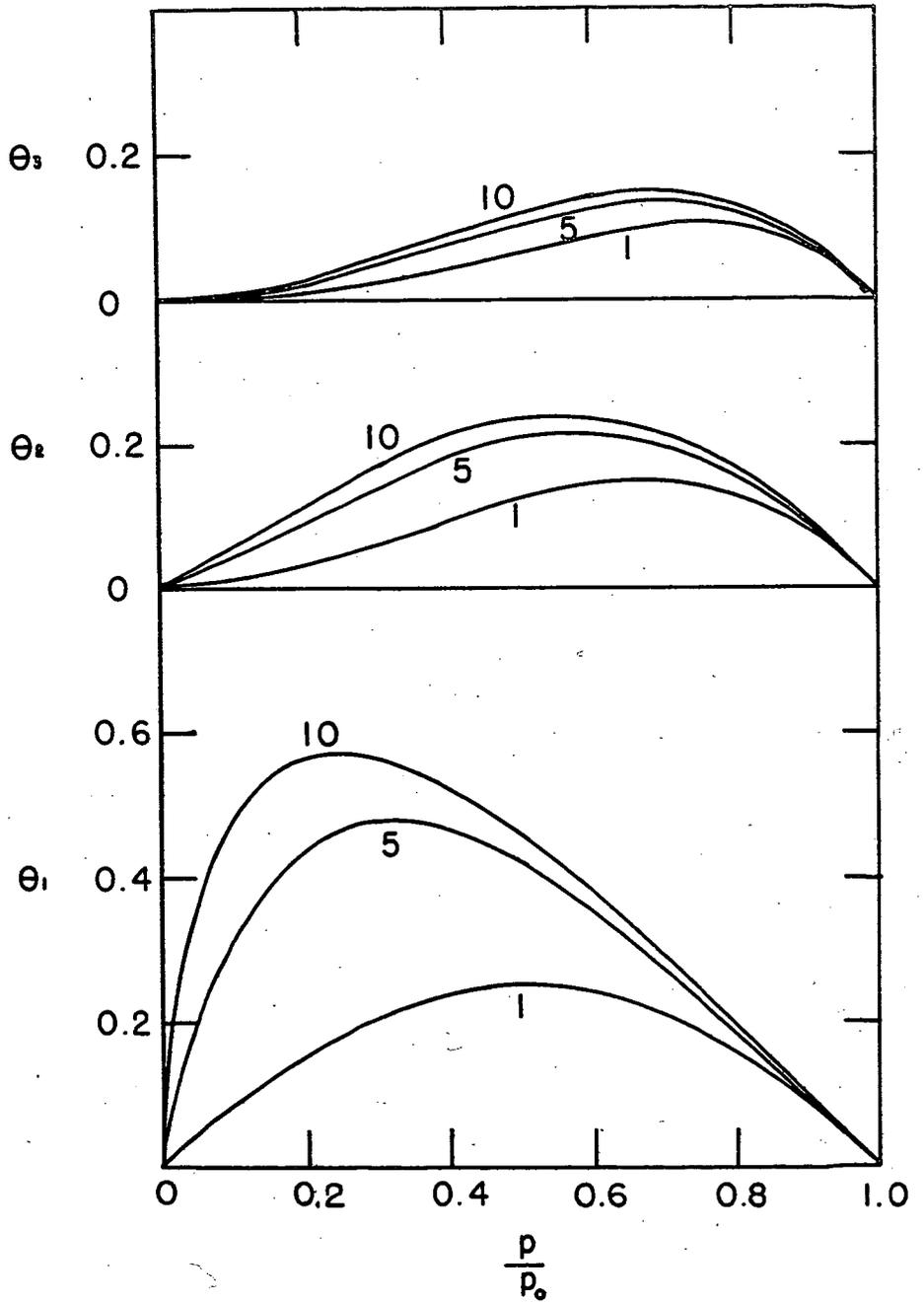


FIGURE 2 - θ AS A FUNCTION OF c

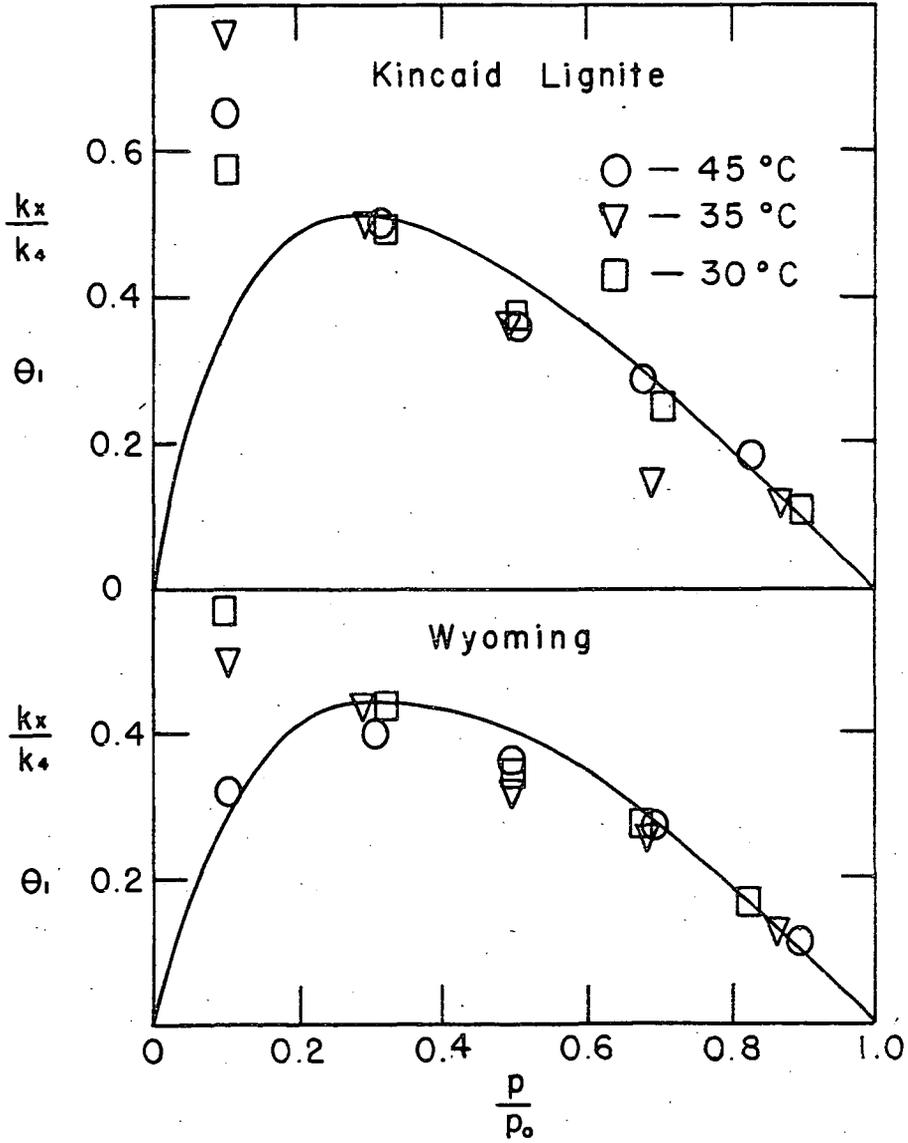


FIGURE 3 - θ_1 AS A FUNCTION OF c

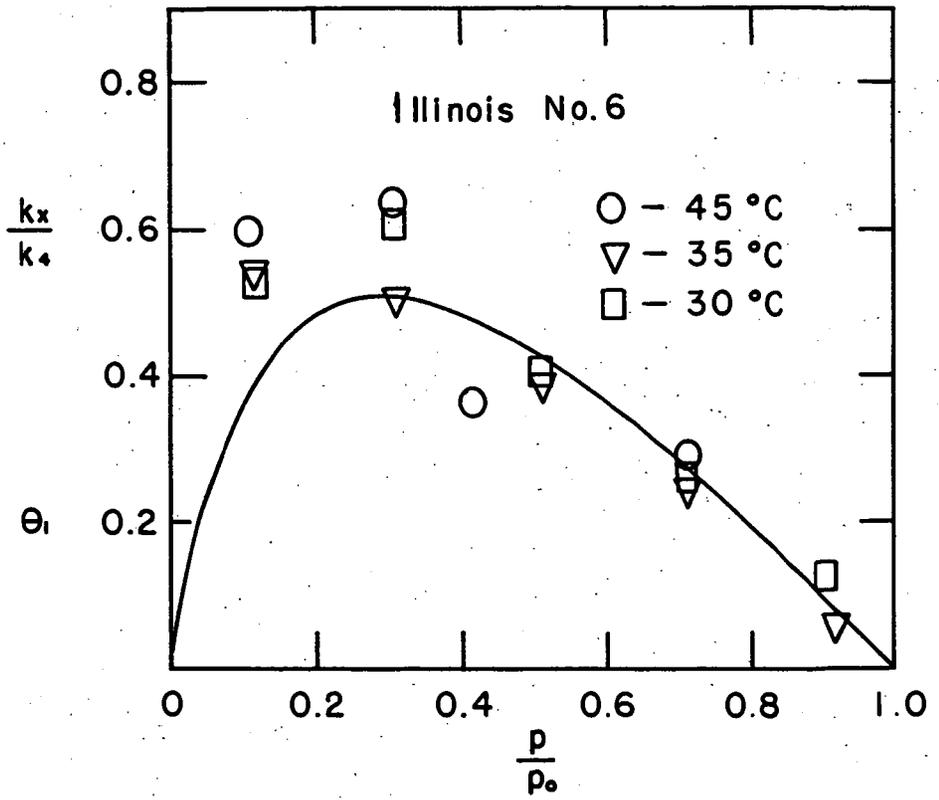


FIGURE 4 - θ_1 AS A FUNCTION OF c

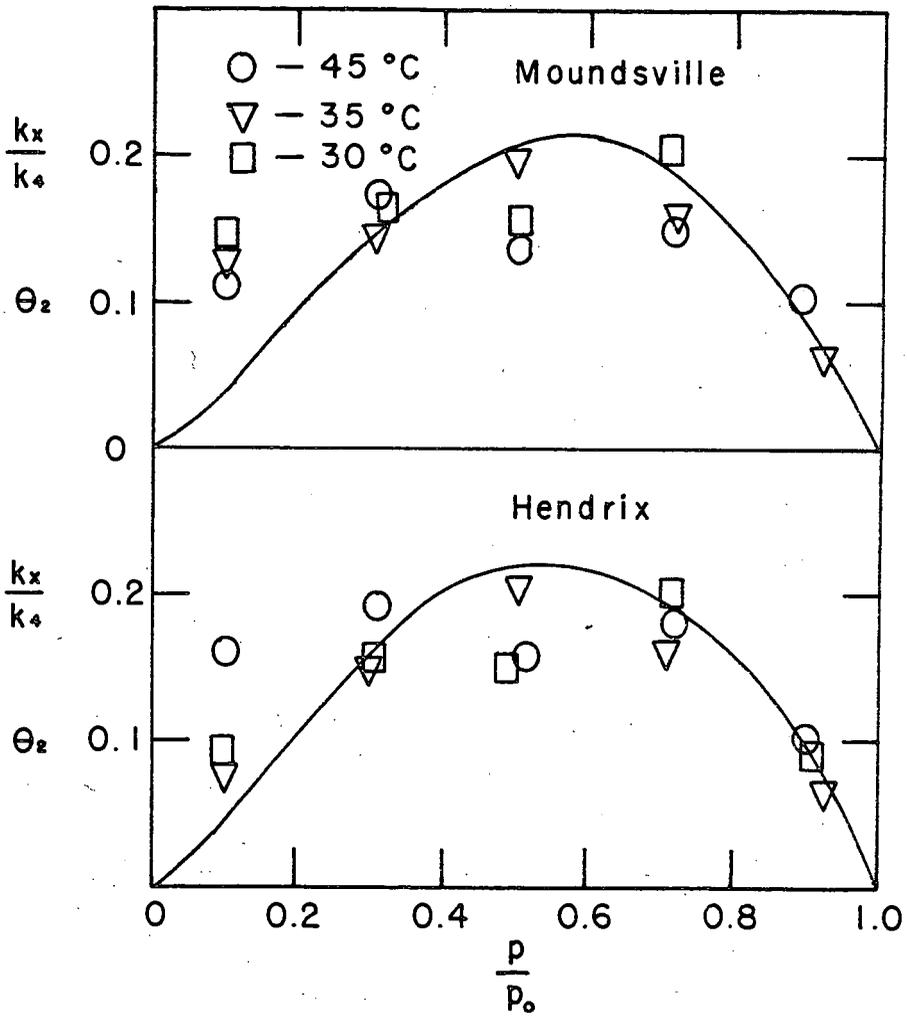


FIGURE 5 - θ_2 AS A FUNCTION OF c

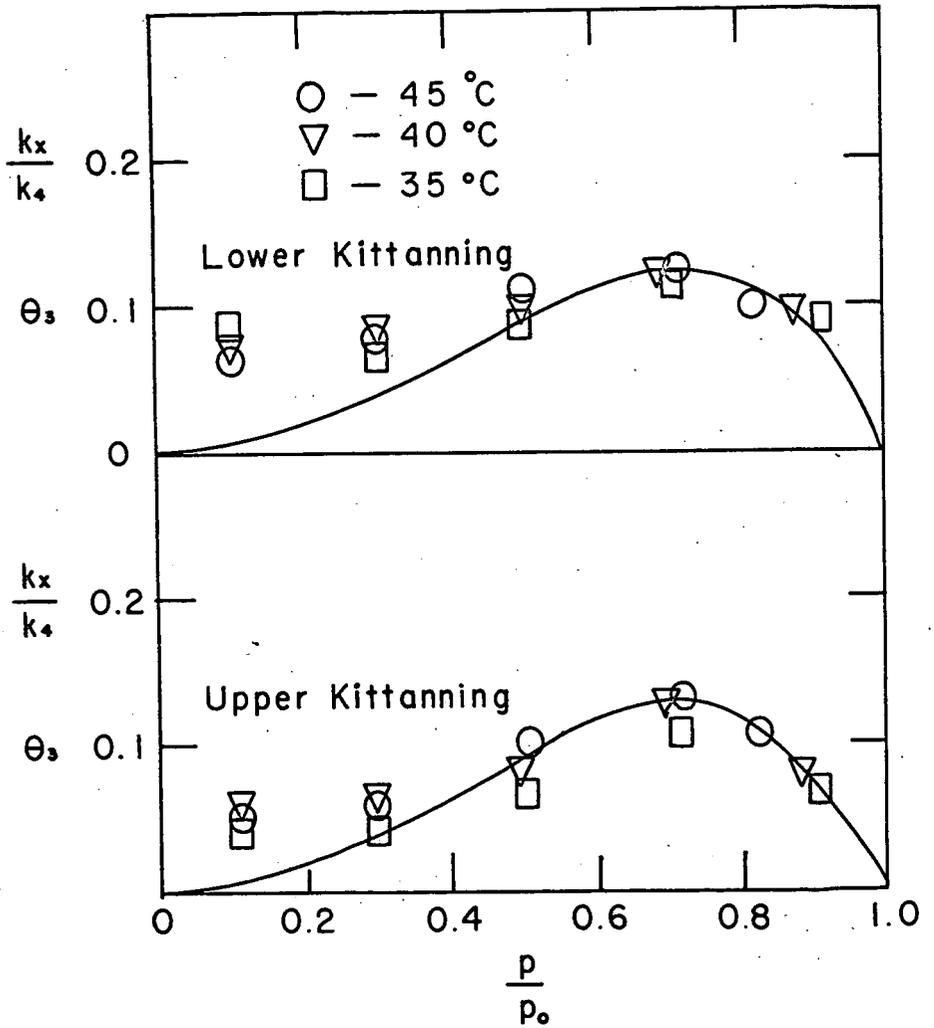


FIGURE 6 - θ_3 AS A FUNCTION OF c

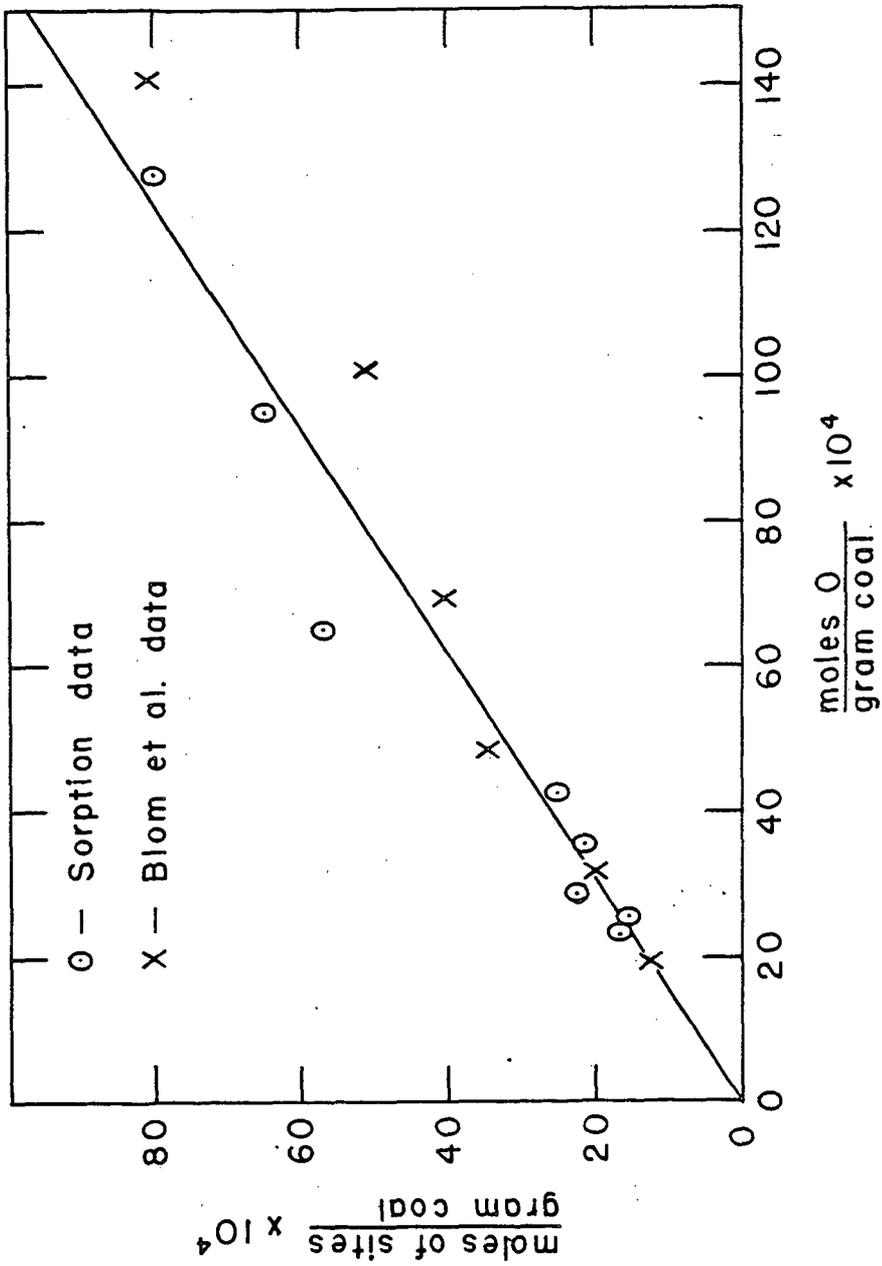


FIGURE 7 - RELATIONSHIP BETWEEN A AND TOTAL OXYGEN CONTENT