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KINETIC AND EQUILIBRIUM MEASUREMENTS OF COAL DRYING

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ABSTRACT

The retention, attachment, and release of water (sorption, adsorption, and desorption) in Fruitland subbituminous coal are shown to be very complex phenomena. The vapor pressure and thermodynamic activity of water in the coal at about 315 K vary sharply with composition. Removal of 60% of the water initially present reduces the vapor pressure by about 60%. The total moisture content of saturated coal also varies with temperature. A 10 K rise in temperature reduces the sorbed water by about 8%. There is strong hysteresis in the sorption behavior, water which is desorbed by reducing the vapor pressure over a coal sample is not fully replaced by adsorption when the vapor pressure is returned to its original level. These measurements of desorption and adsorption reflect stable and metastable equilibria. Kinetic measurements are reported for approach to a new equilibrium if the vapor pressure over the coal is reduced. The kinetic measurements reflect the shape of the pores while equilibrium vapor pressures reflect how tightly the water is bound in the pores. Both types of measurement show changes in behavior at the same compositions. Implications of these results for UCC are discussed.

It is well known that the removal of water greatly increases the permeability and porosity of moist, low-rank coals, e.g., Fruitland coal, San Juan Basin, Four Corners Region of New Mexico[1,2]. In corollary, subsequent coal reactions can proceed to a more suitable conclusion because of many factors including:

- More complete combustion[1]
- Improved characteristics of the UCC pyrolysis char[3,4]
- Increased reaction area[5]
- Advantageous thermodynamic conditions[1]
- Higher gas reaction temperature[1]
- Reduced unavailable heat[1]
- Easier gas flow[1,2]
- Reduced environmental problems[1]

In spite of the very great importance of coal moisture, the subject has received incomplete study. Earlier workers did not resolve questions regarding the nature of coal, the sources of hysteresis in water sorption, or the thermodynamics of moisture sorption on coal. (See Refs. 7,8 regarding the earlier work which includes sorption studies.) More recently there have been a few measurements of the thermodynamics of adsorption and desorption[9-11], but the kinetics associated with the approach to equilibrium have not been studied.

In contrast with the case for coal moisture, there is a large amount of literature on the equilibria developed during adsorption and desorption of vapors on catalyst substrates. In many, but not all, ways the sorption behaviors in the two cases are similar. Like the coal-moisture case, however, there are no kinetic data, because no adequate experimental techniques are available for precise studies of these systems.

The vapor pressure measurements reported in this paper were made by isopiestic balance. This device has been used for many years for precise measurements of alloy vapor pressures at high temperatures[12], but its use for water sorbed on coals and its use for kinetic measurements is new.

EXPERIMENTAL INFORMATION

The Isopiestic Balance

This balance system very precisely measures vapor pressure-composition relationships for systems in which only one component is significantly volatile. Figure 1 indicates part of the system.

A sealed, air free, equilibration tube (a) is attached to a supporting arm (b) which is suspended from a 0.[illegible] mm tungsten wire (c). The supporting arm is connected to an analytical balance above (not shown) by a sidearm and a 0.08 mm tungsten wire (d). In operation, moist coal (e) at one temperature is equilibrated with water vapor from a reservoir of water (f)

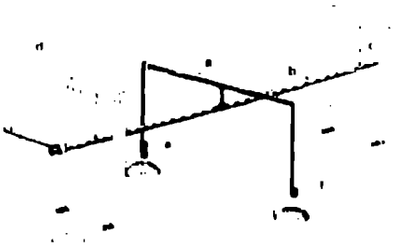

Fig. 1 The isopiestic balance system.

at a lower temperature. The vapor pressure of the reservoir water sets the vapor pressure throughout the system, and the coal adsorbs or desorbs water until the moist coal composition is proper for satisfying the ambient water vapor pressure.

The weight needed to null the analytical balance is related to the composition of the moist coal. Specifically, the suspension system is counterbalanced so that 0.01-mg weight shifts at the balance can be detected. In addition, there is a lever advantage because the moisture transfers six times as far as the balance arm length. Thus, 0.01-mg shifts of moisture can readily be detected. The moist coal sample initially weighed 700 mg in the present experiments.

The thermodynamic activity of the water in the moist coal is essentially the pressure ratio, P/P°, where P is the vapor pressure of water at the water reservoir temperature and P° is the vapor pressure of pure water at the coal temperature. The temperatures of the coal leg and of the water leg of the equilibration tube are measured to about 0.02°F, and the temperature difference is also measured to that precision. At a coal temperature of 311 K, these measurements lead to a precision of about 1/10,000 in the water activity at any coal composition measured.

The time to each equilibrium depends upon the position on the isotherm. At 311 K and water activities over 0.9, the systems come to equilibrium in about eight hours after an alteration of the vapor pressure. For the activities around 0.5, the equilibrations require several days to reach essential equilibrium.

RESULTS

Equilibrium Results

Figure 2 shows the temperature dependence for the desorption of moisture from a Fruitland subbituminous coal which initially was fully wet, i.e., the last droplet of excess moisture had just been removed, and [illegible], the ratio of the vapor pressure over the moist coal to the vapor pressure of pure water at the same temperature, was equal to 1.

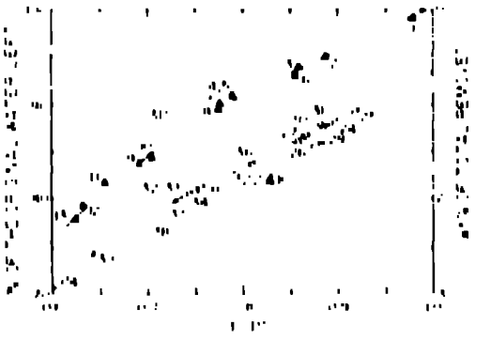

Fig. 2 Temperature dependence for desorption.

These desorption measurements were carried out at two temperatures, 311.1 K and 322.4 K. The numbers of the data points indicate the order in which the data were taken. In most cases the equilibrium was achieved after the temperature of the water reservoir had been dropped a degree or two, thus producing a a small loss in moisture from the coal as the vapor pressure and thermodynamic activity for the water decreased. In a few cases, however, the water reservoir temperature was raised slightly, and adsorption took place. (This adsorption along the desorption leg is to be distinguished from adsorption along scanning curves of the adsorption leg of the isotherm. Such adsorption leads to a hysteresis, as will be discussed regarding Fig. 4.)

The measurements for Fig. 4 start at Point 14. The point follows Point 13 in Fig. 2, which was taken with the coal temperature at 311 K. Between Points 13 and 14, the coal temperature was raised to 322 K.

The Points 14 to 27 along curve d follow what is called a scanning curve in catalyst-substrate terminology. Points 26 and 27 lie on the desorption curve (in a region which will be discussed as corresponding to true equilibrium). Points 26 to 30 are shown in Fig. 2, except that the data in Fig. 2 have been corrected to exactly 322.4 K while the data in Fig. 4 are for a nominal 322 K.

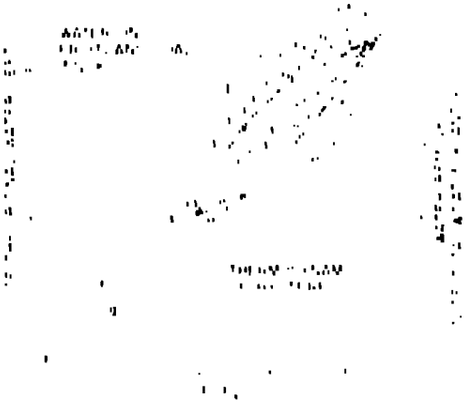

Fig. 4 Hysteresis with stable and metastable equilibria for desorption and adsorption.

Curve segments a, b, and c were followed during desorption for coal at 322 K. For the adsorption along Curve e, the vapor pressure of the water was raised in steps until the desorption curve was again met

Curves f and g are estimated for desorption and adsorption, based on the reported performance of moist coals as published elsewhere[9-11].

Figure 4 indicates the equilibria achieved at the conclusion of the kinetic runs which are presented in the next section.

Kinetic Results

The results of a typical kinetic run are plotted in Fig. 5 as the fraction of the total weight loss which results from a vapor pressure change vs the square root of time. (This type of plot reflects diffusion theory.)

In this case the system was in pressure and composition equilibrium with the coal at 31[illegible] K, the water reservoir at 310.[illegible] K, and the vapor pressure of the water uniform throughout the system as set by the water reservoir temperature. Then the water reservoir temperature was dropped 1 K to 309.1 K, and the moisture in the coal fell as indicated by the data points.

As shown in Fig. 4, the composition and equilibrium activity moved from Point k-1 to Point 1-4.

The different kinetic behavior corresponding to the different levels of moisture content in the coal is shown in Fig. 6. As noted regarding Fig. 5, Run k-5 in Fig. 6 corresponds to a drop of 1.0 K to a condition where the water reservoir temperature is [illegible].9 K below the coal temperature.

Fig. 4 - Equilibria achieved at the conclusion of kinetic runs.

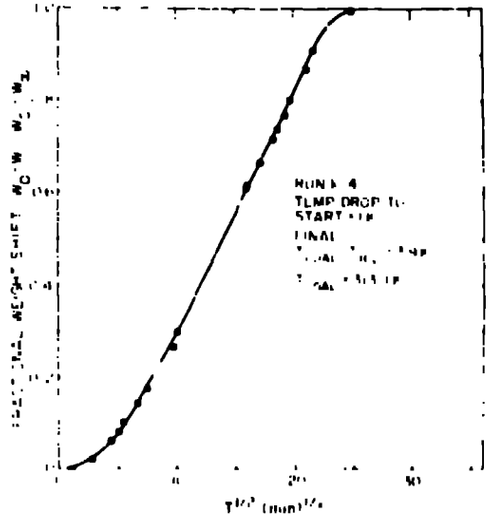

Fig. 5 - A typical kinetic run.

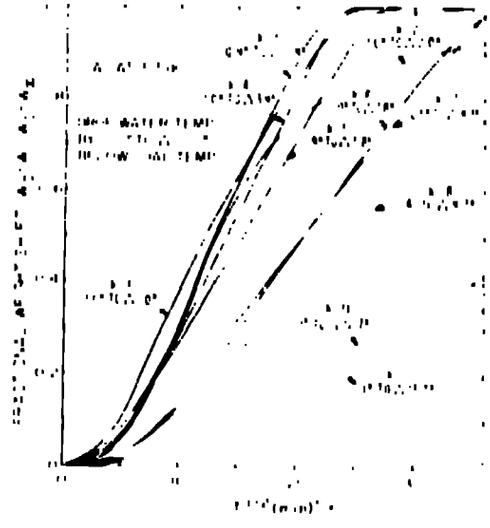

Fig. 6 - Comparison of the various classes of kinetic runs.

TABLE I

FREE ENERGY, ENTROPY, AND ENTHALPY CHANGES ON THE DESORPTION LEG OF THE SORPTION ISOTHERM FOR A COAL

Fruitland subbituminous coal

Fraction of the original water left on the coal	Random entropy for surface sorption 2/3 R ln X	Coal temp. K	Coal-H_2O activity P/P^o	Vaporization process ΔS^o cal/(mole)(K)	Vaporization process ΔH^o kcal/mole
0.950	0.07	311.1 322.4	0.888 (1.032 %)	36.02 %)	(12.97 %)
0.900	0.14	311.1 322.4	0.779 0.932	37.41	13.48
0.850	0.22	311.1 322.4	0.704 0.8[illegible]	36.[illegible]1	13.2[illegible]
0.800	0.30	311.1 322.4	0.6[illegible]5 0.[illegible]	35.96	12.[illegible]
pure liq. water	0.00	317	1.000	27.74	10.32

P is the vapor pressure of the moisture held in the coal at the temperature indicated, P^o is the vapor pressure of pure water at the same temperature. This ratio closely approximates the thermodynamic activity.

DISCUSSION

Thermodynamics

Before proceeding with this discussion it should be noted that these thermodynamic values are for one sample only. Preliminary studies on a different sample indicate substantially (15 %) smaller enthalpies. Other thermodynamic properties appear to be affected quantitatively as well.

Entropies and enthalpies of water vaporization from coal along the top of the desorption leg of the isotherm are indicated in Table I. These values are based on the temperature dependance of the vapor activities, P/P^o, as presented in Fig. 2. (Under these conditions the fugacity ratios and the pressure ratios are essentially identical.)

The enthalpies indicate a strong bonding of water to coal in the upper regions of the desorption leg of the sorption isotherm. Nearly a third more energy must be supplied if water is being vaporized from coal than if it is being vaporized from bulk water. Somewhat surprising is the fact that the energy for vaporization decreases as the coal becomes unsaturated. Perhaps hydrogen bonding is lost as the remaining water molecules lose contact with each other.

A similar phenomenon is observable with the entropies of vaporization. The entropy gained upon vaporization decreases toward the value for vaporization of bulk water. These entropy changes are far larger than anything which could be ascribed to the creation of simple randomness as water molecules are removed. Randomness of vacancies on a surface would add 2/3 R ln (fractional coverage), as indicated in the table. In this case one must look to much larger sources of entropy such as a new rotation of the adsorbed water molecules as part of the adsorbed material is removed.

There can be strong hysteresis depending upon whether water is desorbed or adsorbed. This hysteresis occurs in Fig. 3 for the adsorption scanning curves d and e, but it does not occur in the region listed as a in Fig. 3 and shown also in Fig. 2. Note in Fig. 2 that the sequence of Points 2a-3f involves both desorption and adsorption, yet all the data lie on a single line. Apparently there must be significant removal of moisture before the system generates conditions for the hysteresis shown in the scanning curves.

Our data show that the bonding forces met on desorption can be much stronger than those met on adsorption. Other data show[10] that water adsorbed on coals like ours behaves much like bulk water, and we show strong bonding and loss of entropy for desorption conditions. The true equilibrium conditions show on the desorption

leg; adsorption yields metastable equilibria.

For fractions of 0.0[illegible]-0.7[illegible]2 of the maximum adsorption on lignite, the heats of sorption are 6.8-2.0 kcal/mole[12] of water.

Curves 1 and g for desorption and adsorption in Fig. 5 are estimates based on other measurements of sorption isotherms[9-11].

Kinetics

Typical data-scatter for the runs measuring the approach to equilibrium are indicated in Fig. 5. A collection of data from nine runs of this type are given in Fig. 6, and the equilibria resulting from these runs are shown in Fig. 6.

The kinetic runs lead to the same equilibria as are identified in Figs. 2 and 4. Fig. [illegible] involves measurements on a cylinder of coal, and Figs. 3 and 4 apply to a group of about 20 1-mm pieces. The ordinates of Figs. 2 and 4 are different from that in Fig. 4. If the data from the three figures were plotted on the same ordinate, however, the two groups of data would demonstrate very close agreement.

Now consider Run k-7 in Fig. 6. It [illegible] like k-1 and k-4, but then it drops off unlike any of the other runs. The run behavior is reproducible, and it can be shown that the [illegible] two thirds of the course of the run should not be considered as shown in Fig. 6.

In light of the previous paragraph, Run k-1 to k-[illegible] fall in one family, k-6 to k-8 make a second family, and k-11 and k-12 are in a third family. (k-9 and k-10 cannot be plotted because of lack of a critical point.)

In Fig. 6 the kinetic runs move from one point to the next. For example, Run k-1 moves from START to Point k-1. Thus Runs k-1 to k-4 and the start of Run k-5 describe the same region of linear activity-composition relationships which was also identified by the equilibria in Figs. 2 and 4.

Correlations between equilibrium and kinetics cannot be established as clearly for k-6 to k-8 and k-11 to k-12 as for the group just discussed. However, we are confident that a correlation could be shown if more data were available.

Relationship Between Thermodynamics and Kinetics

Equilibrium can be looked [illegible] as a measure of how tightly water is bound to the coal. The large (2 to 6 kcal/mole) heats of sorption on the desorption leg, and the associated large entropy effects (6 to 10 cal/mole K) indicate that the coal must have very small pores and very large internal surface areas--without pores like those described, the coal moisture would look much more like bulk water.

The kinetics reflect the paths through which the water vapor must move, i.e., the permeability and porosity at various stages of water removal. To yield the behavior shown in Fig. 6, there must be relatively large groups of very similar pores with other large groups of pores of different types.

In the field of catalyst substrates, equilibrium sorption data are analyzed to deduce features of the pore sizes and shapes, e.g., Ref. 14. In many ways the kinetic data offer an even more powerful tool. Until we can cross check the two methods, we do not want to publish an analysis of either type of data alone, however.

Implications for Underground Coal Conversion

1. Although these data indicate a very great complexity in the behavior of moisture in coal, this behavior should not be taken as a basis to reject the more simple kinetic models of drying, e.g., Ref. 2. The true situation is that the simple models are all that can be used in practice, and they may work very well. Also, the complexities we see act almost like a fine structure which deviates off the general trends of behavior; thermodynamic free energies tend to show gradual changes even when the enthalpies and entropies are changing abruptly--ΔG competes with $T\Delta S$, and ΔG holds its trend.

2. The hysteresis in adsorption/desorption is of a form which assists underground coal conversion. If tightly bound water in coal, is desorbed during gasification and recondensed nearby, it will not be as tightly bound in its new location.

3. Much of the moisture is very tightly held and will not exhibit the normal boiling point of water. This factor is important in thermodynamic calculations of drying and later pyrolysis and gasification.

4. This tightly bound water helps to explain why the oxygen and hydrogen of "dried" coal can be treated as H_2O in thermodynamic calculations. Much water will not be removed in the usual moisture determination procedures.

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