# Water in Coal Pores: Low-Temperature Heat Capacity Behavior of the Moisture in Wyodak Coal

Abstract. *The low-temperature heat capacity behavior of naturally occuring water in Wyodak coal indicates that there are two types of water present. More than two-thirds is "nonfreezable," displaying no evidence of a phase transition in the neighborhood of 273 K where normal bulk water melts. The remainder is "freezable," displaying a somewhat distorted heat capacity peak, which is indicative of a phase transition. This evidence suggests that the nonfreezable water is either adsorbed on the internal surfaces of the coal or is in smaller pores, whereas the freezable water is in larger pores. Parallels to the heat capacity behavior of the coal-water system include the water in a porous ceramic, water in the mineral endellite, and water in the protein collagen.*

The physical properties and chemical reactivity of a particular coal are often influenced by the coal's porosity. The coal structure includes an intricate network of pores, ranging by one definition (*1*) from macropores (> 300 Å) to intermediate pores (12 to 300 Å) to micropores (< 12 Å), with the pore-size distribution varying for different coals. In a sample of raw coal, the porous network is usually filled with water, the amount of water reflecting the coal rank and porosity. We have investigated the nature of coal-water interactions by making low-temperature heat capacity measurements of a subbituminous coal (Wyodak) containing its natural water. We found no studies of this type in the literature, although measurements by dilatometry (*2*), nuclear magnetic resonance (*3*), and vapor-pressure isotherms (*4*) indicate that the water in coal does not behave as pure bulk liquid water. Our results indicate that there are two types of water in Wyodak coal, "nonfreezable" (incapable of forming crystalline ice) and "freezable." We speculate that the nonfreezable water is either adsorbed on the coal's internal sufaces or is in the coal's smaller pores, whereas the freezable water is in the coal's larger pores. We also report the heat capacity behavior of water in a porous ceramic, chosen as a model system, and compare the coal and ceramic results to parallels that have been reported in the literature.

"As-received" Wyodak coal contains about 37 g of water per 100 g of dried coal (*5*). We measured heat capacities with a differential scanning calorimeter (Perkin-Elmer DSC-2) from 100 to 300 K with an accuracy of 3 to 4 percent (*6*). For each measurement, about 10 mg of sample (coal particle size, 1.2 to 2.5 mm) was encapsulated in a sealed aluminum sample pan.

We prepared samples of Wyodak coal containing various amounts of naturally occurring water by allowing a weighing bottle of as-received coal to lose water to the ambient laboratory atmosphere and taking samples at intervals. In a separate experiment, the weight gain of a desiccant matched the weight loss of as-received coal when both were enclosed in an air-containing desiccator; this result indicated that the principal weight change that occurs when as-received coal is exposed to air is a simple loss of water. We prepared a sample of dry coal (for comparison with the wet coal samples) by the room-temperature evacuation of as-received coal in a desiccator first over $CaSO_4$ (Drierite) and then $P_2O_5$ for several days. We chose not to dry the coal at elevated temperatures to minimize the possibility of chemical or physical alteration to the pore structure.

Figure 1a shows the heat capacities, measured on heating, of samples of Wyodak coal containing different amounts of water. If the water in coal were behaving as pure bulk water, there would be a large sharp peak at 273 K, where ice melts, indicating a latent heat of 79.7 calories per gram of water present. Figure 1a shows that at most only a small fraction of the water in the coal resembles bulk water. Only the samples containing the larger amounts of water show a phase transition, and the peaks in these samples are largely rounded and contain only a fraction of the enthalpy change expected. A rough calculation of the enthalpy change for the as-received sample containing 37 g of water per 100 g of dried coal indicates that less than one-third of the water in as-received coal undergoes a phase transition. Samples below a threshold water level (19 to 22 percent) exhibit no phase transition (Fig. 1a).

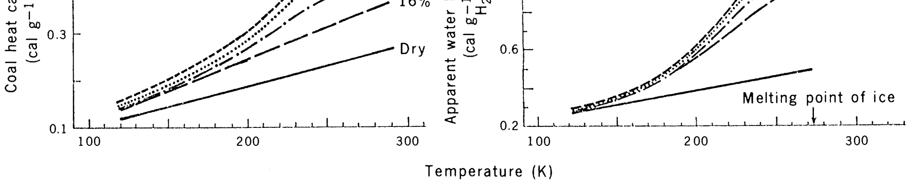

Fig. 1. (a) The specific heat capacity of samples of Wyodak coal containing the indicated amounts [percent defined as the grams of water per 100 g of dried coal (*5*)] of naturally occurring water. (b) The apparent specific heat capacity of the water in the Wyodak coal samples of (a) compared to that of pure water.

If the heat capacity of the coal matrix is unaffected by the presence of the water, one can calculate the apparent heat capacity of the water by subtracting the heat capacity of the appropriate amount of dry coal from that of the wet coals. The apparent specific heat capacities for the water in the samples of Fig. 1a are shown in Fig. 1b. Since these curves result from the subtraction of two experimental quantities, possible errors are magnified but a further feature of the water-coal system is evident. All of the water, regardless of the differences in behavior near 273 K, has a heat capacity that is solid-like at low temperatures and liquid-like at room temperature.

From these observations, we propose that there are two types of water in Wyodak coal, freezable and nonfreezable. We speculate that the nonfreezable water is incapable of forming crystalline ice because it is either adsorbed on the internal surfaces or is in the smaller pores. Starting with solid-like heat capacity at low temperature, the water molecules gradually acquire degrees of freedom as the temperature is raised without ever undergoing a definite phase transition. The freezable water, then, is that fraction of the water away from the perturbing influence of the coal surface and therefore in the coal's larger pores. Even the freezable water, however, does not behave as perfectly pure bulk water since its fusion peak is rounded.

To test this hypothesis, we made parallel measurements on a porous alumina catalyst support whose pore-size distribution and surface area were known (*7*). We studied five samples, containing 0.0,

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9.3, 18.3, 24.1, and 31.6 percent water added to the dried support (*5*). This system shows remarkable similarity to the coal-water system; in this system also there is a threshold water level, this time about 15 to 17 percent, below which no transition is evident and above which a fusion peak begins to appear; moreover, all of the water has solid-like heat capacity at low temperatures and liquid-like heat capacity at room temperature. However, the peak in the ceramic sample containing 31.6 percent water is much larger than the peaks in coal samples containing similar water contents.

From the apparent specific heat capacity of the water in the ceramic samples, the total observed apparent enthalpy change per gram of water, $\Delta H_{\text{obs}}$, from 121 to 295 K can be determined. We propose the following model to explain these enthalpy changes. For each sample the enthalpy change is assumed to consist of two contributions: the water below 17 percent behaves as nonfreezable water with an enthalpy change of 102 cal per gram of water (the average of the experimental enthalpies for the 9.3 percent sample, which had no peak, and the smooth baselines put under the peaks in the other samples); the water above 17 percent has the enthalpy change of pure bulk water, 158 cal $g^{-1}$. The calculated enthaply change from 121 to 295 K for each sample, $\Delta H_{\text{calc}}$ (in calories per gram of water), was determined from this simple two-state model

$$\Delta H_{\text{calc}} = \frac{17}{x}(102) + \frac{x - 17}{x}(158) \qquad (1)$$

where $x$ is the percent total water. For each sample, $\Delta H_{\text{obs}}$ is in good agreement with $\Delta H_{\text{calc}}$: $x = 9.3$, $\Delta H_{\text{calc}} = 102$, $\Delta H_{\text{obs}} = 104$; $x = 18.6$, $\Delta H_{\text{calc}} = 106$, $\Delta H_{\text{obs}} = 107$; $x = 24.1$, $\Delta H_{\text{calc}} = 118$, $\Delta H_{\text{obs}} = 114$; $x = 31.6$ (*8*), $\Delta H_{\text{calc}} = 128$, $\Delta H_{\text{obs}} = 131$. Although this simple model is admittedly dependent upon a variety of assumptions that are open to question, its apparent agreement with the observed results is intriguing. In particular, the agreement tentatively supports a simple two-state description of the water in the porous ceramic and implies that the initial nonfreezable water remains nonfreezable, even in the presence of additional freezable water.

Furthermore, using the known surface area of the ceramic, 316 $m^2 g^{-1}$, and the diameter of a water molecule (*9*), 2.3 to 2.9 Å, we calculate the surface coverage that would produce the threshold value of 17 percent water. The result, depending on the space followed between the adsorbed molecules, falls in the range of one to two monolayers. This supports our original hypothesis that internal surface adsorption is a mechanism for producing nonfreezable water.

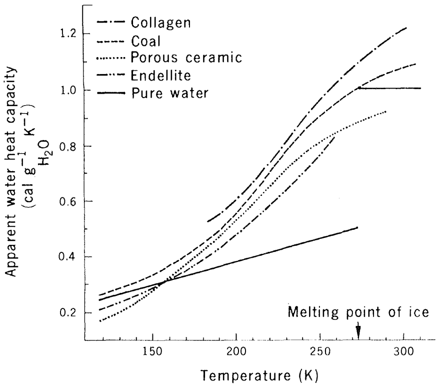

Fig. 2. Similarity of the apparent specific heat capacity of "nonfreezable" water in coal, porous ceramic, collagen (*10*), and endellite (*11*).

Whether the simple two-state model for enthalpy change applies to the water in Wyodak coal is uncertain, since it does not give consistent answers for the amount of nonfreezable water in different samples. This may be due to the fact that there is not enough freezable water in Wyodak coal to allow a coherent calculation. On the other hand, the model assumes that, on drying, all freezable water will leave the coal before any nonfreezable water does. If this is not the case, because of the chemical or physical heterogeneity of the coal, the model would not be expected to fit.

Although we found no earlier studies of this type in the coal science literature, there are parallels to the coal-water system in a variety of materials. Two significant works have appeared recently, on water in the protein collagen (*10*) and in the mineral endellite (*11*). In both of these systems, there appears to be nonfreezable water with very similar behavior to the water in our coal or ceramic samples. Figure 2 compares the specific heat capacities of the water in all four systems at levels below which any transition peak is evident (*12*). Unlike coal, however, collagen and endellite have known structures. The nonfreezable water in collagen is in channels (15 Å in diameter) in the protein, whereas the water in endellite is in interlayer spaces (10 Å wide) of the mineral's crystal. The similarity of the curves for nonfreezable water in Fig. 2 is strong support for our original hypothesis that the nonfreezable water in coal is either adsorbed on the internal surfaces or is in small pores.

There have been many investigations of the behavior of the freezable fraction of a liquid absorbed into a porous material. Litvan has shown that the first two molecular layers of water adsorbed on porous silica glass do not exhibit a phase transition, and he has made extensive studies of the additional water by calorimetry, dilatometry, thermal analysis, and vapor adsorption (*13*). He postulates that the water must move out of its original locations either to larger pores or to the outside of the material before it can freeze, and he relates this theory to the mechanisms of frost action in building materials and of cryoinjury in biological systems. Berezin *et al.* (*14*) have suggested a similar mechanism of vapor transport, to describe their results on benzene and water in silica gel, but Brun *et al.* (*15*, p. 469) have claimed that the carbon tetrachloride absorbed in porous γ-alumina undergoes its solid-liquid phase transition "inside the porous material itself without implying mass transfer." Brun *et al.* (*16*) have also suggested that the freezing behavior of an absorbed liquid, observed on cooling, can be used to determine the pore size and volume distribution of the porous material.

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## References and Notes

1. H. Gan, S. P. Nandi, P. L. Walker, Jr., *Fuel* **51**, 272 (1972).
2. R. L. Bond, M. Griffith, F. A. P. Maggs, *ibid.* **29**, 83 (1950).
3. A. D. Alekseev, R. M. Krivitskaya, B. V. Pestryakov, N. N. Serebrova, *Khim. Tverd. Topl.* **11**, 94 (1977).
4. D. J. Allardice and D. G. Evans, *Fuel* **50**, 236 (1971).
5. We use the term "percent" to mean the number of grams of water per 100 g of dried coal or ceramic. Although we use percent for simplicity, it should not be confused with true percent (by weight).
6. With careful work, we have achieved heat capacities accurate to 1 or 2 percent [see S. C. Mraw and D. F. Naas, *J. Chem. Thermodyn.* **11** (No. 6), 567 (1979)]. We used less time-consuming methods for the present research in order to investigate a large number of samples.
7. We thank M. L. Gorbaty for this suggestion.
8. Heat capacity values for the 31.6 percent sample were not measured below 220 K. Values used in the calculation were extrapolated by comparison with the other curves.
9. W. J. Moore, *Physical Chemistry* (Prentice-Hall, Englewood Cliffs, N.J., ed. 4, 1972).
10. C. A. J. Hoeve and A. S. Tata, *J. Phys. Chem.* **82**, 1660 (1978).
11. M. I. Cruz, M. Letellier, J. J. Fripiat, *J. Chem. Phys.* **69**, 2018 (1978).
12. Unfortunately, the heat capacity of water in endellite was not reported above 250 K.
13. G. G. Litvan, *Adv. Colloid Interface Sci.* **9**, 253 (1978).
14. G. I. Berezin, A. V. Kiselev, A. A. Kozlov, *J. Colloid Interface Sci.* **45**, 190 (1973).
15. M. Brun, J.-F. Quinson, B. Martinie, C. Eyraud, *J. Chim. Phys. Phys-Chim. Biol.* **75** (No. 5), 469 (1978).
16. M. Brun, A. Lallemand, J.-F. Quinson, C. Eyraud, *Thermochim. Acta* **21** (No. 1), 59 (1977).

17. We thank M. L. Gorbaty, G. D. Cody, and R. B. Stephens for helpful discussions.

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