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HIGH-PRESSURE, HIGH-TEMPERATURE THERMODYNAMIC PROPERTIES OF A COAL-DERIVED LIQUID

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ABSTRACT

Heat capacities, compressibilities and enthalpy and entropy changes of a coal-derived liquid at pressures up to 3500 bar and at temperatures up to 448 K are given. The results have been calculated using experimental measurements of thermal expansion as a function of both pressure and temperature, heat capacity as a function of temperature under atmospheric pressure, and volume as a function of pressure at a low reference temperature.

INTRODUCTION

In a previous paper [1] we reported thermal expansion data of two coal-derived liquids measured calorimetrically as a function of both pressure up to 4 kbar and temperature up to 448 K, and their volumes at 298 K as a function of pressure up to 4 kbar. As emphasized previously, these data can also be used to determine other thermodynamic properties of the liquids under investigation. This paper reports the determination of heat capacities, compressibilities, and entropy and enthalpy changes of the coal-derived liquid denoted as liquid 2 in ref. 1. Basic physicochemical characteristics of this liquid, such as density, mean boiling temperature, mean molecular weight and carbon-to-hydrogen ratio, have also been given previously [1].

HEAT CAPACITY

Computation of the heat capacity can be performed on the basis of the following thermodynamic equation [2]

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p = -VT\left(\alpha^2 + \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) \tag{1}$$

Volume, as a function of both pressure and temperature, can be obtained by the integration of thermal expansion data

$$V(T, p) = V(T_0, p)\exp\left[\int_{T_0}^{T} \alpha(T, p)\mathrm{d}T\right] \tag{2}$$

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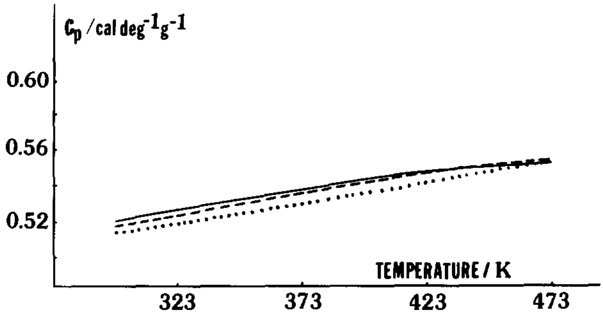

Fig. 1. Heat capacity of coal-derived liquid 1 (— —), of coal liquid 2 (····) and of hexadecane (———) as a function of temperature under normal pressure.

where $V(T_0, p)$ is the reference isotherm reported previously [1]. Introducing eqn. (2) into eqn. (1) and integrating, one can obtain the following equation for the heat capacity as a function of both pressure and temperature for which all parameters have been determined experimentally:

$$C_p(T, p) = C_p(T, p_0) - T\int_{p_0}^{p} V(T_0, p)\exp\left[\int_{T_0}^{T}\alpha(T, p)\mathrm{d}T\right]\left(\alpha^2 + \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\mathrm{d}p \tag{3}$$

where $C_p(T, p_0)$ is the heat capacity of the liquid as a function of temperature under atmospheric pressure. The $C_p(T, p_0)$ data have been collected with a classical DSC apparatus. They are presented graphically in Fig. 1, together with the data for coal-derived liquid 1 and hexadecane, these last two are given for comparison and accuracy testing. The heat capacity of liquid 2 as a function of both pressure and temperature calculated from eqn. (3) is presented in Table 1 in the form of a matrix and plotted in Fig. 2. The plots show an unusual behaviour of the two low-temperature isotherms

TABLE 1

Heat capacity C_p (cal g^{-1} K^{-1}) of coal-derived liquid 2 at different temperatures and pressures

P (bar)	T (K)				
	312.8	339.3	369.0	400.3	447.8
1	0.516	0.523	0.528	0.540	0.547
1000	1.19	0.821	0.364	0.423	0.471
1500	2.44	1.49	0.358	0.466	0.520
2000	3.42	2.14	0.486	0.557	0.619
2500	3.97	2.54	0.653	0.659	0.783
3000	4.17	2.69	0.758	0.781	0.931
3500	4.36	2.11	0.888	0.951	1.09

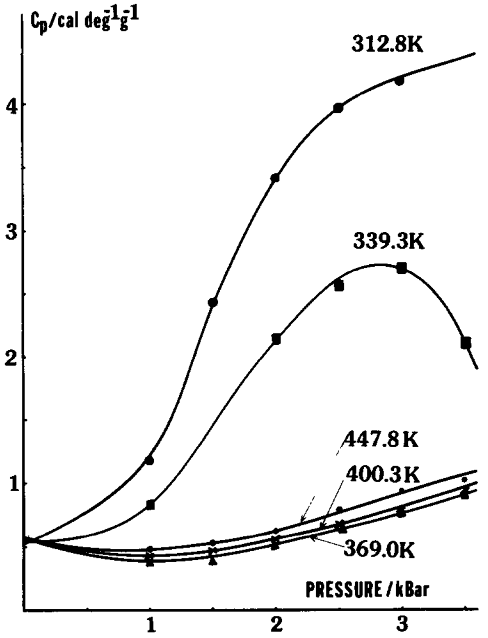

Fig. 2. Heat capacity of coal-derived liquid 2 as a function of pressure at different temperatures.

which is probably caused by the precipitation of high-boiling components. A more precise elucidation of this behaviour will require additional investigations using model coal liquids. The three higher-temperature isotherms demonstrate a behaviour similar to the pressure behaviour of pure liquids, e.g. n-hexane [3,4] or water [1,5], determined by two independent experimental techniques. The existence of a minimum in the heat capacity vs. pressure plots at fixed temperatures is thermodynamically consistent with the temperature–pressure behaviour of thermal expansion. In a recent paper [6] we attempted to explain this behaviour on the molecular level by anharmonic contributions to the heat capacity and a change in the shape of the intermolecular potential caused by the application of pressure.

ENTHALPY

The enthalpy changes caused by pressure and/or temperature variations have been calculated from the following equation

$$\Delta_{312.8}^{T}H = \int_{312.8}^{T} C_p(T, p)\,\mathrm{d}T \tag{4}$$

TABLE 2

Enthalpy changes $\Delta^{T}_{312.8}H$ (cal g^{-1}) of coal liquid 2 at different pressures and temperatures

P (bar)	T (K)			
	339.3	369.0	400.3	447.8
1	13.6	29.4	46.1	72.0
1000	26.3	44.1	56.4	75.9
1500	51.5	79.2	92.1	112.3
2000	72.8	112.2	128.6	156.6
2500	85.3	133.2	153.7	188.1
3000	89.9	141.6	165.7	206.5
3500	84.8	129.7	158.5	207.2

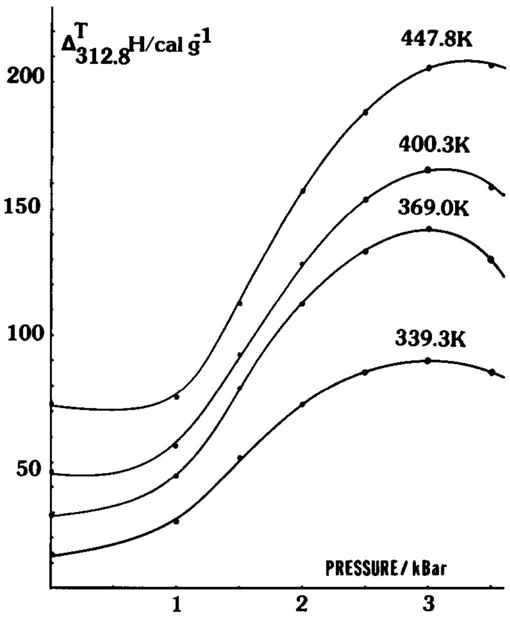

Fig. 3. Enthalpy changes $\Delta^{T}_{312.8}H$ of coal-derived liquid as a function of pressure at different temperatures.

TABLE 3

Entropy changes $\Delta^{T}_{312.8}S$ (cal K^{-1} g^{-1}) of coal-derived liquid 2 at different pressures and temperatures

P (bar)	T (K)			
	339.3	369.0	400.3	447.8
1	0.42	0.86	1.30	1.91
1000	0.82	1.33	1.65	2.11
1500	1.60	2.40	2.74	3.22
2000	2.26	3.40	3.83	4.49
2500	2.64	4.03	4.57	5.38
3000	2.79	4.28	4.91	5.87
3500	2.64	3.94	4.68	5.83

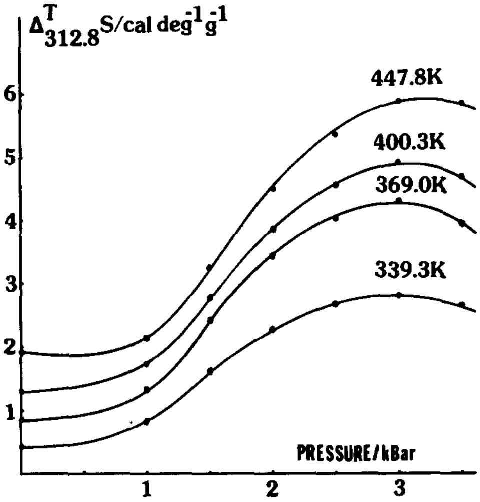

Fig. 4. Entropy changes $\Delta^{T}_{312.8}S$ of coal-derived liquid 2 as a function of pressure at different temperatures.

The calculated enthalpy changes are listed in Table 2 and their graphic presentation is given in Fig. 3.

ENTROPY

The entropy changes caused by pressure and/or temperature variations have been calculated from the following equation

$$\Delta^{T}_{312.8}S = \int_{312.8}^{T} C_p(T, p)\mathrm{d}\ln T \tag{5}$$

The calculated data of entropy changes are listed in Table 3 and their graphic presentation is given in Fig. 4.

COMPRESSIBILITY

The thermodynamic relation between the cross derivatives

$$\left(\frac{\partial \alpha}{\partial p}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_p \tag{6}$$

enables one to compute the compressibility

$$\kappa(T, p) = \kappa(T_0, p) - \int_{T_0}^{T}\left(\frac{\partial \alpha}{\partial p}\right)_T \mathrm{d}T \tag{7}$$

where $\kappa(T_0, p)$ is the compressibility along a reference isotherm. Values of

TABLE 4

Compressibility κ ($\text{bar}^{-1} \times 10^5$) of coal-derived liquid 2 at different pressures and temperatures

P (bar)	*T* (K)				
	312.8	339.3	369.0	400.3	447.8
500	3.98	4.24	4.79	5.46	6.68
1000	3.53	3.70	4.08	4.50	5.20
1500	3.07	3.29	3.51	3.81	4.30
2000	2.46	2.76	3.00	3.21	3.54
2500	2.46	2.73	2.91	3.07	3.33
3000	2.25	2.44	2.55	2.67	2.89
3500	2.09	2.23	2.24	2.38	2.55

compressibility computed from eqn. (4) with the use of previously reported data [1] are listed in Table 4 with a graphical presentation in Fig. 5. These plots show typical compressibility behaviour; the changes occurring in the liquid under pressure at lower temperatures, visible on both the thermal expansion and heat capacity isotherms, are not detectable on the compressibility plots.

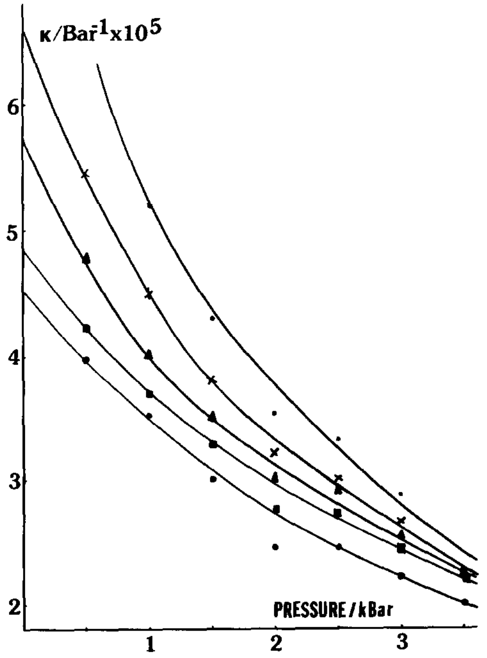

Fig. 5. Compressibility of coal-derived liquid 2 as a function of pressure at different temperatures.

CONCLUSIONS

The thermodynamic data of a coal-derived liquid presented in this paper show how one can get a complete thermodynamic description of such a liquid over very large pressure and temperature ranges. To this aim one needs two types of calorimetric measurements: (1) thermal expansion as a function of both pressure and temperature, (2) heat capacity as a function of temperature at a lower reference pressure, and (3) a measurement of volume as a function of pressure at a lower reference temperature. The precision of the primary measurements is not completely reproduced in the calculated thermodynamic quantities, but the computation uses only integration and first-order differentiation, thus not degrading the precision as much as with double differentiation of volumetric data. The quality of the graphic presentations of the data is satisfactory. It is estimated that the accuracy of the data presented in this paper is of the order of a few per cent over the entire pressure and temperature ranges.

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