

Liquid Association and the Critical Temperature

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difficult to estimate. It resides wholly in the error in determination of the parameter u_2 . The best estimate (on the basis of intensity computations for various values of u_2) is that the OHO distance in boehmite is $2.47 \pm 0.07\text{\AA}$. Therefore even assuming maximum error, the hydrogen bridge distance for boehmite is only equal to the shortest previously known; namely, 2.54\AA for the tetragonal crystal KH_2PO_4 .¹⁶

The OHO bonds are relatively weak in character and hence are easily sheared. This accounts for the apparent cleavage of boehmite and its existence in orthorhombic plates, such as are shown in the electron micrograph of Sample *B* (see Fig. 2). This factor may also account for the greater half-width of the (020) reflection which was consistently observed on a large number of preparations of synthetic boehmite. The weak hydrogen bonds would permit distortion of the "b" axis direction and this crystalline distortion could account for the varying values of line breadth observed from sample to sample and from diffraction line to diffraction line. Aside from the factor of distortion, the tendency for the crystal

TABLE VI. Interatomic distances in boehmite.

Atom	In the same octahedron	In other octahedra In same layer	In other octahedra In next layer
Al	2O _{II} at 1.87\AA 2O _I at 2.06\AA 2O _I at 1.93\AA	2Al at 2.86\AA 2Al at 3.69\AA	
O _I	2O _I at 2.86\AA 4O _{II} at 2.94\AA 4O _I at 2.50\AA 1O _{II} at 2.69\AA		
O _{II}	2O _{II} at 2.86\AA 1O _I at 2.69\AA 4O _I at 2.94\AA		2O _I at 4.66\AA 4O _{II} at 3.78\AA 2O _{II} at 2.47\AA

to occur in the form of thin crystalline plates would also account for the increased breadth of the (020) reflection.

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A THEORETICAL basis for a critical region instead of a critical point is furnished by Mayer who has calculated on a statistical mechanical basis¹ the general form of the pressure volume curve for a number of temperatures in the region of the critical temperature. The type of P - V diagram obtained for a pure liquid-saturated vapor system is such that two critical or characteristic temperatures, T_m and T_c , may exist. T_m is interpreted to correspond to the temperature at which the meniscus disappears and the surface tension becomes zero. This temperature is lower than the true critical temperature, T_c , the temperature at which the

P - V curve has an inflection point for only one volume. At and above T_c , no differences exist between gas and liquid. Below T_m , a definite meniscus exists and the condensed phase has a surface tension. Between T_m and T_c , the P - V curve is horizontal over a finite volume and no surface tension exists. The magnitude of the temperature interval between T_m and T_c has not been theoretically calculated. This interval according to the Van der Waals equation is, of course, zero.

Since a liquid possesses a more definite structure (order) than a gas,² this structure may be regarded as persistent beyond T_m and not com-

¹ Mayer and Harrison, *J. Chem. Phys.* **6**, 87 (1938); Harrison and Mayer, *ibid.*, 101.

² Stewart, *Chem. Rev.* **6**, 483 (1929); *Rev. Mod. Phys.*, **2** 116 (1930).

TABLE I. Critical temperatures determined from meniscus disappearance and from P - V isotherms.

System	T_m , stationary bomb	T_m , shaken bomb	Ref.	T_c	Ref.
Carbon dioxide	30.96°C		a	31.04°C	b
Ethane		32.23°C	c	32.27	d
Propane	96.85		e	96.81	d
Butane	152.2		f	152.01	d
Pentane	197.2		g	197	h
Ethylene		9.21	i	9.90	j
Propylene	91.4		k	91.4	k
	91.9		m	91.9	l
				96.4	n
Methyl ether	126.9		o	138	p
Ethyl ether	192.3		q	194.6	r
Methyl alcohol	240.6		q	not determined	
Ethyl alcohol	241.7		q		
	243.6		s	243.6	s
Water	374.2		t	380	u

^a Kennedy, J. Am. Chem. Soc. 51, 1360 (1929).

^b Michaels, Blaisse, and Michaels, Proc. Roy. Soc. (London) 160A, 358 (1937).

^c See reference 3 in text.

^d Beattie *et al.*, J. Am. Chem. Soc. 59, 1589 (1937); 61, 24, 924 (1939).

^e Deschner and Brown, Ind. Eng. Chem. 32, 836 (1940).

^f Kay, Ind. Eng. Chem. 32, 358 (1940).

^g Young, J. Chem. Soc. (London) 71, 446 (1897).

^h Sage and Lacey, Ind. Eng. Chem. 34, 730 (1942).

ⁱ See reference 4 in text.

^j McIntosh and Maass, Can. J. Research 16B, 289 (1938); Dacey, McIntosh, and Maass, *ibid.* 17B, 206 (1939); McIntosh, Dacey, and Maass, *ibid.*, 241.

^k Vaughan and Graves, Ind. Eng. Chem. 32, 1252 (1940).

^l Souders, Ind. Eng. Chem. 32, 1252 (1940).

^m Winkler and Maass, Can. J. Research 9, 613 (1933).

ⁿ This temperature is the temperature at which the dielectric constant of the vapor equals that of the liquid. Marsden and Maass, Can. J. Research 13B, 296 (1935).

^o Tapp, Steacie and Maass, Can. J. Research 9, 217 (1933).

^p Approximate extrapolation from the measured (17) difference in densities of liquid and saturated vapor plotted as a function of temperature to the temperature at which density difference is zero.

^q Fisher and Reichel, Mikrochemie V. Mikrophim. Acta 31, 102 (1943).

^r Schroer, Zeits. f. physik. Chemie. 140, 381 (1929).

^s Ramsay and Young, Phil. Trans. Roy. Soc. (London) A177, 123 (1886).

^t Schroer, Zeits. f. physik. Chemie. 129, 79 (1927); Callendar, Proc. Roy. Soc. (London) A120, 460 (1928); Khitarov and Ivanov, Zentr. Mineral. Geol. 1936A, 46.

^u This temperature is the temperature at which the density of the liquid equals that of its saturated vapor. Callendar, reference t.

pletely broken until T_c is reached, at which temperature the complete disorder characteristic of the gas state is finally attained. One would thus expect associated liquids to have

larger intervals between T_m and T_c than the non-associated liquids. Data given in Table I show that carbon dioxide and the saturated lower hydrocarbons, typical unassociated liquids, possess, within the errors of the data, zero intervals or intervals too small for experimental detection. The more strongly associated lower ethers, alcohols, and water appear to have measurable intervals. A quantitative relationship between the degree of association and magnitude of the interval cannot be deduced, however, from the presently available data. Also, the physical significance of the T_m measurements made in stationary bombs is seriously questioned by the discovery that shaking the bomb vigorously has a profound effect not only upon the temperature at which the meniscus disappears but also increases greatly the precision with which such measurements may be made.³ Shaking the bomb causes the meniscus to disappear at a lower temperature. Thus with ethylene, T_m is 9.50°C in a stationary bomb and 9.21°±0.015°C in a shaken bomb.⁴ It is thus probable that the interval between T_m and T_c is small but also real for non-associated liquids.

Temperatures given as T_c in the table have been determined, unless otherwise noted in the references, from isotherms carefully measured through the critical region at small temperature intervals, as the temperature at which the tangent to the inflection point for an isotherm is horizontal.

³ Mason, Naldrett, and Maass, Can. J. Research 18B, 103 (1940).

⁴ Naldrett and Maass, Can. J. Research 18B, 118 (1940).