

conclusion ascribed to us by Subramanian,² namely, that the hydrate, if a clathrate, has a low guest to host ratio. On the contrary, the stability of this hydrate under pressure, the electrically conductive properties of solution permeated solids⁸ and of aqueous tetraalkylammonium halide solutions⁴ under pressure, and the partial molar volumes of the tetraalkylammonium cations in aqueous solution⁵ all point to the conclusion that hydrophobic hydration such as that enveloping the *n*-tetrabutylammonium cation represents a low specific volume type of water structure. This in turn implies that, in order to achieve high density, if the structure is of a clathrate type, then the cages in the host structure surrounding the cations must be filled with one or more water molecules. Also the structure cannot be that of the ordinary hexagonal ice-I, a high specific volume form.

If the structure is not ice-like, there is no reason to expect it to facilitate ice formation in the bulk solution. Furthermore the nucleation of supercooled water is a rate, not an equilibrium phenomenon, and examination of Bridgman's phase diagram for water⁶ shows that there are no stable forms in the temperature and pressure range of the experiments in question.

Thus we feel that some explanation other than the nucleation of ice-I must be proposed in explanation of Evans' results,^{7,8} but we most heartily agree that, in view of the biological significance of the structure involved, further studies, such as X-ray examination, of these structures should prove to be worthwhile.

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The Pressure at the Maximum in Adsorption Isotherms at High Pressures

Sir: The maximum in adsorption isotherms at high pressures and above the critical temperature of the adsorbate has been observed in all cases where the measurements have been carried out to sufficiently high pressures, *e.g.*, CH₄ and H₂ on charcoal,¹ CO₂, N₂O, and SiF₄ on charcoal,² CH₄ on coal,³⁻⁶ A and N₂ on active carbon,⁷ N₂ and CO on alumina,^{8,9} and CH₄ and C₂H₄ on silica gel.¹⁰ According to the ordinary definition of

Table I: Comparison of $\tau^2 p_c$ with p_{max} from High-Pressure Adsorption Data

Gas	Adsorbent	Temp, °C	$\tau^2 p_c$, atm	p_{max} , atm	Ref
A. Adsorbents of Second Structural Type					
CH ₄	Coal	25	112	100-115	3-6
N ₂	Alumina	-0.76	156	154	8
		25.1	188	200	
		50.0	220	227	
		74.9	256	260	
		99.7	293	300	
CO	Alumina	-0.77	142	146	9
		25.0	170	180	
		50.0	200	216	
CH ₄	Silica gel	0	94	96	10
		-20	81	82	
		-40	68	63	
C ₂ H ₄	Silica gel	25	56	52	10
CO ₂	Porous plug of lampblack	32	73.6	74	13
B. Adsorbents of First Structural Type					
CH ₄	Charcoal	25	112	85	1
		50	131	100	
		100	175	124	
		180	258	132	
H ₂	Charcoal	25	1169	80	1
CO ₂	Coconut shell charcoal	35	75	44	2
		50	82	54	
		100	110	85	
N ₂ O	Coconut shell charcoal	60	83	52	2
		100	104	85	
SiF ₄	Coconut shell charcoal	25	60	19	2
		50	71	28	
		100	94	41	
N ₂	Active carbon	-76	82	60	7
		-25	130	80	
		0	157	95	
		20	181	120	
A	Active carbon	-76	85	60	7
		-25	134	95	
		0	163	105	
CH ₄	Molecular sieve (Ca-substituted)	20	187	120	
		-78	48	32	14
N ₂	Molecular sieve (Ca-substituted)	-78	80	57	14

adsorption, the amount adsorbed is the *excess* material present in the pores and on the surface of the adsorbent over and above that corresponding to the density of the

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gas in the gas phase at that temperature and pressure. With increasing pressure this excess or differential adsorption soon reaches a maximum. As the pressure is increased further, the density of the gas phase (ρ_g) gradually approaches that of the adsorbed phase (ρ_a). This can continue till $\rho_g = \rho_a$ and the amount adsorbed, measured experimentally and calculated according to the above definition, must become zero.¹¹ Hence the high-pressure adsorption isotherms must exhibit a maximum even by elementary considerations.

In the application of Polanyi's potential theory of adsorption for gases above their critical temperatures, Dubinin¹² has shown that the filled volumes of adsorption space can be expressed as

$$W = ab \quad (1)$$

where a is the amount adsorbed and b is the constant in the van der Waals equation, while the adsorption potential ϵ can be calculated from

$$\epsilon = 2.30RT \log (\tau^2 p_c / p) \quad (2)$$

where $\tau = T/T_c$ is the reduced temperature and p_c is the critical pressure of the adsorbate.

Application of eq 2 to high-pressure adsorption data shows that in many cases a is maximum when $\tau^2 p_c = p$ and hence $\epsilon = 0$. The equilibrium pressure p_{\max} at which the adsorption isotherm at any temperature exhibits a maximum can thus be calculated from critical temperature and pressure of the gas; it does not seem to depend on the type or nature of the adsorbent surface. In Table IA^{13,14} the values of $\tau^2 p_c$ are compared with literature data on pressure p_{\max} at which experimental adsorption isotherms exhibit a maximum. The agreement between the two is quite satisfactory especially in view of the numerous inaccuracies and uncertainties in usual high-pressure adsorption measurements,¹⁵ and the added difficulty of locating p_{\max} in cases where the maximum in the isotherm is not sharp but is rather flattened over a pressure range of 10–30 atm.

Adsorbents with extremely small micropores of molecular dimensions, *e.g.*, charcoal, active carbon of high surface area, and molecular sieves, exhibit a dif-

ferent behavior (Table IB). In their case p_{\max} is always much lower than $\tau^2 p_c$, the ratio of the two often being 0.6–0.8. These adsorbents for which the effect of increasing adsorption potentials as a result of overlapping of the fields of opposite walls of the pore is prominent, are designated by Dubinin¹² as adsorbents of the first structural type. In adsorbents with larger pores this overlapping of fields does not take place, and these are referred to as adsorbents of the second structural type. It is for this second type, given in Table IA, that the relation $\tau^2 p_c = p_{\max}$ holds good, although eq 2 has been found to be equally applicable¹² to adsorbents of both structural types.

A consequence of the relation $\tau^2 p_c = p_{\max}$ will be that $p_c = p_{\max}$ when $T = T_c$. Thus p_{\max} seems to have the role of a critical pressure for the gas adsorbed above its critical temperature, as if above this pressure the adsorbed gas forms a continuous film or "condensed" layer. An adsorption isotherm measured at the critical temperature of a gas should show a maximum at the critical pressure. The closest approach to critical temperature can be seen in the measurement of adsorption of CO₂ on a porous plug of lampblack¹³ at 32° ($T_c = 31^\circ$) where a maximum in the isotherm is observed at 74 atm, which agrees very well with the calculated value $\tau^2 p_c = 73.6$ atm and the critical pressure of CO₂ of 73 atm.

(11) In practice, this has not been observed for any rigid noncompressible adsorbent. The behavior of the adsorption isotherms at very high pressures is quite different.^{8,9}

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