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Some Calculated Properties of Tritium*

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December 16, 1949

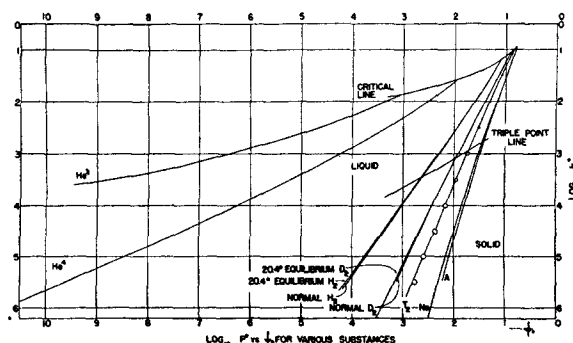
APPPLICATION of quantum theory to the condensed permanent gases by J. De Boer¹ resulted in a modified law of corresponding states in terms of reduced P , V , and T variables, plus a parameter Λ^* . On the basis of this theory, De Boer and Lunbeck² predicted a number of properties of the helium isotope of mass three. Several of these properties, including the vapor pressure, were subsequently determined,³ and the experimental results agree quite closely with those predicted by De Boer and Lunbeck.² In the present paper, De Boer's theory is applied to tritium. Since the prediction of the He^3 properties involved a graphical extrapolation, whereas the prediction of the tritium properties involves an interpolation, it is hoped that an even closer agreement between theoretical and experimental results will be observed when data on tritium become available.

In Table I, the constants pertinent to the calculation are collected. Corresponding values for H_2 and D_2 are included for comparison where $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$, k is Boltzmann's constant, N is Avogadro's number, and σ and ϵ are characteristic quantities of the intermolecular field defined by the potential function representing the interaction between two molecules of the gas, viz:

$$\varphi(r) = \epsilon \left(\frac{4}{(r/\sigma)^{12}} - \frac{4}{(r/\sigma)^6} \right).$$

TABLE I.

	Λ^*	ϵ/k (°K)	N/σ^3 (cm ³ /mol)	ϵ/σ^3 (atmos.)	ϵ (10 ⁻¹⁶ ergs)	σ (AU)
H_2	1.73	37.0	15.12	203	50.75	2.92
D_2	1.22	37.0	15.12	203	50.75	2.92
T_2	1.00	37.0	15.12	203	50.75	2.92

FIG. 1. $\text{Log}_{10} P^*$ vs $1/T^*$ for various substances

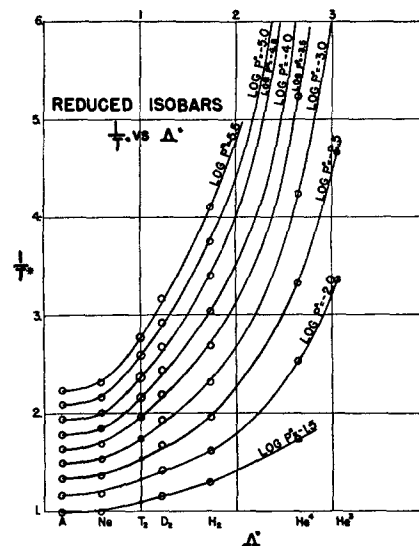
Thus for $r = \sigma$, $\varphi(r) = 0$; and $\epsilon = \varphi(r)$

for the value of r satisfying the equation $\partial \varphi / \partial r = 0$.

The variables of the reduced equation of state are defined in terms of "molecular" units as follows:

$$\begin{aligned} P^* &= P\sigma^3/\epsilon, \\ V^* &= V/N\sigma^3, \\ T^* &= kT/\epsilon. \end{aligned}$$

The vapor pressures of tritium may be obtained from the theory by plotting experimental $\text{log } P^*$ vs. $1/T^*$ curves for the light elements as in Fig. 1; from this, a series of reduced isobars is constructed, viz., Fig. 2. From the latter graph, the vapor pressure vs. temperature curve (Fig. 1 or Fig. 3) for tritium is immediately

FIG. 2. Reduced isobars $1/T^*$ vs Λ^* .

obtainable. The results are tabulated in Table II, which also includes calculated data for deuterium above the boiling point.

Using the modified law of corresponding states, a plot of a given reduced property vs. Λ^* permits a prediction of that property for other substances with different Λ^* 's. In Table III, the critical

TABLE II.*

Tritium		P (mm Hg)
T (°K)		
12.2		0.154
13.3		0.488
14.3		1.54
15.6		4.88
17.1		15.4
18.9		48.8
20.2		95.1
21.3		154.4
21.58		181.2
22.2		233.8
23.0		322.6
24.2		488.0
25.0		643.5
26.0		867.3
27.0		1162.0
27.9		1544.0
33.9		4880.0
Deuterium (Above boiling point)		P (mm Hg)
T (°K)		
24.2		919.5
24.5		1007.5
25.0		1143.0
25.5		1304.0
26.0		1462.0

* Estimated uncertainty in the various temperatures associated with each vapor pressure: $\pm 0.3^\circ\text{K}$

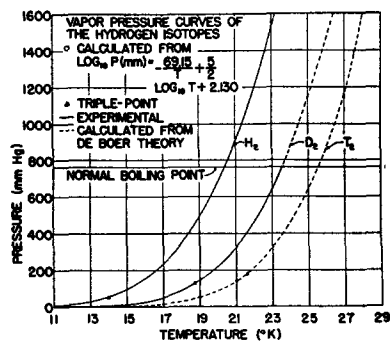


FIG. 3 Vapor-pressure curves of the hydrogen isotopes

TABLE III.

Critical constants.					
	T_c (°K)	V_c (cm ³ /mole)	P_c (atmos.)		
H ₂	33.19†	66.95†	12.98†		
D ₂	41.1*	56.7*	18.9*		
T ₂	43.7*	53.7*	20.8*		
Triple-point constants					
	T_{tr} (°K)	V_{tr} (liq.) (cm ³ /mole)	V_{tr} (solid) (cm ³ /mole)	P_{tr} (atmos.)	P_{tr} (mm Hg)
H ₂	13.96†	26.10†	23.25†	0.071†	53.7†
D ₂	18.72†	23.14†	20.48†	0.168†	128.0†
T ₂	21.65*	21.90*	19.24*	0.248*	188.0*
Molecular constants					
	θ (°K)	V_0 (cm ³ /mole)	U_0 (cal./mole)		
H ₂	105†	22.57†	183†		
D ₂	97†	19.49†	276†		
T ₂	87*	18.6*	316*		

* Calculated by De Boer's Theory (see reference 1 of text)

† From "Compilation of thermal properties of hydrogen in its various isotopic and other para modifications," Woolley, Scott, and Brickwedde, J. Research Nat. Bur. of Stand. 41, 379 (1948).

‡ Scott, Brickwedde, Urey, and Wahl, J. Chem. Phys. 2, 454 (1934).

constants, triple-point constants, and several molecular constants for D₂ and T₂ so calculated are presented for comparison with corresponding experimental data for H₂.

The value of U_0 can be inserted into the theoretical equation for the vapor pressure, viz:

$$\log_{10} P = U_0 / (2.303RT) + 5/2 \log_{10} T + \text{const.},$$

where the contribution of the thermal motion is neglected. This equation should be fairly accurate over a limited temperature range, especially at low temperatures. By choosing the constant equal to 2.130, an analytical representation of the calculated vapor pressures in mm Hg, of solid tritium previously presented in Table II is obtained.

* This document is based on work performed at Los Alamos Scientific Laboratory of the University of California under AEC Contract W-7405-Eng-36.

† J. De Boer, Physica XIV, 139 (1948).

‡ J. De Boer and Lunbeck, Physica XIV, 1101 (1948).

§ Sydoriak, Grilly, and Hammel, Phys. Rev. 75, 303 (1949)

The Diffusion of AgNO₃ and Ag⁺ Ion in Aqueous Solution

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December 10, 1949

ADAMSON and co-workers have recently published^{1,2} curves showing that at low concentrations the observed self-diffusion coefficients of Na⁺ ion in aqueous solution are appreciably greater than the theoretical. In their experiments the diffusion

volume was defined by a porous diaphragm of sintered glass and a radioactive isotope was used as a tracer for sodium. They suggest that this increased diffusion is due to the enhanced mobility of Na⁺ ion on the glass walls of the microscopic channels in the porous disk and point out that a similar effect has been observed in the conductance of alkali metal salt solutions.³ The object of this note is to present some data obtained in this laboratory on the diffusion of AgNO₃ and Ag⁺ ion which do not exhibit the effect observed by Adamson.

These measurements were made at 25° in McBain-Northrup diffusion cells⁴ calibrated with 0.1N KCl as outlined by Gordon.⁵ The amount of AgNO₃ diffusing from solutions of various concentrations into water (bulk-diffusion) was determined by titration with standard KSCN solutions. At the lowest concentrations radioactive silver (Ag¹¹⁰, half-life 225 days) was used as an indicator. The diffusion of Ag⁺ ions between AgNO₃ solutions of identical concentration (self-diffusion) was followed with the same radioactive isotope. All counting was done on aliquots with an end window G-M tube. Except for several self-diffusion experiments referred to later, the only stirring was that due to difference in density.

The results of these measurements are shown in Figs. 1 and 2. The former refers to bulk-diffusion and the latter to self-diffusion. The points represent experimental data. The curve in Fig. 1 is drawn through values calculated from the Onsager-Fuoss Equation⁶ for a 1:1 electrolyte at 25°, viz.,

$$D(\text{cm}^2/\text{sec.}) = 2RT \left(\frac{\bar{M}}{c} \right) \left(1 + \frac{c \partial \ln \gamma}{\partial c} \right) 10^8, \quad (1)$$

where

$$\frac{\bar{M}}{c} = \left(1.0748 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0}{\Lambda^0} \right) - \left(\frac{[\lambda_1^0 - \lambda_2^0]^2}{2[\Lambda^0]^2} \right) \frac{3.1322 \times 10^{-19}}{\eta_0 (DT)^{\frac{1}{2}}} \times \frac{(\Gamma)^{\frac{1}{2}}}{(1 + \kappa a)} + \left(\frac{9.304 \times 10^{-13}}{\eta_0 (DT)^2} c \phi(\kappa a) \right).$$

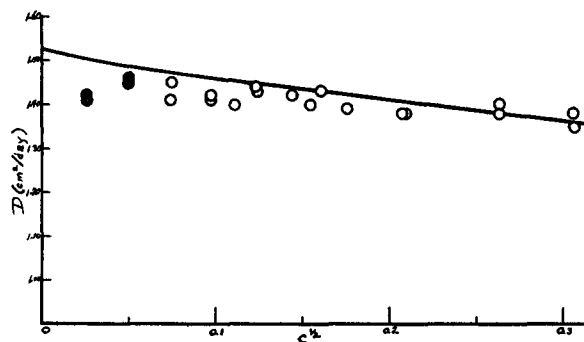


FIG. 1 Diffusion constants of AgNO₃ at 25°. The points represent experimental results. Filled circles are runs with radioactive silver. The curve is that of Eq. (1).

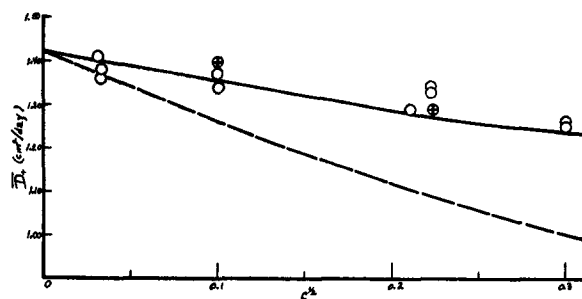


FIG. 2 Diffusion constants of Ag⁺ at 25°. The points represent experimental results. Circles with crosses are runs with mechanical stirring. The lower curve is that of Eq. (2). The upper curve is that of Eq. (3).