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HYDROGEN VAPOR PRESSURES FROM 4 TO 30 K: A REVIEW

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Contents

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Abstract

In this report, we review the following properties for the hydrogens from 4 to 30 K: liquid-gas and solid-gas vapor pressures, triple-point values, virial coefficients, liquid and solid densities, and heats of transformation. We have correlated these properties with as much consistency as the data allow. Empirical equations are given for virial coefficients and densities.

Clausius-Clapeyron equations relate vapor pressure and temperature with the other properties. Data are frequently available with H_2 and D_2 and are sometimes available for HD and T_2. We have, therefore, estimated HT and DT values to complete the set. We have also reviewed work on binary H-D mixtures and have estimated the expected behavior for H-T and D-T systems.

Introduction

The current research programs in hydrogen fusion (e.g., magnetic confinement, electron beams, heavy ions, plasma focus, and lasers) all use a D_2-DT-T_2 mixture as thermonuclear fuel. Most of these programs plan eventually to use the D-T in cryogenic conditions, either for cryopumping, tritium recovery, or fuel pellet manufacture. Therefore, we have embarked on a series of review and extrapolation reports in an attempt to provide information on the physical and chemical properties of heavy hydrogen.[1-7] In this paper, we consider the saturated-vapor pressure of the hydrogens from 4.2 to 30 K.

The vapor pressure along the solid-gas and liquid-gas phase boundaries is perhaps the most basic property of cryogenic hydrogen. It is certainly the most measured property and a staggering amount of information exists. Much of this has been summarized in recent cryogenic hydrogen surveys.[8,9]

However, the literature on vapor pressure is quite confusing. Even the better reviews have made no attempt to correlate the data throughout the isotopes or across the triple point from liquid to solid. In addition, much of the data in the reviews are obsolete; scattered errors propagate down through the years. The most recent papers containing the best data are written in stark outline, presumably for a narrow and already

well-informed audience. To the outsider, however, the field appears chaotic; in this report, we shall try to bring some order to this chaos.

The Clausius-Clapeyron Equation

The saturated-vapor pressure is usually given some theoretical substance with the Clausius-Clapeyron equation. This equates the free energy, G, of two phases in equilibrium (e.g., liquid and gas[10]) for a pure component;

$$\left(\frac{\partial G}{\partial P^\circ}\right)_T dP^\circ + \left(\frac{\partial G}{\partial T}\right)_{P^\circ} dT \Bigg|_\ell$$
$$= \left(\frac{\partial G}{\partial P^\circ}\right)_T dP^\circ + \left(\frac{\partial G}{\partial T}\right)_{P^\circ} dT \Bigg|_g , \qquad (1)$$

where P° is the pressure, T is the temperature, and the letters ℓ and g denote liquid and gas. We can now use the thermodynamic identities,

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \qquad (2)$$

and

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \qquad (3)$$

where V is the volume and S is the entropy. From this we obtain

$$\frac{dP^\circ}{dT} = \frac{S_g - S_\ell}{V_g - V_\ell} = \frac{H_v}{T(V_g - V_\ell)} , \qquad (4)$$

where the entropy difference is converted into the heat of vaporization, H_v, divided by the temperature. The subscripts g and ℓ again denote gas and liquid. We use the gas equation to substitute for the gas volume, V_g, and obtain,

$$\frac{dP^\circ}{dT} = \frac{P^\circ H_v}{ZRT^2 \left(1 - \frac{V_\ell}{V_g}\right)} , \qquad (5)$$

where Z is the compressibility and R is the gas constant. Inverting the volumes to densities, we find

$$\frac{d\ln P^\circ}{dT} = \frac{1}{Z\left(1 - \frac{\rho_g}{\rho_\ell}\right)} \frac{H_v}{RT^2} . \qquad (6)$$

If we had a perfect gas with $Z = 1$ and if $\rho_g \ll \rho_\ell$, then we could easily integrate Eq. (6) to obtain P°. Although the constants of integration must be determined experimentally, we have nevertheless related P° and H_v.

We replace the real heat of vaporization, H_v, with an "effective" one, $H_v(\text{eff})$, where

$$H_v(eff) = \frac{H_v}{Z\left(1 - \frac{\rho_g}{\rho_\ell}\right)} \,, \qquad (7)$$

and also,

$$H_v(eff) = RT^2 \frac{d\ln P}{dT} \,. \qquad (8)$$

For solids and gases in equilibrium, we use the corresponding solid density, ρ_s, and the heats of sublimation, H_s and $H_s(eff)$. We consider only the solid-liquid equilibrium and just at the triple point. Again, we may use the Clausius-Clapeyron equation with the heat of fusion, H_f.

From a practical point of view, we would like to know what $H_v(eff)$ or $H_s(eff)$ look like. We may, therefore, take experimental data points that are close together and use a variation of Eq. (8):

$$H_v(eff) = R(\overline{T})^2 \left(\frac{\ln P_2^\circ - \ln P_1^\circ}{T_2 - T_1}\right) \,. \,(9)$$

The subscripts 1 and 2 refer to the data points in a pair. The $\overline{T}$ is an average between T_1 and T_2. If ($T_2 - T_1$) is small (i.e., a Kelvin or less), a linear average may be used without great error. (After presenting our sources of data, we use Eq. (9) for the analysis.)

The Saturated Liquid-Gas Vapor Pressure

The literature is extensive and, unfortunately, most of it is obsolete. In this latter category, we include the following references from 1948 to the present: eH_2 (Refs. 11-18), nH_2 (Refs. 11, 13, 16, 19), HD (Ref. 12), and D_2 (Refs. 12, 20-22). We also include an early effort to use H_2 and nH_2 liquid-gas vapor pressures as part of the temperature scale.[23]

Selecting the best data is not easy because the differences are subtle and the background data are sparse. For eH_2 and nH_2, we select the equations listed as part of the International Practical Temperature Scale of 1968.[24] This is a strange paper, the product of the Comité International des Poids et Mesures. It is obviously the work of many people but only the communicator's name is given. However, neither details nor references are given so that it is impossible to trace its continuity with earlier work. Preceding the temperature scale work, the paper with the greatest reported detail was written in 1967 by the Dutch[18]; yet, their work does not appear to have been incorporated to

any degree into the 1968 temperature scale. Moreover, the 1975 temperature-measurement conference[25] includes even less of the work of the Dutch. The nH_2 data are not repeated and there are no vapor pressure curves. Three fixed points from 13.8 to 30.3 K are listed for eH_2; these are obviously from the 1968 temperature scale.

Returning to the 1968 temperature scale work for our hydrogen vapor pressures,[24] we conclude that, from the triple point to 23 K, the eH_2 data are valid. They are almost certainly as good as anybody else's up to 30 K because they are a close derivative of the triple point to 30-K equation of the famous 1948 Woolley review.[11] The nH_2 data, only slightly different, are listed to apply from the triple point to 30 K.[24] These, too, are similar to the old Woolley equation.[11]

For the HD data, there are only two choices available[12] and we select the 1948 data of Woolley.[11] For the D_2 data, we select the 1951 data of Grilly.[26] The later review of Prydz does not seem to us to be internally consistent.[22] For T_2, we select some 1975 data by Sherman and Grilly of Los Alamos.[27] These are partly re-measured data by Sherman and partly the readjusted 1951 data of Grilly.[26] The D_2 data are normal and the difference between these and the equilibrium form is probably less than

their accuracy. The T_2 value is listed as normal but could be equilibrium because it could have been converted during the experiment by beta-particle catalysis.[28,29]

Now, we consider the form of the effective heat of vaporization, $H_v(eff)$, as a function of temperature. We have taken the data on H_2, HD, and D_2 from the sources listed above and have processed pairs of adjacent data points according to Eq. (9). Figure 1 shows the resultant $H_v(eff)$ vs temperature curves from the triple points to 30 K.

At first glance, the form of $H_v(eff)$ appears to be linear with a quadratic component,

$$H_v(eff) = R[-B + B'T + CT^2], \quad (10)$$

where B, B', and C are constants and B is a negative number. We substitute for $H_v(eff)$ in Eq. (8) and integrate to obtain

$$\ln P° = A + \frac{B}{T} + B'\ln T + CT, \quad (11)$$

where A is the constant of integration. The term P° denotes the saturation liquid-gas, pure-component vapor pressure. This equation produces a fairly self-consistent set of constants for H_2, HD, D_2, and T_2 (see Ref. 3).

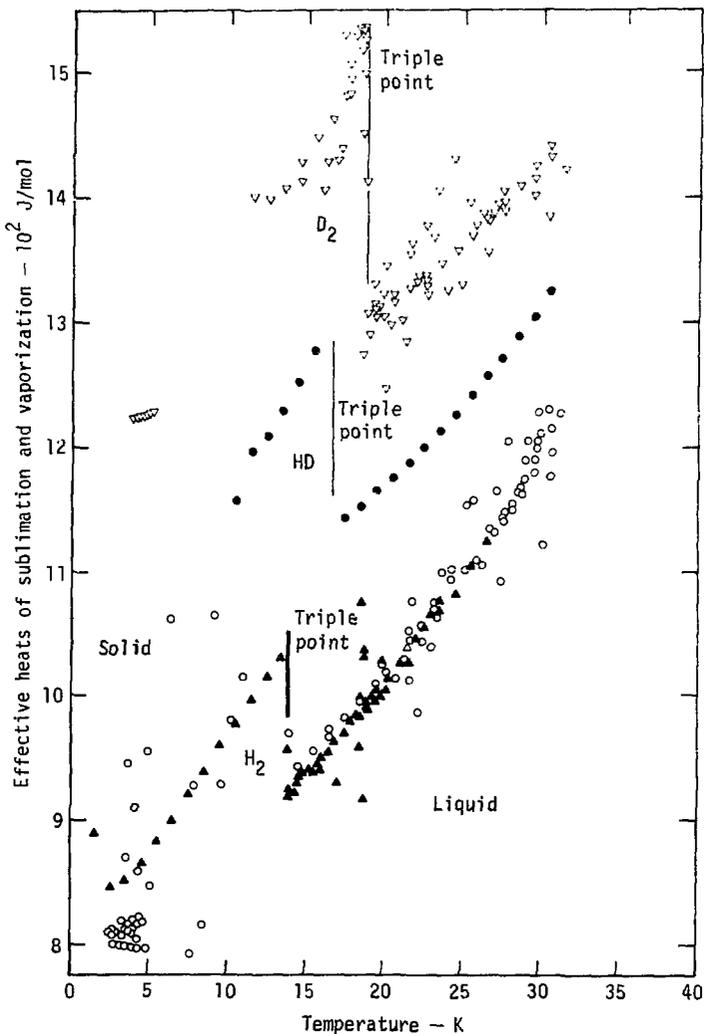However, liquid-gas vapor pressures have not been cast in the form of

-4-

Fig. 1. Effective heats of sublimation and vaporization for H_2, HD, and D_2 from many sources. Most of the strings of points contain unknown *amounts* of smoothing. Here, ▲ = eH_2, ○ = nH_2, ● = HD, and ▽ = D_2.

Eq. (11). From Woolley's 1948 review to the present, the accepted form has been

$$H_v(eff) = R[-B + CT^2 + 2DT^3] \ , (12)$$

where B, C, and D are constants and B, again, is a negative number. This integrates to

$$\ln P° = A + \frac{B}{T} + CT + DT^2 \ ; \qquad (13)$$

again, A is the constant of integration. This is the form used in all our selected references, including the 1968 temperature scale; we shall, therefore, also follow the form of Eq. (13).

The actual constants for eH_2, nH_2, HD, D_2, and T_2 are listed in Table 1. We see that the H_2, HD, D_2, and T_2

values as well as constants A and B follow a smooth sequence through the isotopes; however, C and D do not. For the present, we will have to live with these discrepancies. Sherman[27] at Los Alamos Scientific Laboratory is currently working on the H_2, D_2, and T_2 vapor pressures and hopefully he will be able to smooth the sequence of equations.

The equations of Table 1 must, of course, yield the proper triple-point temperatures and pressures. These are: eH_2 = 13.81 K and 7030 Pa (52.73 Torr),[24] nH_2 = 13.956 K and 7199 Pa (54.00 Torr),[24] HD = 16.604 K and 12400 Pa (92.8 Torr),[11] nD_2 = 18.73 K and 17140 Pa (128.6 Torr),[26] and T_2 = 20.63 K and 21600 Pa (162.0 Torr).[27] The normal boiling points at one atmosphere that fit

Table 1. Saturated liquid-gas vapor pressures of the pure-component hydrogens from the triple point to 30 K. The HT and DT pressures are estimated from the rule of the Geometric Mean.

Hydrogen Isotope	$\ln P° = A + \frac{B}{T} + CT + DT^2$				
	A(Pa)	A(Torr)	B	C	D
eH_2	15.46688	10.57411	-1.013378×10^2	5.432005×10^{-2}	-1.105632×10^{-4}
nH_2	15.52059	10.62782	-1.027498×10^2	5.338981×10^{-2}	-1.105632×10^{-4}
HD	16.52000	11.62723	-1.272167×10^2	3.405523×10^{-2}	0
nD_2	18.89988	14.00711	-1.612823×10^2	-4.861678×10^{-2}	10.56887×10^{-4}
T_2	19.11365	14.22088	-1.820038×10^2	-2.560401×10^{-2}	5.133943×10^{-4}

these equations are: $eH_2 = 20.280$ K, $nH_2 = 20.397$ K, HD = 22.13 K, $nD_2 = 23.66$ K, and $T_2 = 25.04$ K. Because these values are taken from different sources, they are not comple.ely consistent as a set. The H_2 and T_2 temperatures are set to the 1968 temperature scale; the HD and D_2 values have not and could be 0.01 K higher.

Now the problem arises: What shall we do with HT and DT? These have never been isolated in bulk quantities as pure components and their vapor pressures have never been measured. Mittelhauser and Thodos studied the question and used the following method.[30] They possessed an older version of the triple-point and normal boiling-point data for H_2, HD, D_2, and T_2. They also knew that, experimentally, HT has a lower isothermal vapor pressure than does D_2; both have the same mass.[31] They then used the rule of the Geometric Mean to obtain the vapor pressures of HT and DT. This rule applies to hydrogen species in isothermal chemical equilibrium. Thus, for the chemical reaction,

$$X_2 + Y_2 \rightleftharpoons 2XY, \qquad (14)$$

where

$$X,Y = H,D,T,$$
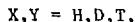
the law of the Geometric Mean proposes the pure-component vapor pressure relation,

$$P^\circ_{XY} = \sqrt{P^\circ_{X_2} \cdot P^\circ_{Y_2}} \ . \qquad (15)$$

Mittelhauser and Thodos analyzed the data of the day and decided that Eq. (15) is true to within 0.5%, although there is a 1.1% deviation at 19 K. They used Eq. (15) to find the normal boiling point of the unknown species, XY. Then they plotted a normal boiling-point vs triple-point curve and interpolated to obtain the XY triple-point temperature. At that temperature, Eq. (15) gave them the corresponding pressure. They then derived equations for HT and DT like those of Table 1. Their final estimated XY pressures were only a few tenths of a percent below those of the Geometric Mean. Their triple-point estimates were: HT = 17.62 K and 14600 Pa (109.5 Torr) and DT = 19.71 K and 19420 Pa (145.7 Torr). These values have been taken as official ever since, including by us. They have never been measured, and, as we shall see, could be somewhat in error.

We shall use the rule of the Geometric Mean to calculate HT and DT vapor pressures. This procedure is also recommended by Sherman at Los Alamos.[27] However, our accepted H_2, D_2, and T_2 vapor pressures are slightly different from those used by Mittelhauser and Thodos. If we generate vapor pressures from Table 1, we find

that the measured HD values are con-
sistently less than those calculated
from the Geometric Mean. Figure 2
shows that these results vary
from 3% deviation at the HD triple
point to 1.3% at 30 K. We do not
know if this is a real effect, and,

therefore, have not made any cor-
rection for the observed deviation.

Let us suppose that the deviation
from the Geometric Mean is a real
effect. It will probably be larger
for HT where the two masses are the
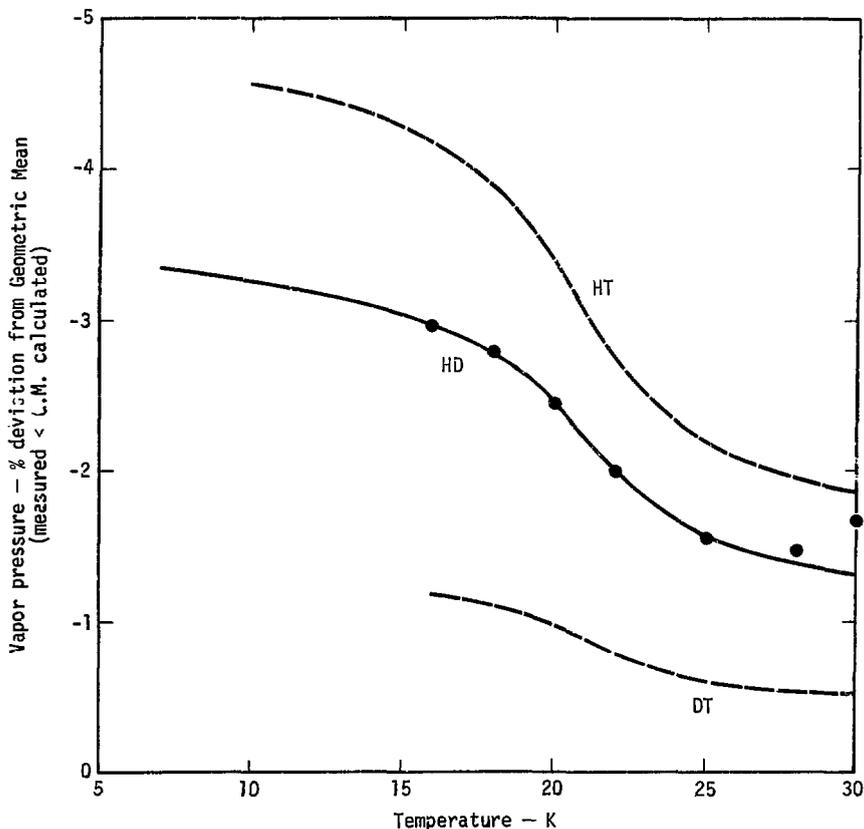most different. In Fig. 2, we have

Fig. 2. Deviation of vapor pressures from the rule of the Geometric Mean. The
HD data are taken from Table 1; other data are estimates.

estimated an HT value from the relative difference of H_2-T_2 and H_2-D_2 triple-point temperature differences. We find a possible deviation of 4.5% which could change the triple-point temperature by as much as 0.2 K. For DT, the effect will be smaller, perhaps 1% or less. This effect is important when analyzing mixtures of isotopes where nonidealities of mixing are expected to be a few percent.

Virial Coefficients

As seen in Fig. 1, there is not much data on the solid-gas vapor pressures. Good low-temperature data have appeared only in the past five years. The strings of points in Fig. 1 represent previous smoothings, the validity of which is uncertain. The data must also connect across the triple points.

To work our way from liquid to solid vapor pressures, we have collected several peripheral bits of data. The effective heat of vaporization must be converted into a real heat. This requires, first, a value for the compressibility of the gas. In this section, we derive virial coefficients for use along the saturation line.

We write the compressibility, Z, as

$$Z = 1 + B_g \rho_g + C_g \rho_g^2 , \qquad (16)$$

where ρ is the gas density, B_g is the second virial coefficient, and C_g is the third virial coefficient.

Second virial coefficients for the hydrogens have been measured for: eH_2 (Refs. 32-34), probably eH_2 (Ref. 11), nH_2 (Refs. 13,35-36), HD (Refs. 13,36), and nD_2 (Refs. 13,36). A plot of these data is shown in Fig. 3 from the triple point to 30 K. The reported difference between eH_2 and nH_2 is about 1%,[37] which is less than the scatter of the data. We have, therefore, drawn a single H_2 curve and describe these curves with the empirical equation,

$$B_g = \frac{B_0}{T^n} , \qquad (17)$$

where B_0 and n are constants. See Table 2 for a list of these constants and for estimates of HT, DT, and T_2.
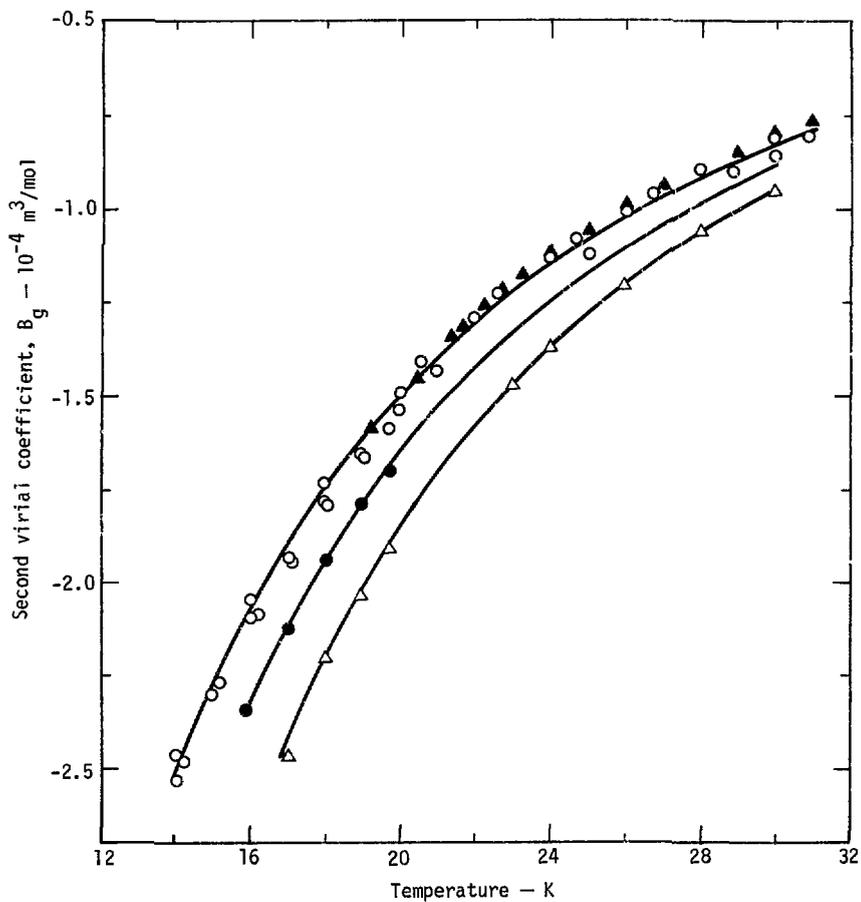
Fig. 3. Second virial coefficient data for hydrogen gas from 14 to 30 K. Here, ▲ = eH_2, o = nH_2, ● = HD, and △ = D_2.

Table 2. Second virial coefficients of the hydrogens from 14 to 30 K.
Estimates, as derived from a triple-point temperature plot, are
in parentheses.

| Hydrogen Isotope | $B_g = B_0/T^n$ | |
	B_0, 10^{-6} $m^3 \cdot K^n/mol$	n
H_2	$-11,178$	1.44
HD	$-16,170$	1.53
HT	$(-20,468)$	(1.59)
D_2	$-25,168$	1.64
DT	$(-29,310)$	(1.705)
T_2	$(-33,189)$	(1.765)

These estimates are obtained by plotting the constants vs the triple-point temperature and extrapolating.*

The third virial coefficient has been measured for eH_2 and nH_2 (Refs. 11,33,35). We do not include the Prydz review data[22] for D_2 for either virial coefficient. The third virial coefficient data are shown in Fig. 4

*This empirical method accounts for the saturation of a given property, progressing from H_2 to T_2. It also accounts for the probable differences expected (from the vapor pressure) for HT and D_2. It is, actually, almost equivalent to plotting a property vs the reduced mass of the isotope.

and the data extend in two opposite directions. The Woolley data[11] are probably the more correct. However, we need only concern ourselves with the high-temperature end of the saturation curve. We use the C_g-limiting value of 1600×10^{-12} $(m^3/mol)^2$; at 30 K, both sets of data approach this value. At lower temperatures, the saturation pressure falls so rapidly that the effect of the third virial coefficient, whatever its value, may be ignored. Thus, we have calculated the compressibility and gas density at the triple points of the hydrogens and present the data in Table 3.

Table 3. Hydrogen heats of transformation at the triple points. Estimates are in parentheses. For purposes of calculation, more digits than the true accuracy are given.

Hydrogen Isotope	T (K)	P (Torr)	ρ_g, Gas Density (mol/m³)	Z, Compress- ibility	H_v(eff) (J/mol)	$Z\left(1 - \frac{\rho}{\cdot}\right)$	H_v (J/mol)	H_f (J/mol)	H_s (J/mol)	$Z\left(1 - \frac{\rho}{s}\right)$	H_s(eff) (J/mol)
eH_2	13.810	52.73	62.213	0.9841	923.85	0.9825	907.7	117.3	1025.0	0.9822	1043.0
nH_2	13.956	54.00	63.043	0.9842	935.76	0.9826	919.5	117.2	1036.7	0.9826	1054.8
HD	16.604	92.8	91.498	0.9799	1135.78	0.9777	1110.5	159.4	1269.9	0.9779	1298.6
HT	(17.62)	(109.5)	(101.87)	(0.9782)	(1246.57)	(0.9758)	(1216.4)	(176)	(1392.4)	(0.9761)	(1426.5)
nD_2	18.731	128.6	112.67	0.9768	1314.63	0.9742	1280.7	196.6	1477.3	0.9745	1516.0
DT	(19.71)	(145.7)	(121.20)	(0.9780)	(1417.31)	(0.9753)	(1382.3)	(215)	(1597.3)	(0.9756)	(1637.3)
T_2	20.627	162.0	(128.56)	(0.9796)	(1497.59)	(0.9768)	(1462.8)	(232)	(1694.8)	(0.9771)	(1734.6)

Fig. 4. Third virial coefficient data for hydrogen gas from 14 to 30 K.
Here, ● = data from Ref. 11, □ = data from Ref. 33, and △ = data from Ref. 35.
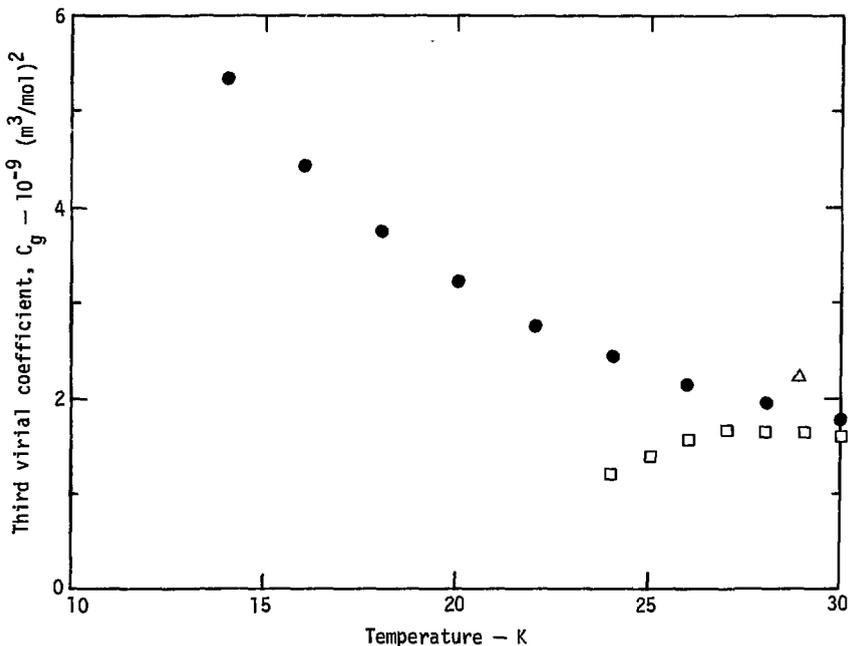
Saturated Solid and Liquid Densities

As we can see in Eq. (7), the next item needed (in addition to gas compressibility and density) to relate H_v and $H_v(eff)$ is the liquid (or solid) density. The available liquid-density data taken for H_2, HD, D_2, and T_2 (Refs. 17,22,38-40) are probably good to ±0.5%. We use the following empirical equation for the saturated liquid density, ρ_ℓ:

$$\rho_\ell = A_\ell - B_\ell T^2 , \qquad (18)$$

where A_ℓ and B_ℓ are constants for each isotope. The constants are listed in Table 4. The H_2 equation begins to deviate from ±0.5% above 26 K and is off by 5% at 30 K. The other measured isotopes should have densities to ±0.5% up to 30 K. We have interpolated for HT and DT by plotting ρ_ℓ (at constant T), A_ℓ and B_ℓ vs the triple-point temperature, and smoothing.

The density data for solid H_2, HD, D_2, and T_2 are extremely scattered. Measurements have been taken by both bulk[11,41-42] and lattice parameter techniques.[43-52] The data are shown in Fig. 5 for both the hexagonal close-packed and face-centered cubic phases. The error in the data is much larger than the 0.5% volume change

Table 4. Equations for saturated solid and liquid densities of the hydrogens. Estimates are in parentheses.

Hydrogen Isotope	SOLID $\rho_s = \rho_s^o - B_s T^3$		LIQUID $\rho_\ell = A_\ell - B_\ell T^2$	
	ρ_s^o (10^4 mol/m^3)	B_s $(\text{mol/m}^3 \cdot K^3)$	A_ℓ (10^4 mol/m^3)	B_ℓ $(\text{mol/m}^3 \cdot K^2)$
eH_2	4.434	0.5483	4.093	14.30
nH_2	4.434	0.4887	4.109	14.34
HD	4.742	0.3556	4.420	13.35
HT	4.892	0.3188	4.580	13.25
nD_2	5.072	0.2886	4.778	13.20
DT	(5.219)	(0.2642)	(4.900)	(13.36)
T_2	.5.368	0.2450	5.116	13.68
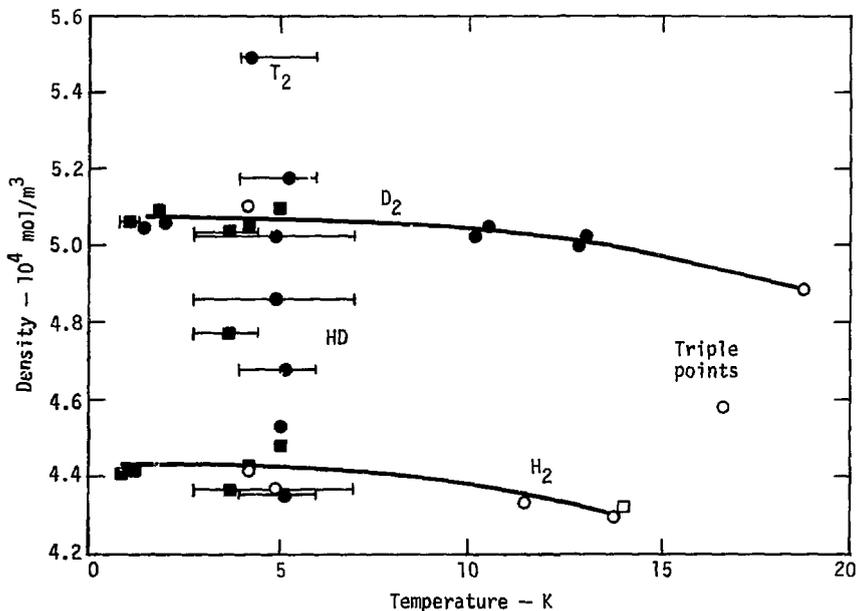
Fig. 5. Densities of the solid hydrogen isotopes as a function of temperature. The open symbols represent data obtained in bulk determinations; the solid symbols are data obtained in lattice parameter determinations.

that occurs in the crystallographic transition in the 2- to 4-K range.[53] We use another empirical equation for the saturated solid density, ρ_s:

$$\rho_s = \rho_s^o - B_s T^3 \, , \qquad (19)$$

where ρ_s^o and B_s are constants for each isotope (see Table 4). The constant ρ_s^o is the solid density at 0 K. The cubed exponent is set by the few H_2 and D_2 points in the 10- to 13-K range and, quite possibly, is not the correct power.

We have modified our opinion of the single T_2 x-ray diffraction point from that expressed in earlier papers.[3,5] This density was first reported by the Soviets as 5.36×10^4 mol/m^3 for an incorrect tetragonal structure.[43] The authors then revised it to 5.49×10^4 mol/m^3 for the correct hexagonal structure.[44] The first value is probably more correct because the second is too large to fit into any isotopic sequence. We use the first value, 5.36×10^4 mol/m^3. In any case, we

-14-

Table 5. Solid and liquid hydrogen densities at 0 K, 4.2 K, and the triple points (TP). Estimates are in parentheses.

Hydrogen Isotope	Density (10^4 mol/m^3)				Density Ratios	
	Solid 0 K	Solid 4.216 K	Solid TP	Liquid TP	4.2 K solid TP liquid	TP solid TP liquid
eH_2	(4.434)	4.430	4.290	3.820	1.1594	1.1227
nH_2	(4.434)	4.430	4.301	3.830	1.1567	1.1230
HD	(4.742)	(4.739)	4.579	4.063	(1.1664)	1.1270
HT	(4.892)	(4.890)	(4.718)	(4.179)	(1.1702)	(1.1290)
nD_2	(5.072)	5.070	4.883	4.316	1.1747	1.1314
DT	(5.219)	(5.217)	(5.017)	(4.425)	(1.1790)	(1.1337)
T_2	(5.368)	(5.366)	(5.153)	4.535	(1.1832)	(1.1362)

see that the HD and T_2 curves basically are estimates, to say nothing of the HT and DT values. We have, therefore, used the same triple-point temperature plot, fixed mainly on H_2 and D_2 values, to obtain all solid density curves. It would be desirable to have better experimental values for all these isotopes.

In Table 5, we have collected the equation-derived densities for the solid hydrogens at 0 K, 4.2 K, and at the triple point as well as for the liquid at the triple point.

Saturated Vapor Pressure of the Solid Hydrogens

We can now consider the deviation of the solid-hydrogen vapor pressures. We start with the effective heat of vaporization, $H_v(eff)$, for the liquid at the triple point. We multiply it by $Z(1 - \rho_g/\rho_\ell)$, as shown in Eq. (7), to obtain the true heat of vaporization. We now add to it the triple-point heat of fusion to find the heat of sublimation. We use the measured values of eH_2 = 117.3 J/mol,[54] nH_2 = 117.2 J/mol,[55] HD = 159.4 J/mol,[11]*

-15-

and nD_2 = 196.6 J/mol.[56] These form a good sequence when plotted empirically vs the triple-point temperatures. We, therefore, estimate other triple-point heats of fusion as: HT = 176 J/mol, DT = 215 J/mol, and T_2 = 232 J/mol. We add the heats of fusion and vaporization to obtain the *true heat of sublimation*, H_s. We then divide H_s by $Z(1 - \rho_g/\rho_s)$ to finally obtain the effective heat of sublimation, $H_s(eff)$, at the triple point. All these steps are shown for the isotopes in Table 3.

Now, we consider the form of $H_s(eff)$ as a function of temperature. Many sources from Woolley[11] have used Eq. (12) with constant D = 0; i.e., they have a quadratic temperature increase for $H_s(eff)$. Using this equation does not produce a good sequence of constants B and C for the measured isotopes H_2, HD, and D_2. The reason can be seen in Fig. 1, which plots the good solid-gas data (Refs. 11, 57, 58) with the obsolete references for eH_2 (Refs. 11,14), nH_2 (Refs. 11, 59-61), and D_2 (Refs. 11,26), We have not included the solid-T_2 data in the plot because the scatter is considerable.[26]

The good data in Fig. 1 are the two clusters about 4 K by Lee for nH_2[57] and nD_2[58]. The precision of these points is outstanding, even considering the smoothed data nearby. It

is apparent that $H_2(eff)$ is at least a straight line with temperature. It may even be concave downward (rather than concave upward like T^2). We assume $H_2(eff)$ to be a linear function of temperature, at least from 4 K to the triple point. We use Eq. (10) with constant C = 0. We find

$$H_s(eff) = R[-B + B'T] . \qquad (10a)$$

We need two points to calculate the constants B and B'. We already have the $H_s(eff)$ triple-point values. From Lee's work, we take average values of 818 J/mol at 4 K for nH_2[57] and 1224.5 J/mol at 4.5 K for nD_2.[58] The third good reference is Woolley's HD value of 1155 J/mol at 10 K.[11] Woolley's point is not of the quality of Lee's data but it is all we have for HD. For eH_2, we assume the same slope as nH_2, i.e., we expect a value of 806.2 J/mol at 4 K. For HT, DT, and T_2, we must use our usual triple-point temperature estimates. As an aid, we have Grilly's triple-point T_2 values for $H_s(eff)$ and $H_v(eff)$ of 1700 and 1500 J/mol (each ±50 J/mol, respectively).[26]

Next, we integrate Eq. (8) to obtain the pressure,

$$\ln Q° = A + \frac{B}{T} + B'\ln T . \qquad (11a)$$

-16-

Table 6. Saturated solid-gas vapor pressure of the hydrogens. Estimates are in parentheses.

Hydrogen Isotope	$\ln Q^\circ = A + \dfrac{B}{T} + B' \ln T$			
	A(Pa)	A(Torr)	B	B'
eH_2	7.416223	2.523453	-85.35199	2.903253
nH_2	7.570953	2.678183	-86.94152	2.860678
HD	8.866980	3.974210	-112.7637	2.615288
HT	(9.451935)	(4.559165)	(-126.6)	(2.552)
$nD_2^{\cdot}$	9.801089	4.908319	-136.1893	2.463629
DT	(10.32667)	(5.433901)	(-149.7)	(2.396)
T_2	(10.73882)	(5.846049)	(-160.7)	(2.3235)

Here, the term Q° denotes the saturated solid-gas, pure-component vapor pressure. The use of Γ° for liquid-gas and Q° for solid-gas will prove to be convenient when discussing hydrogen mixtures. The constant of integration, A, is obtained by substituting the triple-point temperatures and pressures. The solid-gas, vapor-pressure constants for the isotopes are listed in Table 4.

Binary Hydrogen Mixtures

All work with mixtures of hydrogens has been done with binary combinations. The first substantial work concerned the liquid-gas equilibria of H_2-HD and H_2-D_2 mixtures.[62] Some H_2-D_2 liquid-solid work was done, primarily to demonstrate the absence of a phase separation down to 8 K.[63] This was followed by considerable work by the Soviets, mostly on eH-eD_2, but partly on H_2-HD and HD-D_2.[64-67] Much of this work also involved the three-phase region.

The three-phase eH_2-eD_2 phase diagram is shown in the temperature-composition plot of Fig. 6.[63,67] The solid-line data were taken by melting a slowly-frozen sample, i.e.,
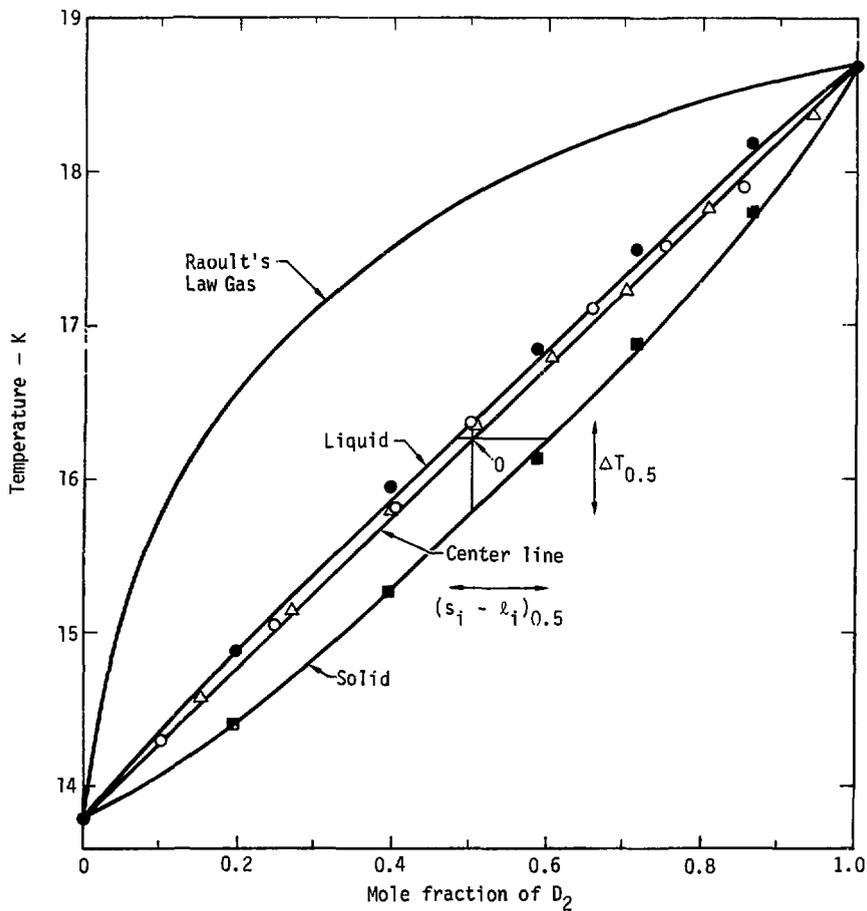
Fig. 6. Three-phase, temperature-composition diagram for eH_2-eD_2. Here, ● = corrected calorimetric freezing of liquid-gas,[63] ■ = corrected calorimetric melting of solid-gas,[63] o = calorimetric freezing,[67] and Δ = volume shrinkage upon freezing.[67]

one that fractionated away from the known input composition. Hence, the experimental values were extensively corrected to produce those shown in Fig. 6.[63] The gas line is our Raoult's-Law calculation.

In Fig. 6, the binary phase diagram resembles a "cigar" that closes at each end at the triple-point temperature, θ_i (for the ith species). We use the center line, connecting the two triple points, as our reference. For a two-phase system (e.g., liquid and gas), about half of the cigar is above and half is below this center line. We may imagine two such two-phase cigars, liquid-gas and solid-liquid (from the melting curve), overlapping almost completely. The liquid line then moves almost onto the center line. For H_2-D_2, the vertical-temperature spread of the liquid-solid cigar at 0.5 mole fraction, $\Delta T_{0.5}$, is 0.6 K with less than 20% of this above the center line. The corresponding horizontal-composition spread occurs at the temperature where the center line and the $\Delta T_{0.5}$ line intersect (point 0 in Fig. 6). This spread, $(s_i - \ell_i)_{0.5}$, for H_2-D_2 is 0.12. Similar liquid-solid cigars have been measured for H_2-HD and HD-D_2.[64] It is difficult to measure the cigar widths from the small graph, but we obtain $\Delta T_{0.5}$ values of 0.17 and 0.10 K and $(s_i - \ell_i)_{0.5}$ values of 0.052 and 0.038 for

H_2-HD and HD-D_2, respectively. If we correlate these with the difference in triple-point temperatures of the pure components, $\theta_i - \theta_j$, we find that the temperature spread increases as approximately the 2.2 power. The composition spread increases as the 1.2 to 1.5 power. All mixtures are assumed to be completely miscible.

Assuming that these mixtures are essentially ideal, we consider the following relations. Raoult's Law, generalized for three equilibrated phases with components i and j, becomes

$$\ell_i P_i^\circ = s_i Q_i^\circ \; , \tag{20}$$

and

$$g_i = \frac{P_i}{P_T^\circ} \; , \tag{21}$$

where

$$P_T^\circ = \sum_{i=1}^{6} \ell_i P_i^\circ \; . \tag{22}$$

Here, the mole fractions of component i in the gas, liquid, and solid phases are g_i, ℓ_i, and s_i. Also, P_i° is the ith pure-component, liquid-vapor pressure, derived in the last section after much effort and Q_i° is the same for the solid code. Lastly, P_i is the partial pressure of component i in the mixture and P_T° is the Raoult's Law total pressure of the

-19-

mixture. We substract $\ell_i Q_i^\circ$ from each side of Eq. (20) to obtain the composition spread at a given temperature,

$$(s_i - \ell_i) = \ell_i \left(\frac{P_i^\circ}{Q_i^\circ} - 1 \right) . \qquad (23)$$

Using the codes of this report, we have plotted $(P_i^\circ/Q_i^\circ - 1)$ as a function of $T - \theta_i$ in Fig. 7. The farther we move from the ith component's triple point, the more $(P_i^\circ/Q_i^\circ - 1)$ will diverge. For most of the isotopes, temperatures both below and above the triple points must be considered because all conceivable mixtures can exist between the lowest Q_i of 13.81 K for eH_2 and the highest Q_i of 20.63 K for T_2. This necessitates extrapolating our pure component codes into nonphysical regions with unknown error. Because both the liquid and solid codes are used over the entire three-phase hydrogen range from 13.81 to 20.63 K, the two symbols P_i° and Q_i° are used to avoid confusion.

From Fig. 7, we find that

$$\frac{P_i^\circ}{Q_i^\circ} - 1 \simeq |T - \theta_i|^{0.8-1.2} . \qquad (24)$$

The relationship is close to linear and a coefficient equal to 0.068 may be obtained from Fig. 7. If we equate the liquid line and center line, then the temperature may be found to approximate

$$T \simeq \sum_{i=1}^{6} \ell_i \theta_i , \qquad (25)$$

and

$$(s_i - \ell_i) \simeq 0.068 \, \ell_i \ell_j \, (\theta_i - \theta_j) . \quad (26)$$

For eH_2-eD_2, $(\theta_i - \theta_j)$ is 4.92 K and we calculate $(s_i - \ell_i)_{0.5}$ to be 0.084, compared to the measured value of 0.12. If we return to the phase diagram in Fig. 6, we see that for a thin cigar, we may derive the following approximate statement. At the 0.50-mole fraction point, the ratio $\Delta T_{0.5}/(s_i - \ell_i)_{0.5}$ is approximately equal to the ratio of $(\theta_i - \theta_j)$ divided by the total composition range, which is always one. From Eq. (26), we see that the temperature spread of the liquid-solid cigar, ΔT, will follow the square of $(\theta_i - \theta_j)$.

We calculate $\Delta T_{0.5}$ to be 0.41 K, compared to 0.6 K for the experimental value. We may roughly summarize the three H-D binary systems by empirically changing the coefficient assigned to Eq. (26).

We have

$$(s_i - \ell_i) \simeq 0.09 \, \ell_i \ell_j \, (\theta_i - \theta_j) , \text{(26a)}$$

and

$$\Delta T \simeq 0.09 \, \ell_i \ell_j \, (\theta_i - \theta_j)^2 . \qquad (27)$$

We may now estimate values for systems that have not yet been measured. For
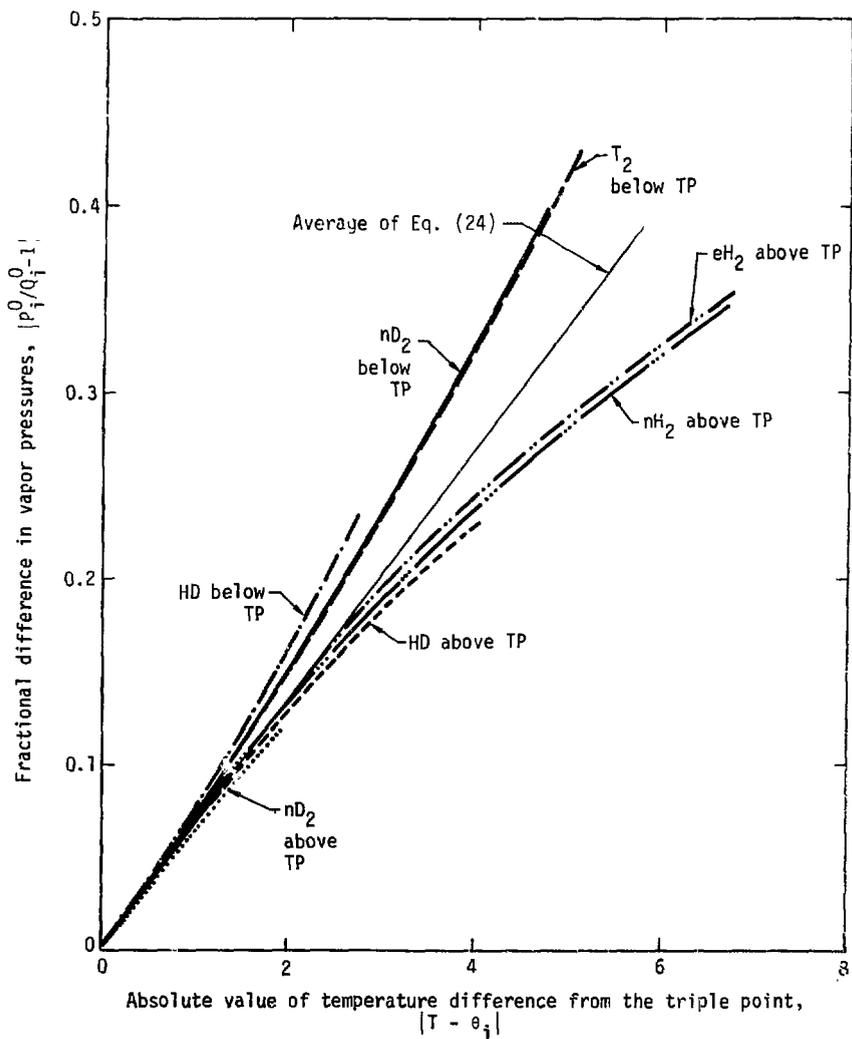
Fig. 7. Fractional difference of the pure-component liquid and solid vapor pressures as a function of the distance from the triple-point temperature.

D_2-T_2, $(\theta_i - \theta_j)$ is 1.90 K and we calculate $(s_i - \ell_i)_{0.5}$ to be 0.043 (i.e., 50% liquid T_2 yields 54% solid T_2). Also, we calculate $\Delta T_{0.5}$ to be 0.081, quite a thin phase-diagram cigar. For H_2-T_2 (providing there is no phase separation) we calculate $(\theta_i - \theta_j)$, $(s_i - \ell_i)_{0.5}$, and $\Delta T_{0.5}$ to be 6.82 K, 0.15 mole fraction, and 1.05 K, respectively.

We now turn to the percent deviation of the mixture vapor pressure, I, from Raoult's Law. This is defined as

$$I(T_m) = \frac{(P_m - P_T^\circ)}{P_m} \ (100) \ , \qquad (28)$$

where P_m is the measured total pressure of the mixture and I is calculated at the measured temperature, T_m. We see that I has an empirical aspect in that T_m may be shifted from the ideal (but unknown) temperature. Figure 8 shows available data for H_2-D_2. The highest curve is in the three-phase equilibrium data, taken for freezing liquid where we know the composition and for freezing gas where the Raoult's Law is used to estimate the liquid mole fraction.[67] We have used our vapor pressure codes to expand the Soviet raw data into this form. The three-phase curve is neither isothermal nor isobaric. The temperature increases left to right from 13.81 K

to 18.73 K. The pressure peaks at approximately 0.83 mole fraction D_2 (17.90 K).[65] The two lower curves are for two-phase, liquid-gas equilibrium, taken from the boiling-point table of Ref. 62 where the liquid mole fractions are given. The two curves are isobaric in terms of the Raoult's-Law pressure, P_T°. They are not isothermal and the temperatures are not given. Thus, it is impossible to modify the data (or use the authors' dew-point table). On each of the lower curves, the temperature obviously increases with the mole fractions of D_2. Also, the 2500-Torr curve represents higher temperatures than the 500-Torr line. There are two major features of the Raoult's-Law, mixed-vapor pressure data. The data are peaked towards the D_2 side, about at the gas mole fraction of 0.5. Secondly, I increases with decreasing temperature. This seems surprising because the gas pressure drops rapidly as the temperature falls. The gas becomes more nearly ideal in the sense of the Perfect Gas Law, even while it is becoming more nonideal with respect to Raoult's Law. There are also some H_2-HD liquid-gas data of P_T° values from 500 to 2500 Torr.[62] These show the same general form but are lower than the corresponding H_2-D_2 points by a factor of 0.34 to 0.87.
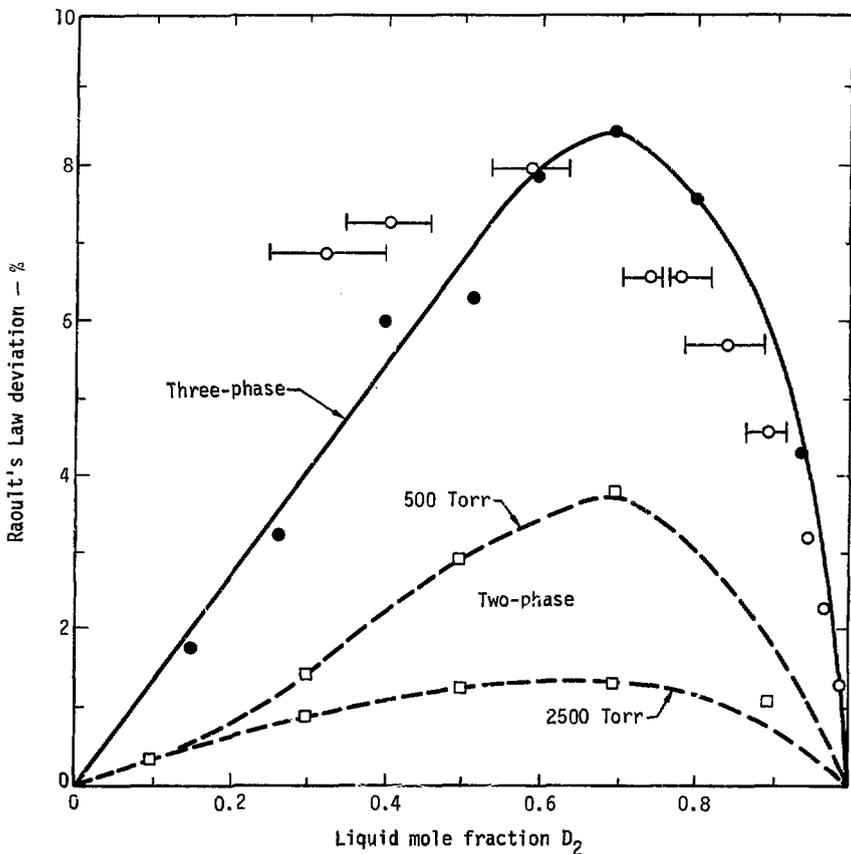
Fig. 8. Percent deviation from Raoult's Law for H_2-D_2 mixtures. The two-phase pressures are Raoult's Law values, P_T^o. Here, ● = calorimetric freezing of liquid-gas,[67] o = volume shinkage upon freezing,[67] and □ = two-phase boiling points.[62]

Acknowledgments

-23-

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PLL/gw/vt

Appendix. List of Symbols

A, B, B', C, D   Constants for vapor pressure, temperature equations.

A_ℓ, B_ℓ Constants for liquid density, temperature equations.

B_g, C_g Second and third virial coefficient for gas.

B_s Constant for the solid density, temperature equation.

B_0 Constant for the second virial coefficient, temperature equation.

G   Gibbs free energy (J/mol).

g_{D_2}, g_{H_2}, g_i, g_j Mole fractions of the D_2, H_2, i^{th}, and j^{th} components in the gaseous phase of a mixture.

H_f, H_s, H_v Real heats of fusion, sublimation, and vaporization (J/mol).

H_s(eff),H_v(eff)   Effective heats of sublimation and vaporization (J/mol).

I   Percent deviation of gas pressure from Raoult's Law.

ℓ_{D_2}, ℓ_{H_2}, ℓ_i, ℓ_j Mole fraction of the D_2, H_2, i^{th}, and j^{th} components in the liquid phase of a mixture.

n   Constant for the second virial coefficient, temperature equation.

P_i Partial pressure of the ith component in a mixture (Torr).

P_m Measured total vapor pressure of a mixture (Torr).

P°   Pure component, saturated, liquid-gas vapor pressure. Subscripts D_2, H_2, X_2, XY, and Y_2 refer to specific hydrogen species. Subscript i refers to the ith component in a mixture. Subscripts 1 and 2 refer to two consecutive data points in a series (Torr).

P_T° Raoult's Law total-vapor pressure of a mixture (Torr).

Q°   Pure component, saturated, solid-gas vapor pressure. Subscript i refers to the ith component in a mixture (Torr).

R   Gas constant (8.314 J/mol·K or 62.361 Torr-litres).

S   Entropy. Subscripts g and ℓ refer to gas and liquid (J/mol·K).

s_i Mole fraction of the ith component of a mixture in the solid phase.

$(s_i - \ell_i)_{0.5}$ Difference in solid and liquid mole fractions for the ith component of a mixture at the temperature of the center line-0.5-mole fraction intersection.

$T, \overline{T}$ Temperature, average temperature between two data points. Subscripts 1 and 2 refer to temperatures of two consecutive data points of a series (K).

$\Delta T_{0.5}$ Temperature difference between solid and liquid lines at 0.5-mole fraction (K).

V Volume. Subscripts g and ℓ refer to gas and liquid (m^3).

X_2, XY, Y_2 Diatomic hydrogen species (H, D, T).

Z Compressibility of gas.

ρ_g, ρ_ℓ Density of gas, liquid (mol/m^3).

θ_i, θ_j Triple-point temperatures of the ith and j^{th} hydrogens (K).