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Some thermodynamic properties of hydrogen and deuterium

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In the twenty-odd years which have elapsed since the existence of isotopes was first well established, isotopes of most of the chemical elements have been discovered and their individual masses determined. Of the several hundred now known, by far the majority have been revealed by Aston's mass spectrograph[11]. In recent years rare isotopes of exceptional interest have been found by the molecular spectrum method, the first being the isotopes 17 and 18 of oxygen, discovered by Giauque and Johnston[12]. Then the isotopes 15 of nitrogen and 13 of carbon, detected in studies of molecular spectra by Naudé[13] and by Birge and King[14] respectively, were added to the list of known isotopes.

Due to these discoveries the abundant isotopes of the light elements were known when the existence of the hydrogen isotope of atomic weight two, now called deuterium, was first demonstrated in 1931. Previous to the experimental detection of deuterium an empirical regularity among the known isotopes which indicated the possible existence of ^{2}H(D), ^{3}H(T) and ^{5}He had been recognized[29]. Figure 1 *a* shows this regularity in the form of a plot of the number of neutrons and protons in atomic nuclei calculated on the assumption that nuclei consist of a number of protons equal to the atomic number and of an additional number of neutrons sufficient to account for the approximate atomic weight. (This regularity was originally presented in the form of an electron-proton plot.) Though without adequate theoretical support the relationships in the plot cannot be regarded as a definite prediction of the existence of ^{2}H, ^{3}H and ^{5}He, the knowledge of them served to stimulate the search for isotopes of the lighter elements. Since 1931 the existence of ^{2}H, of ^{3}H and also of ^{5}He, which is not expected on the basis of the plot, have been revealed; ^{5}He, however, has not been detected. Figure 1 *b* shows this plot as it is now. The recently discovered unstable nuclei are not included.

The determination of the exact atomic weight of ^{1}H relative to ^{16}O, taken as the standard of atomic weights equal to 16 units, and the determination of
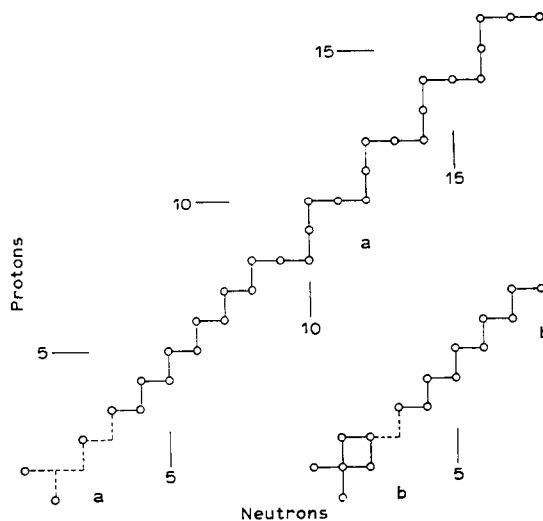
Fig. 1. (a) The plot of the numbers of protons and neutrons in the nuclei of the lighter elements known in 1931; (b) a same plot for the first few elements as of January 1935.

the chemical atomic weight of the natural mixture of the oxygen isotopes showed, as was first pointed out by Birge and Menzel[15], that a hydrogen isotope of mass 2 might be present to the extent of 1 part in 4,500 of the light variety. This was the maximum abundance that could be expected, since the presence of any heavier isotope of hydrogen would have meant that all additional isotopes must be less abundant than one part in 4,500. This estimate is based upon a difference of 2 in the fourth decimal place in atomic weights when reduced to the same standard; this is only slightly greater than a reasonable estimate of the probable error of the chemical determinations. More recent determinations of the abundance of ^{18}O necessitate a revision of this estimate to 1 : 3,700 instead of 1 : 4,500. (See Addendum, p. 354.)

In order to demonstrate the existence of such a rare isotope, it seemed to be necessary to concentrate it in some way, for no isotope so rare as this had been found by any of the methods known at that time. This was subsequently shown not to be true because of the adoption of a very sensitive method for the detection of this isotope, namely the use of the atomic spectra, which can be used in this case because of the relatively large atomic isotope effect to be expected from the theory of Bohr. However, the isotope of hydrogen of atomic weight 2, or deuterium, was concentrated by the distillation of hydrogen in order to facilitate its detection.

Previous to the carrying out of the experiments on the concentration of

this substance, calculations were made on the vapor pressures of the mole-cules* H_2 HD and HT, on the basis of the following postulates: (i) the internal rotational and vibrational energies of the molecules are the same in the solid and gaseous states and thus were not considered in the calculation of the vapor pressures; (ii) the free energy of the solids may be calculated from the Debye theory of the solid state: the Debye Θ''s ($= h\nu/k$) of the three solids** are inversely proportional to the square roots of the molecular weights; (iii) the free energy of the gas is given by the free energy equation for an ideal monatomic gas[16]. Further, the Θ'_{I} used in these calculations for the hydrogen molecule, H_2, was that required to describe the heat capacity of the solid hydrogen under its saturation pressure, using the Debye theory for the heat capacities of a monatomic solid. Also, it was assumed that the heats of vaporization of the hypothetical vibrationless solid hydrogen, solid hydrogen deuteride and solid hydrogen tritide to the gaseous phase are the same, in the neighbourhood of absolute zero. The vapor pressure of one of the solids on the basis of these assumptions is given by the equation:

$$\ln P = \frac{E_0}{RT} + \frac{F_s}{RT} + \ln M^{3/2} T^{5/2} - \frac{\chi}{RT} + \text{const.} \qquad (1)$$

where χ is the heat of vaporization of the vibrationless solid to the motionless gas at absolute zero. E_0 is the zero point energy of the solid due to the Debye vibrations, and F_s is the free energy of the solid at temperature T, exclusive of the zero point energy. The vapor pressure equation depends upon the mass only through the dependence of the zero point energy and the free energy of the solid on the mass and through the dependence of the free energy of the gas on the ln M term. Hence, for the ratio of the two vapor pressures, we secure

$$\ln \frac{P(H_2)}{P(HD)} = \frac{E_0(H_2) - E_0(HD)}{RT} + \frac{F_s(H_2) - F_s(HD)}{RT} + \frac{3}{2} \ln \frac{M(H_2)}{M(HD)} \quad (2)$$

Simon and Lange[17] have shown that the value of the Θ'_{I} for the hydrogen is 91 and from this the value of the Θ''s for hydrogen deuteride and hydrogen tritide are easily calculated to be 74.3 and 64.4 respectively, assuming that the molecular weights of the three molecules are in the ratio 2 : 3 : 4.

* H, D and T and the names hydrogen, deuterium and tritium are used for the atoms and substances represented by the symbols ^{1}H, ^{2}H and [3]H.
* * The prime is used to distinguish this approximate Θ' from the true Θ used below.

The use of this simple theory gives for the ratios of vapor pressures of hydrogen to hydrogen deuteride and of hydrogen to hydrogen tritide, the values 2.23 and 3.35 respectively. Using these values for the ratio of vapor pressures, simple calculations showed that very effective concentration of deuterium should be secured by the simple distillation of solid hydrogen at the triple point. Of course, it was impossible to be certain that these differences would apply to the liquid state, but it was a reasonable postulate that at least some of the effect would persist into the liquid state.

Bohr's theory, given some twenty years ago, permits the calculation of the Balmer spectrum of the heavier isotopes of hydrogen from this spectrum of hydrogen by the well-known theoretical formula for the Rydberg constant. The value of the Rydberg constant for the hydrogen isotopes can be calculated from the atomic weights of the isotopes and the known atomic weight of the electron. The expected wavelengths of the Balmer series, using the most recent determinations for the atomic weights of hydrogen, deuterium and tritium, and of the electron, are given in Table I.

Dr. F. G. Brickwedde, of the United States Bureau of Standards, very kindly prepared samples of hydrogen evaporated in accordance with the conditions indicated by the theory outlined above. The best sample was obtained from 4,000 cc. of liquid hydrogen which was evaporated near the triple point until a residue of approximately 1 cc. remained. My research assistant, Dr. G. M. Murphy, and I, in the fall of 1931, investigated the atomic spectrum of this sample and other samples of fractionated hydrogen as well as natural hydrogen, using a 21-ft. concave grating having 15,000 lines to the inch. We found three members of the Balmer series of deuterium even when commercial electrolytic hydrogen was used. The light of these

Table I. Calculated wavelengths *(in vacuo)* of the Balmer lines of hydrogen, deuterium, and tritium.

	λ (H)	λ (D)	λ (T)	$\Delta\lambda$ (calc.) (H — D)	$\Delta\lambda$ (obs.) (H — D)
α	6564.686	6562.899	6562.304	1.787	1.79
β	4862.730	4861.407	4860.966	1.323	1.33
γ	4341.723	4340.541	4340.148	1.182	1.19
δ	4102.929	4101.812	4101.440	1.117	1.12

The values have been calculated by using $M_H = 1.007775$, $M_D = 2.01363$, $M_T = 3.0151$ and $m_e = 5.491 \times 10^{-4}$ and taking R_H equal to 109677.759 cm^{-1}.

wavelengths was increased by a factor of four or five times in the samples prepared by Dr. Brickwedde. Moreover, the $D\alpha$ line was found in the concentrated samples and was found to be a doublet of approximately the separation required by the fine structure theory for the hydrogen lines. It was concluded that these additional lines were to be interpreted as due to the hydrogen isotope of atomic weight two, since (i) their wavelengths agreed within the experimental error of about 0.02 Å unit with the predicted theory for the wavelengths for this isotope, (ii) the $D\alpha$ line was found to be a doublet as required by theory and by experiments on the hydrogen lines, (iii) these wavelengths of deuterium appeared on our plates only when the discharge was run in the so-called black stage, which produces an intense atomic spectrum, indicating that they were atomic lines and not lines of the molecular spectrum of ordinary hydrogen, and (iv) the deuterium lines were stronger in the concentrated samples, thus showing that a concentration had been effected and that the lines were not due to ghosts. Further, it was shown that there were no recorded molecular lines which agreed with the calculated and observed positions of the $D\alpha, D\beta, D\gamma$ and $D\delta$ lines. The mean value of the wavelength differences for the hydrogen and deuterium lines, as observed in all the samples of hydrogen investigated at that time, are recorded in Table I. No evidence was secured for the presence of a hydrogen isotope of atomic weight 3.

Though the deuterium line is easily detectable in the natural hydrogen, it would have been very difficult to have definitely established its existence if the more concentrated samples prepared by distillation had not been used, for irregular "ghosts" of a ruled grating might conceivably have accounted for the observed additional lines. Thus, the method of concentration devised for and used in these original researches, was important in proving the existence of this isotope[1].

The theory of hydrogen and deuterium vapor pressures

The practically complete separation of hydrogen and deuterium has permitted an investigation of the vapor pressure of pure deuterium and the direct comparison of its vapor pressures with that of hydrogen. Lewis and Hanson[18], and Scott, Brickwedde, Urey and Wahl[8] have investigated these vapor pressures experimentally. The results are in essential agreement, though they deviate from each other in a direction which could be accounted for by the

assumption that Lewis and Hanson used a less pure sample than the latter authors*.

The vapor pressure of deuterium in terms of the vapor pressure of liquid hydrogen is given by the following equations:

$$\log_{10} P\,(D_2\text{liquid}) = -1.363 + 1.310 \log P\,(H_2\text{liquid}) \qquad (3)$$
$$\log_{10} P\,(D_2\text{solid}) = -1.954 + 1.534 \log P\,(H_2\text{liquid}) \qquad (4)$$

Using an equation for the vapor pressure of liquid hydrogen devised by Scott, Brickwedde, Urey and Wahl, namely:

$$\log_{10} P\,(\text{mm of Hg}) = 4.6633 - 44.7291/T + 0.02023\ T \qquad (5)$$

the equations for the vapor pressure of solid and liquid deuterium become:

$$\log_{10} P\,(D_2\text{liquid}) = 4.7459 - 58.5951/T + 0.02650\ T \qquad (6)$$
$$\log_{10} P\,(D_2\text{solid}) = 5.1995 - 68.6144/T + 0.03103\ T \qquad (7)$$

Equations (3) and (4) are independent of the temperature scale, since the vapor pressures of hydrogen and deuterium were compared directly, but equations (6) and (7) depend upon the temperature scale. The vapor pressures at the temperatures for which measurements were made, together with the heats of transition derived from them, are given in Table 2.

In a more exact theory of the vapor pressures of hydrogen and deuterium than that given above it is necessary to include the deviations from the ideal gas law as well as slight corrections for the free energy of the solid at varying pressures. To do this it is necessary to adopt an equation of state for deuterium, and as a first approximation we may assume that hydrogen and deuterium follow the same equation of state. The equation:

$$PV = RT\ \{1 - (0.0381/V)\ (1 + 1150/T^2)\} \qquad (8)$$

is in accord with the latest experimental determinations of the virial coeffi-

* Dr. Brickwedde informs me that he has investigated samples supplied to him by Professor H. S. Taylor and found lower vapor pressures than those reported by Scott, Brickwedde, Urey and Wahl by an amount which would indicate that the samples of Professor Taylor are purer deuterium by about 0.3 percent than the ones used in the vapor pressure experiments.

Table 2.[1]

T	H_2			D_2			
	$P(H_2)$	ΔH	ΔH (ideal)	$P(D_2)$	$^2\Delta H$	$^2\Delta H$ (ideal)	$^3\Delta H$ (ideal)
13.92	(54)	245.7 (28.0)	247.7 [4](28.0)				
13.92	(54)	217.7	219.7	(5)	340.8	340.9	341.1
15.188	106.1			14.2	345.4	345.7	345.8
16.430	190.3			35.0	349.6	350.2	350.0
17.479	287.0			65.5	352.7	353.7	353.7
18.182	372.4			97.7	354.5	355.9	355.9
19.58	(429)	218.7	224.8	(121)	355.4	357.1	357.2
					(52.3)	(52.3)	[4](52.4)
18.58	(429)			(121)	303.1	304.8	
18.945	484.9			142.4	304.0	305.9	
18.953	486.0			143.2	304.0	305.9	
19.167	521.7			157.1	304.4	306.5	
19.330	550.0			168.5	304.8	306.9	
19.969	672.0			218.5	306.0	308.6	
20.334	749.8			252.0	306.6	309.6	
20.38	760	215.9	225.3	(257)			
23.5	(1760)			(760)			

[1] The values of the vapor pressures enclosed in parentheses are interpolated or extrapolated values.

[2] ΔH recorded in this column is the heat of vaporization of deuterium in the condensed phase to the gas at the saturation pressure calculated from the empirical vapor pressure equation. ΔH (ideal) is the heat of vaporization to the gas at zero pressure.

[3] ΔH (ideal) recorded in this column is the heat of vaporization of the solid to the gas at zero pressure calculated from equation (10) using $\Theta_2' = 100$.

[4] The heats of fusion are enclosed in parentheses.

cients for hydrogen. The vapor pressure equation for solid hydrogen or deuterium then takes the form:

$$\ln P = -\frac{\Delta H_o}{RT} + \frac{5}{2}\ln T + \frac{3}{2}\ln M + 2.30259\,i + \frac{V_sP}{RT} + \frac{F_s}{RT}$$

$$+ \ln\left[1 - \frac{0.0381}{V}\left(1 + \frac{1150}{T^2}\right)\right] + \frac{2 \times 0.0381}{V}\left(1 + \frac{1150}{T^2}\right) \qquad (9)$$

where ΔH_o is the heat of vaporization at absolute zero, i is the chemical constant and is equal to -1.5882, V_s is the gram molecular volume of the solid,

F_s is the free energy of the solid at zero pressure exclusive of the zero point energy, and the other symbols have their usual significance.

Since the heat capacity of solid hydrogen under the saturation pressure can be calculated empirically by the theoretical Debye formula, using Θ_1' equal to 91, as mentioned above, the free energy F_s may be calculated from the same theory and it may be assumed that the F_s for deuterium may be calculated in a similar way, using an appropriate value for Θ_2'. By trial and error it was found that the adoption of a $\Theta_2' = 100$ gave constant values for ΔH_o, as shown in Table 3.

Table 3. ΔH_0 calculated from the vapor pressures (using $\Theta_2' = 100$).

T	15.188	16.463	17.479	18.182	
ΔH_0	276.11	275.97	276.09	276.08	**Av.** 276.06

In making these calculations it was necessary to compute the value of V at the pressure P from the equation of state, and then substitute its value as well as that of P in equation(9), and thus solve for ΔH_o. By this method, we find that the average value of ΔH_0 in the case of deuterium is 276.0 cal per gram molecule.

Recently Bartholomé and Clusius[19] have found, from experimental determinations of the heat capacity of solid deuterium, that the Θ_2' is equal to 89, instead of 100 as deduced from the vapor pressure equation. The values of ΔH_o, using this value of Θ_2' in the vapor pressure equation, are not constant, when calculated at the four different temperatures at which vapor pressures were observed, as can be seen from Table 4.

Table 4. ΔH_0 calculated from the vapor pressures (using $\Theta_2' = 89$).

T	15.188	16.463	17.479	18.182
ΔH_0	275.33	274.96	274.89	274.72

This may mean that the equation of state for deuterium is not the same as that for hydrogen, and in fact the deviation is such that the imperfection of deuterium gas is greater than that of hydrogen gas at the same gram molecular volume. A similar effect has been noted by Rabi, who has found that the collisional areas of hydrogen and deuterium molecules are not the same for collisions with potassium and sodium atoms. Such differences are probably associated with the large differences in the internal zero point energies of these molecules.

The change in the value of ΔH_o for deuterium necessitated by the difference in equations of state, as indicated by the values given in Tables 3 and 4, does not in itself affect the conclusions which follow, though indirectly it may be important. It has been assumed that χ, the energy of separation of the molecules of the solid, is the same for hydrogen and deuterium, an assumption which must be questioned seriously, if the forces between the gaseous molecules are not the same. At present I am not able to estimate how large this difference in the χ's may be, but since the Raman frequencies of hydrogen are nearly the same in the gas and liquid this effect will probably not be very large.

Making use of the equation of state (8), the heat of vaporization is:

$$\Delta H = \Delta H_o + \frac{5}{2} RT - (RT/V)\ 0.0381\ (1 + 3450/T^2) - H_s \qquad (10)$$

H_s, the heat content of the solid under the saturation pressure, may be taken as the Debye energy with Θ_1' equal to 91 in the case of hydrogen. Using Simon and Lange's value for the heat of vaporization of solid hydrogen at the triple point, ΔH_o for hydrogen is found to be 182.9 cals per molecule.

It will be noted, first of all, that the ΔH_o's cannot be accounted for on the assumption that the heats of vaporization of the vibrationless solid hydrogen and solid deuterium are the same, and that the zero point energies have the values $9/8\,\Theta_1'R$ and $9/8\,\Theta_2'R$ *since the* values of Θ_1' and Θ_2' are so nearly the same. This result is to be expected, for the zero point energy of a solid should be equal to $9/8\ OR$, where Θ is the Debye function $(h\nu/k)$, secured from the heat capacity at constant volume, and since the heat capacity at constant volume should be less than that at constant pressure, Θ_1 and Θ_2 should be larger than Θ_1' and Θ_2' respectively. Assuming that the heats of vaporization of the vibrationless solids are the same for hydrogen and deuterium and that the ratio of the zero point energies varies inversely as the square roots of the reduced masses, we then have the equations:

$$\chi = E_o(H_2) + 182.9 = E_o(D_2) + 276.0 \qquad (11)$$
$$E_o(H_2)/E_o(D_2) = (4.0273/2.0156)^{1/2} \qquad (12)$$

From these equations we find that $\chi = 501.2$, $E_0\ (H_2) = 3\ 18.3$ and $E_0\ (D_2) = 225.2$. The corresponding Θ's are $\Theta_1 = 142.4$ and $\Theta_2 = 100.7$. These Θ's should be used to calculate the heat capacities and other thermodynamic

properties at constant volume. The striking thing about these results is that, whereas Θ_1 and Θ_1' are markedly different, being 142.4 and 91 respectively, Θ_2 and Θ_2' are nearly the same, being 100.7 and 100 (or, using Bartholomé and Clusius' value, 89) respectively. This shows that the heat capacities at constant pressure and constant volume are markedly different for hydrogen but nearly the same for deuterium, and since $C_p - C_v = \alpha^2 VT/\beta$, where α and β are the coefficients of thermal expansion and compressibility respectively it follows that the ratio α^2/β must be smaller in the case of deuterium than in the case of hydrogen.

It should be noted that the zero point energy of hydrogen is about 64 per cent of the value of χ, while for deuterium it is 46 per cent of this quantity. Thus it seems probable that the oscillators for both hydrogen and deuterium which are responsible for the heat capacity are markedly anharmonic. Moreover, the oscillators of hydrogen should be considerably more anharmanic in character than those of deuterium, and hence the coefficient of expansion of hydrogen should be considerably greater than that of deuterium. This indicates that the heat capacities of hydrogen at constant volume and at constant pressure should differ more than these heat capacities for deuterium, which is in agreement with the observation. Moreover, the observation of Bartholomé and Clusius[19] that the gram molecular volume of solid hydrogen is some 11 per cent greater than that of deuterium is in agreement with this view. This difference is to be regarded as due to the greater amplitudes of oscillation in solid hydrogen and their greater anharmonic character, and this difference in gram molecular volume should persist to the absolute zero, as was observed by these authors.*

Throughout this calculation it has been assumed that the molecules of hydrogen and deuterium rotate freely in the solid state, and that the internal vibrational zero point energy is the same in the condensed and gaseous phases. It is well known that the rotational energy in the solid state is not exactly the same as that of the gaseous state, since the heat capacity of ortho hydrogen below 11° absolute is markedly different from that of para hydrogen in this temperature range. The difference can be accounted for qualitatively by assuming a simple potential energy function for rotation in the solid state. A consideration of the differences in rotational states to be expected in the case of hydrogen and deuterium indicates that no large correc-

* Clusius and Bartholomé have independently come to similar conclusions to those expressed here. (Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-Physikalische Klasse, Fachgruppe III, p. 29.)

tion to the theory given above needs to be made on this ground. Studies on the Raman effect of liquid hydrogen indicate that the vibrational energy levels are not greatly perturbed in this phase. This indicates that the assumption of equal $\chi's$ for these two solids should be approximately correct and that the calculations of zero point energies and $\Theta's$ and thermodynamic properties at constant volume are a good first approximation.

From the vapor pressure data, it is also possible to conclude that the heat capacity of deuterium in the liquid state is much lower than that of hydrogen in the liquid state, though the equation of state assumed for deuterium affects the calculated values more in the case of the liquid than in that of the solid because of the higher vapor pressures.

The vapor pressures of hydrogen deuteride have not been investigated as yet because of the difficulty of preparing this molecule in the pure state. It is not at all certain that one can calculate the vapor pressure from the data on hydrogen and deuterium using the theory outlined above. The rotational states of the HD molecule in the solid state may be considerably different from those of H_2 and D_2 since rotation occurs about the center of mass which is the mid point between the nuclei in the case of H_2 and D_2 but not in the case of HD. The rotational energy might enter in an important way in this case. However, if we assume that the χ for the mixed molecule is about the same as that for the hydrogen and deuterium molecules, and that its Θ is equal to $\sqrt{\frac{2}{3}}\,\Theta_I$, the vapor pressure ratio of solid hydrogen and solid hydrogen deuteride at the triple point is found to be approximately 2.42.

Using this ratio in the Rayleigh distillation formula, it is possible to calculate what the increased concentration should have been in the original distillation of liquid hydrogen as carried out by Dr. Brickwedde. The hydrogen used in this distillation was prepared by electrolysis of ordinary water and, as we know now, the gas delivered from such a cell contains a smaller fraction of deuterium than does the water within the cell. It seems probable that the liquid hydrogen used contained about one part in 25,000 of deuterium. The ratio of the original to the final volume was about 4,000 and hence the concentration of deuterium should have been increased approximately 125 times instead of about 25, as actually observed. Or, if the observed fractionation factor is calculated by using one part in 25,000 for the original concentration and one part in 1,100 for the final concentration, one finds that this factor was 2.1 instead of 2.42 as required by the theory. It appears, therefore, that the enrichment secured was about what could be expected from the theory considering the difficulties of distilling liquid hydrogen.

The equilibria of exchange reactions involving hydrogen and deuterium

The equilibrium constants of exchange reactions of the general type, AH + BD = AD + BH, can be calculated in the case of diatomic molecules, providing the rotational and vibrational energy levels are known from molecular spectra. The theory of molecular spectra is now so well developed that a knowledge of these levels for the molecules containing hydrogen enables us to calculate these levels for the molecules containing deuterium. The standard free energy of a gas is given by the equation:

$$F^\circ = -\ RT\ \ln\ M^{3/2}T^{5/2}QP^{-1} + 7.2646T + E^\circ \ (P = 1) \qquad (13)$$

Q is the summation of state and equals Σp exp(- *E/kT),* E being the energy of the molecule in a steady state relative to the lowest energy level and the summation being extended over all the steady states; E° *is* the zero point energy per gram molecule. The equilibrium constant of the typical reaction then becomes:

$$\ln K = -\ \frac{E^\circ}{RT} + \ln \left[\frac{M_{AD}\ M_{BH}}{M_{AH}\ M_{BD}}\right]^{3/2} \frac{Q_{AD}\ Q_{BH}}{Q_{AH}\ Q_{BD}} \qquad (14)$$

The appropriate expressions for other exchange reactions are easily derived.

Rittenberg and I have used this theory to show that easily detectable differences in the equilibrium constants of reactions involving hydrogen and deuterium should exist, and subsequent experimental work confirmed these calculations in the case of the reaction of hydrogen and deuterium with iodine to give hydrogen iodide and deuterium iodide. This confirmation was confidently to be expected, but this seems to have been the first time that an equilibrium constant of a chemical reaction had been calculated before one of the elements involved had been prepared in sufficient quantities to confirm the theory.

The equilibrium constants calculated for the reactions

$$H_2 + 2\,DCl = D_2 + 2\,HCl$$
$$H_2 + 2\,DI \ \ = \ \ D_2 + 2\,HI$$
$$H_2 + D_2 \ \ \ \ = 2HD$$
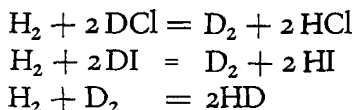
are given in Table 5 for a number of temperatures. Table 6 gives the ex-

perimental values for the percentage dissociation for mixtures of hydrogen and deuterium iodide of the composition shown in column 2. The constants

Table 5. Calculated equilibrium constants of exchange reactions.[4,5,20]

T (°C)	$H_2 + D_2 =$ 2 HD	$H_2 + 2\,DCl =$ $D_2 + 2\,HCl$	$H_2 + 2\,DI =$ $D_2 + 2\,HI$
0	0	0	0
50	1.345		
100	2.265		
200	2.903	0.309	
298.1	3.269	0.502	1.164
400	3.494	0.647	1.212
575	3.710	0.807	1.234
700	3.800	0.874	1.222

Table 6. The dissociation of hydrogen iodide and deuterium iodide.[6]

T (°C)	Conc. of D	Percent dissociation		Difference	
		Exp.	Calc.	Exp.	Calc.
398	0.0	[3]20.72	(20.72)	0	0
398	[1]14.3	20.84	20.89	0.12	0.175
468	0.0	[3]22.72	(22.72)	0	0
468	[1]41.7	23.29	23.33	0.57	0.602
468	[2]75.5	23.88	23.94	1.16	1.222

[1] Concentration of deuterium in the hydrogen iodide – deuterium iodide used.
[2] Concentration of deuterium in the hydrogen–deuterium gas at equilibrium.
[3] Bodenstein's value for 398° C is 20.70 and at 468° C, 22.77.

for the last reaction given above have been confirmed very beautifully by Gould, Bleakney and Taylor[20].

  In the original work various values for the spin of the deuteron were used and the Bose-Einstein and Fermi-Dirac statistics were considered. The first two values of column 2 are dependent on the spin and statistics, though all other values are independent of these. A spin of 1 and the Bose-Einstein statistics are used in the calculation of the constants recorded here.

  Calculations of a similar kind have been made by others (Farkas and Farkas[21], Crist and Dalin[22], Topley and Eyring[23]) and these have been confirmed experimentally. It is, of course, to be expected that similar deviations from the equilibrium constants computed on the assumption of a simple statistical

distribution of hydrogen and of deuterium atoms between their compounds in condensed phases will occur, though the calculations cannot be made exactly in these cases.

The differences in vapor pressure of compounds of hydrogen and deuterium observed by Lewis and his co-workers[26,27] and others, cannot be accounted for by the theory presented above for the differences in vapor pressures of hydrogen and deuterium. If the heat capacity due to the Debye vibrations of a solid is nearly equal to the Dulong and Petit value, no differences in vapor pressures of isotopic substances can be expected from the contribution of these vibrations to the free energy. The differences in vapor pressures of these substances, such as water, ammonia, etc., must be related to the equilibria considered in this section, the differences being due to differences in zero point energies, distribution functions, etc., in the gaseous and condensed phases. At present we have no satisfactory theory for such vapor pressure differences.

The separation of isotopes

The extensive researches which have been carried out with the use of deuterium in the last two years were made possible in a large part by the discovery by Washburn[3] of the electrolytic method for the separation of hydrogen and deuterium. Other methods could be used at the present time for the separation of these isotopes. The exchange reaction between water and hydrogen could probably be adapted to counter-current scrubbing methods, and could be used effectively for the separation of the hydrogen isotopes as suggested by Farkas.

A major problem which challenges chemistry and physics today is the separation of the isotopes of the lighter elements. Orienting experiments have been made in this direction by Lewis and Cornish[24], who discovered a difference in the vapor pressures of the two waters $H_2^{16}O$ and $H_2^{18}O$, and by Hertz[28] using his ingenious diffusion apparatus.

The beautiful confirmation of the theoretical calculation in the case of exchange reactions involving hydrogen and deuterium encourages us to apply the same sort of calculation to exchange reactions involving the isotopes of other elements. Recently such calculations have been made by Dr. L. Greiff and myself[25] for a number of such exchange reactions. In the case of the exchange reaction with respect to ^{16}O and ^{18}O between water and CO_2, it is

found that the ratio of ^{18}O to ^{16}O in the CO_2 in equilibrium with water is increased by approximately 5 per cent over that of the water, and this result has been confirmed experimentally. The ratio of ^{13}C to ^{12}C in CO_2 in equilibrium with CO with respect to the carbon isotopes is about 8 or 9 per cent greater than this ratio in the CO. The isotopic composition of chlorine in equilibrium with hydrogen chloride is sufficiently different to affect the atomic weight of chlorine in the third decimal place. In general, exchange reactions for the lighter isotopes have equilibrium constants sufficiently different from unity, so that the ratios of concentrations of the isotopes in two compounds which are in equilibrium differ by a few per cents in nearly all cases. Some reactions of this kind can be adapted to counter-current scrubbing processes, using apparatus similar to fractionation columns. I believe that these calculations indicate that it will be possible to separate the isotopes of the lighter elements in considerable quantities by the use of these equilibria, though it may be that even better methods will be developed.

The discovery of deuterium and the marked differences in the physical and chemical properties of hydrogen and deuterium, together with an efficient method for the separation of these isotopes, have opened an interesting field of research in several of the major branches of science. It is my expectation that the next few years will witness the separation of the isotopes of the lighter elements in sufficient quantities for effective research in chemistry, physics and biology. If this can be effected, the work on deuterium is only the beginning of a very interesting scientific development.

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Addendum

Since this was written, Aston has revised his mass-spectrographic atomic weight of hydrogen (H) to 1.0081 instead of 1.0078 [F. W.Aston, *Nature,* 135 (1935) 5411. With this mass for hydrogen, the argument by Birge and Menzel is invalid. However, I prefer to allow the argument of this paragraph to stand, even though it now appears incorrect, because this prediction was of importance in the discovery of deuterium. Without it, it is probable that we would not have made a search for it and the discovery of deuterium might have been delayed for some time.