Classic Paper

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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[2,9]. 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 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 molecules* H_2HD 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'_1 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:

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

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

wavelengths was increased by a factor of four or five times in the samples prepared by Dr. Brickwedde. Moreover, the Dα 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 Dα 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 Dα, Dβ, Dγ and Dδ 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].

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

	λ (H)	λ (D)	λ (T)	Δλ (*calc.*) (H — D)	Δλ (*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}.

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[19] 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:

$$\log_{10} P(D_2 \text{liquid}) = -1.363 + 1.310 \log P(H_2 \text{liquid}) \quad (3)$$

$$\log_{10} P(D_2 \text{solid}) = -1.954 + 1.534 \log P(H_2 \text{liquid}) \quad (4)$$

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

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

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

$$\log_{10} P(D_2 \text{liquid}) = 4.7459 - 58.5951/T + 0.02650\ T \quad (6)$$

$$\log_{10} P(D_2 \text{solid}) = 5.1995 - 68.6144/T + 0.03103\ T \quad (7)$$

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_0, 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_0. By this method, we find that the average value of ΔH_0 in the case of deuterium is 276.0 cal per gram molecule.

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.

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.*

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 $\sqrt{\frac{1}{2}}\,\Theta_1$, the vapor pressure ratio of solid hydrogen and solid hydrogen deuteride at the triple point is found to be approximately 2.42.

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.

Biography

Harold Clayton Urey
The Nobel Prize in Chemistry 1934

Born: 29 April 1893, Walkerton, IN, USA

Died: 5 January 1981, La Jolla, CA, USA

Affiliation at the time of the award: Columbia University, New York, NY, USA

Prize motivation: “for his discovery of heavy hydrogen”

Prize share: 1/1

Born	Harold Clayton Urey April 29, 1893 Walkerton, Indiana, U.S.
Died	January 5, 1981 (aged 87) La Jolla, California, U.S.
Alma mater	Earlham College University of Montana (BSc) University of California, Berkeley (PhD)
Known for	Discovery of deuterium Miller–Urey experiment Carbonate–silicate cycle, aka "Urey reactions"
Awards	Nobel Prize for Chemistry (1934) Willard Gibbs Award (1934) Davy Medal (1940) Franklin Medal (1943) Medal for Merit (1946) Foreign Member of the Royal Society (1947) J. Lawrence Smith Medal (1962) National Medal of Science (1964) Gold Medal of the Royal Astronomical Society (1966) Priestley Medal (1973) V. M. Goldschmidt Award (1975)

-Thank you

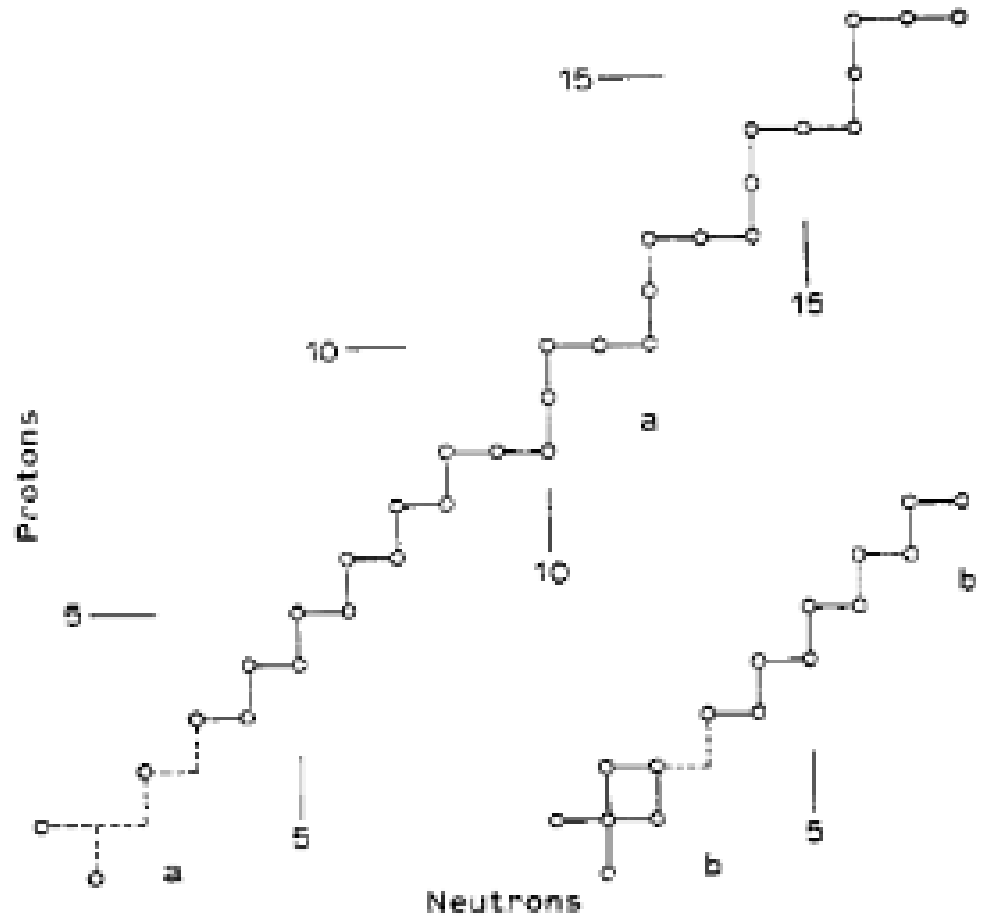

Fig. 1. (a) The plot of the numbers of protons and neutrons in the nuclei of the lighter elements known in 1931; (b) a same plot for the first few elements as of January 1935.