According to Ostwald it is only the un-ionized portion of the molecule that is effective in producing adsorption. The degree of dissociation was determined up to 50 % ionization, using the Ostwald dilution law. This factor is one that caused considerable difficulty, as the dilute solutions were calculated to be over 50% ionized. An attempt was made to determine this value by the hydrogen-ion method but it was impossible to secure checks on any of the solutions used and this method was abandoned.

Summary

1. A general explanation of the chemical theory of capillarity is given.

2. This is shown to serve as an explanation of catalysis.

3. Tables are given showing the adsorption, surface tension, drop weight and density of the different concentrations of oxalic, malonic, succinic, malic, d-tartaric, maleic and fumaric acids and for the diethyl esters of malonic, succinic, d-tartaric and fumaric acids.

4. The absorption of the dibasic acids is less than that of the monobasic acids.

5. The degree of adsorption of the dibasic acids increases with increase in carbon content; however, the increase is not regular for each carbon atom added to the chain.

6. The presence of an hydroxyl group in the molecule decreases the amount adsorbed and raises the surface tension as shown by malic and d-tartaric acids.

7. The esters are adsorbed more than the acids, due to the replacement of the polar carboxyl group by the group $-C(=O)-O-C_2H_5$.

8. The molecules are orientated in the surface with the polar groups in the liquid and the least active portions of the molecule forming the surface.

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THERMODYNAMIC TREATMENT OF THE POSSIBLE FORMATION OF HELIUM FROM HYDROGEN

By Richard C. Tolman

In the light of our newer knowledge concerning the structure of the atom, the suggestion has frequently been made that the nucleus of the helium atom consists of 4 hydrogen nuclei bound together by 2 electrons. If this be the case it is evident that we may write the equation 4H = He as expressing a quasi-chemical reaction.[1]

[1] Reactions for the formation of helium from hydrogen might be written in such forms as $4H^+ + 2E^- = He^{++}$; $4H^+ + 3E^- = He^+$, etc. We have chosen the particular reaction given in the text, since we shall later consider the spectroscopic evidence for the presence of un-ionized hydrogen and un-ionized helium.

If we take the mass of 1 gram atom of hydrogen as 1.0076 and the mass of 1 gram atom of helium as exactly 4.0, it is evident that the above reaction is accompanied by a decrease in mass of 0.0304 g.   In accordance with the theory of the relativity of motion, this loss of mass must correspond to an enormous evolution of energy, and it has been frequently suggested that such a loss of energy when helium is formed would account for the great stability of the α-particle or helium nucleus.[2]   It has also recently been suggested that such an emission of energy would account for the magnitude of the radiation from the giant stars.[3]

If we tentatively assume the validity of the above ideas as to the formation of helium from hydrogen, *and add to them the idea that the entropies of hydrogen and helium would be correctly given by the accepted formula for the entropy of a monatomic gas, even when inter-nuclear reactions are under consideration*, the possibility presents itself of subjecting the above reaction between hydrogen and helium to a thermodynamic treatment. It will be shown in this paper that such a thermodynamic treatment leads to values for the equilibrium between hydrogen and helium which do not accord with the relative amounts of hydrogen and helium in the sun and stars.   The conclusions that can be drawn from this discrepancy will then be discussed.

The Heat of the Reaction

In accordance with the theory of relativity, energy and mass are connected by the equation

$$E = m\,c^2 \tag{1}$$

where c is the velocity of light.   Considering the reaction between monatomic hydrogen and helium, $4H = He$, to be accompanied at the absolute zero by a decrease in mass of 0.0304 g., we may write for the heat of the reaction at the absolute zero

$$\Delta H_0 = -0.0304 \times (2.9994 \times 10^{10})^2 = -2.733 \times 10^{19} \text{ ergs} = -6.535 \times 10^{11} \text{ cal.}$$

and taking the heat capacity of a mol of monatomic gas at constant pressure to be $5/2\,R$, we may write for the heat of reaction at any temperature, T,

$$\Delta H = \Delta H_0 - 3 \times 5/2RT = -6.535 \times 10^{-11} - 14.91\,T \text{ cal.} \tag{2}$$

The Entropy Change Accompanying the Reaction

It has been shown that the entropy of a monatomic gas of molecular weight m is given by the equation[4]

$$S = 5/2\,R\,\ln T - R\,\ln p + \frac{3}{2}R\,\ln m + S_1 \tag{3}$$

[2] The earliest complete expression of these views as to the formation of helium from hydrogen, the loss of energy accompanying the formation, and the resulting stability of the α-particle is due to Harkins and Wilson, THIS JOURNAL, 37, 1367, 1383. 1396 (1915).

[3] Eddington, *Rept. 88th Meeting, Brit. Assoc. Adv. Science*, p. 46 (1920).

[4] For a discussion of this equation see Tolman, THIS JOURNAL, 42, 1185 (1920); 43, 1592 (1921).

where S_1 is the same constant for all monatomic gases. For the change in entropy, when the above reaction takes place under *standard conditions* of unit partial pressure for each of the two gases, we may write,

$$\Delta S = \left(\frac{5}{2} R \ln T + \frac{3}{2} R \ln 4 + S_1\right) - 4\left(\frac{5}{2} R \ln T + \frac{3}{2} R \ln 1.0076 + S_1\right)$$

Taking S_1 as —2.67 cal./deg.,[5] where pressure is expressed in atmospheres, and R as 1.989 cal./deg. and changing to common logarithms we obtain

$$\Delta S = -34.33 \log T + 12.06 \tag{4}$$

The Free Energy Change Accompanying the Reaction

Free energy change is connected with change in heat content and entropy content by the fundamental equation

$$\Delta F = \Delta H - T \Delta S \tag{5}$$

Substituting the values for ΔH and ΔS given above by Equations 2 and 4, we obtain

$$\Delta F = -6.535 \times 10^{11} + 34.33\, T \log T - 26.97\, T \tag{6}$$

for the increase in free energy accompanying the reaction under standard conditions. An examination of this equation shows that even for temperatures as high as a million degrees, the value of the free energy is substantially determined by the heat of reaction at the absolute zero.

The Equilibrium for the Reaction

Free energy change under standard conditions and equilibrium constant are connected by the equation

$$\Delta F = -RT \ln K_p \tag{7}$$

where K_p is the equilibrium constant for the reaction expressed in partial pressures.

Substituting the value for ΔF given by Equation 6 and expressing K_p in terms of the partial pressures we obtain

$$\log \frac{p_{He}}{p^4_H} = \frac{1.426 \times 10^{11}}{T} - 7.5 \log T + 5.85 \tag{8}$$

where the pressures of helium and hydrogen are in atmospheres. An examination of Equation 8 shows at once that even at very high temperatures and very low pressures, hydrogen should combine practically completely to form helium provided equilibrium is attained.

This can perhaps be more easily seen if we rewrite Equation 8 in a slightly different form. Denoting the total pressure of a mixture of hydrogen and helium by

$$p = p_H + p_{He} \tag{9}$$

and the fraction of the helium which is dissociated into hydrogen by x, Equation 8 can easily be written in the form

$$\log \frac{16 x^4 p^3}{(1-x)\,(1+3x)^3} = \frac{-1.426 \times 10^{11}}{T} + 7.5 \log T - 5.85 \tag{10}$$

[5] This is the value given by the theory of ultimate rational units of Lewis and Adams. See Lewis, *Phys. Rev.*, **18**, 121 (1921). It is certainly correct within our present experimental knowledge.

Making use of this equation, we find that the fraction of helium dissociated into monatomic hydrogen even at a temperature as high as 10^6 degrees absolute and a pressure as low as 10^{-100} atmospheres would not be greater than

$$x = 10^{-30000} \tag{11}$$

If we temporarily admit the assumptions upon which the above calculations are based we shall be forced to the conclusion that no appreciable amount of monatomic hydrogen can exist in equilibrium with helium at temperatures below a million degrees and pressures above 10^{-100} atmospheres.

Comparison with Terrestrial, Solar and Stellar Phenomena

It is interesting to compare this extraordinary conclusion with the facts concerning the presence of hydrogen and helium on the earth, in the sun and in the stars.

On the earth it is well known that hydrogen shows no apparent tendency to go over into helium. Hydrogen at terrestrial temperatures is, of course, largely in the diatomic form. Nevertheless, it can easily be shown from the known equilibrium between monatomic and diatomic hydrogen that under terrestrial conditions practically all hydrogen gas should have gone over into helium if equilibrium had been obtained. From the known equilibrium between hydrogen, oxygen and water it can also be shown that this applies to hydrogen combined in the form of water as well as to free hydrogen gas.

In the sun, it is well known from spectral data that monatomic hydrogen and un-ionized helium are both present in appreciable amounts in the chromosphere, at temperatures in the neighborhood of 6000° K. and pressures probably within the range of 1 to 10^{-6} atmospheres, certainly far greater than 10^{-100} atmospheres.[6]

Finally in stars of the classes Oe, Oe5, B0, B2, B3, B5, B8 and B9, lines both from monatomic hydrogen and un-ionized helium are produced under conditions where the temperatures range approximately between 20,000 and 10,000° K.[7] and pressures which again must certainly be great compared with 10^{-100} atmospheres.

Discussion

The problem now presents itself of reconciling the mutual presence of hydrogen and helium under terrestrial, solar and stellar conditions with the tentative thermodynamic prediction of practically complete conversion of hydrogen into helium when equilibrium is attained under the conditions in question.

[6] If the pressures should fall as low as 10^{-100} atmospheres, we should have such complete ionization of hydrogen and helium that the lines of the un-ionized atoms would no longer appear.

[7] See the table of Saha, *Proc. Roy. Soc.*, 99A, 137 (1921).

A number of points of attack present themselves and their discussion will be of interest in suggesting new lines of investigation.

a. One method of meeting the dilemma would be to give up the hypothesis that the helium nucleus is formed from hydrogen nuclei and electrons. At the present time there seems to be no evidence for this assumption beyond the simplification which it introduces into our modes of thought. This simplification, however, is so enormous that we should all be loath to give up the hypothesis as long as other alternatives present themselves.

b. Another method of solving our difficulties would be to assume that the rate of formation of helium from hydrogen is so slow that equilibrium is not attained under the conditions in question. This solution of the problem would have much to recommend itself. The actual mechanism of the reaction for the formation of helium would presumably contain steps of a high order and this would certainly tend to make it slow.[8] Furthermore, it seems to be a general rule that those gas reactions which are accompanied by a great evolution of energy are the very ones which go most slowly at ordinary temperatures. This would easily account for the stability of terrestrial hydrogen. It is more difficult to believe, however, that the rate of reaction at the temperatures in the sun and the classes of stars mentioned above would be slow enough to prevent the establishment of equilibrium in the long time intervals that have been available. A decision as to the probable rate of reaction, however, must await further theoretical developments in the field of chemical kinetics.

c. A third possibility, which presents itself, is that of error in the value taken for the evolution of energy when hydrogen combines to form helium.

In this connection, exception might be taken to the relation between mass and energy which has been used. This relation, however, has been so extraordinarily useful in many other considerations and seems to be so intimately determined by all our present day physical conceptions, that its abandonment must certainly be postponed as long as possible.

The value used for the evolution of energy would also be incorrect if hydrogen does not consist of particles of mass 1.0076, but is really a mixture containing one isotope of mass more nearly unity. The positive-ray analysis of Aston,[9] has apparently checked the chemical value 1.0076 within 0.1%. Nevertheless, the present writer is inclined to believe that the possibility that hydrogen is a mixture of isotopes is not yet definitely excluded.

d. As a fourth possibility, we must consider the justification for taking the heat capacity of our monatomic gases as $5/2\ R$ per mol up to the high temperatures of the sun and stars, since it is evident from the very fact

[8] The actual mechanism of the reaction might even be of higher order than the fourth; see Ref. 1.

[9] Aston, *Phil. Mag.*, **39**, 611 (1920).

that we get spectral emission at all, that electrons in some of the atoms have been displaced from their stable innermost positions or rings, and that more energy has been absorbed than would correspond to the value $5/2\ R$ for a simple particle which can obtain only energy of translation. Consideration, however, will show that neither the value which we have used for ΔH or ΔS would be enough affected to change our main conclusion, even if we increased the values for the heat content and entropy content of hydrogen and helium to the figures which they would obtain on complete dissociation of the atoms in question into nuclei and free electrons.

e. As a fifth consideration we must examine the justification for giving the entropy constant S_1 in the formula for the entropy of monatomic gases

$$S = \frac{5}{2}\,R\,\ln\,T - R\,\ln\,p + \frac{3}{2}\,R\,\ln\,m\,+\,S_1$$

the same value as usually ascribed to it, even though internuclear reactions are to be considered.   An examination of the various methods for deriving the above formula will show that it apparently gives that part of the entropy of the system which is due to the unordered spatial arrangement and to the unordered energy of motion of the monatomic particles as a whole.   The question arises whether there is not an additional quantity of entropy associated with some type of unordered arrangement or unordered energy within the nucleus which would give different values to S_1 for monatomic hydrogen and helium.   Reflection, however, makes this possibility seem improbable, since we must certainly regard the nucleus of an atom as a very tightly bound system of such a nature as not to permit any lack of order in its internal arrangement.   Hence, just as we find the entropy of a crystal at the absolute zero to be zero, we shall be inclined to take the entropy inside the nucleus itself to be zero.   It may further be pointed out that the chance for disorder within the nucleus, if any, would presumably be greater for the complex nucleus of the helium atom than for the presumably simple nucleus of hydrogen, and this would still further decrease the tendency for helium to dissociate into hydrogen.

f. As a final way of explaining the dissociation of helium into hydrogen to an extent far greater than that corresponding to the temperatures and pressures in the sun and stars, we may consider the possibility that the helium atoms are broken down by the action of a very short wavelength radiation which is so penetrating to matter that its amount is not determined by the temperature at the solar or stellar level where the dissociation of helium into hydrogen takes place.   This radiation might have its origin at the very high temperature in the interior of the sun or star and would presumably be of such a short wavelength that a quantum $h\nu$ would be as great as the amount of energy absorbed when a helium atom dissociates

into hydrogen. It will be seen that this hypothesis is entirely similar to that which has already been proposed by Perrin[10] to account for the mechanism of radio-active dissociation.

Summary and Conclusion

By combining the older ideas as to the possible formation of helium from hydrogen, with the newer ideas as to the entropy of monatomic gases, it has been found possible to subject the reaction, 4H = He, to a complete thermodynamic treatment.

The equilibrium constant calculated from this treatment shows that hydrogen should combine practically completely to form helium at all temperatures below a million degrees and pressures above 10^{-100} atmospheres.

The conflict between this conclusion and the mutual presence of hydrogen and helium under terrestrial, solar and stellar conditions has been discussed.

Of the various possibilities presented for reconciling the thermodynamic conclusion as to equilibrium constant and the facts, the present writer is inclined to look with most hope on three of the possibilities,—that the reaction to form helium from hydrogen is an extremely slow one even at 20,000°,—or that hydrogen consists of a mixture of isotopes one of which has an atomic weight nearly unity,—or that helium is decomposed in the sun and stars by the action of an extremely short wavelength radiation which is so penetrating as not to be in temperature equilibrium with the helium affected.

Experimental evidence as to the rate of formation of helium would seem unattainable at the present time, but further theoretical research in the field of chemical kinetics might solve the problem. Further experimental evidence as to the possibility of isotopes of hydrogen would be attainable and very important. Aston's beautiful work certainly seems to show that isotopes do not exist. Nevertheless, the possibility of isotopes is perhaps not yet definitely precluded. Further theoretical consideration of the possibility of the dissociation of helium by very short wavelength radiations, similar to those already postulated by Perrin to explain radio-active decompositions, would be very interesting.

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[10] Perrin, *Ann. phys.*, **11**, 5 (1919).