Sleep is then due to a reversible coagulation of some of the proteins of the centers of consciousness by a substance or group of substances which we will call X and which is produced during work. The coagulating effect of X can be counteracted to some extent by the effect due to the irritability of the sensory nerves. A peptizing agent, such as sodium rhodanate, will decrease this irritability and thereby make sleep possible, though not causing it. A larger dose of the peptizing agent may act also on the centers of consciousness and thereby prevent sleep. Use is made of this when counteracting morphine.

During sleep there is excess production of a substance or group of substances which we will call Y—possibly adrenalin—and which irritates the sensory nerves, waking the sleeper eventually unless he is waked sooner by some other cause—hunger, thirst, digestive disturbances, light on the face, or an alarm clock, for instance.

[1] Hollingworth, *The Psychology of Thought*, 38 (1926).

[2] Piéron, "Le problème physiologique du sommeil," 145, 147, 192, 193, 247 (1913); Dubois, "Physiologie comparée de la marmotte," 27, 28, 44, 235, 248 (1896).

[3] Laird and Muller, *Sleep*, 57 (1930).

[4] Dubois, loc. cit., 76 (1896).

[5] Piéron, loc. cit., 432 (1913).

[6] Laird and Muller, loc. cit., 124 (1930).

[7] Dubois, loc. cit., 248 (1896).

[8] Dubois, loc. cit., 240, 249 (1896).

[9] Marguerite Bellion, *Recherches expérimentales sur l'hibernation de l'escargot*, 23 (1909).

[10] Pavlov, *Conditioned Reflexes*, 251, 253 (1927).

THE ZERO POINT ENERGY AND THE SEPARATION OF ISOTOPES

BY HENRY EYRING

FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY

The very interesting research of Washburn and Urey[1] has shown that as water is electrolyzed the residual portion grows richer in H^2. The purpose of the present note is again to point out the effect of the zero point energy on reaction rates[2] and to show that the greater zero point energy of the lighter isotope effectually aids it in passing over the potential

barriers in the surface reaction $2H^+ + 2$ electrons $= H_2$. For discussion this process may be conveniently separated into two steps. In the first step the hydrogen ion gains an electron and then becomes attached to the surface. The second step corresponds to two of these attached hydrogen atoms approaching each other so that a bond forms between them while the bond to the two surface atoms grows continuously weaker. This second process is of course simply the reverse of an adsorption process and has already been discussed in considerable detail from the point of view of quantum mechanics.[3]

Gurney[4] has considered step one as being chiefly responsible for over-
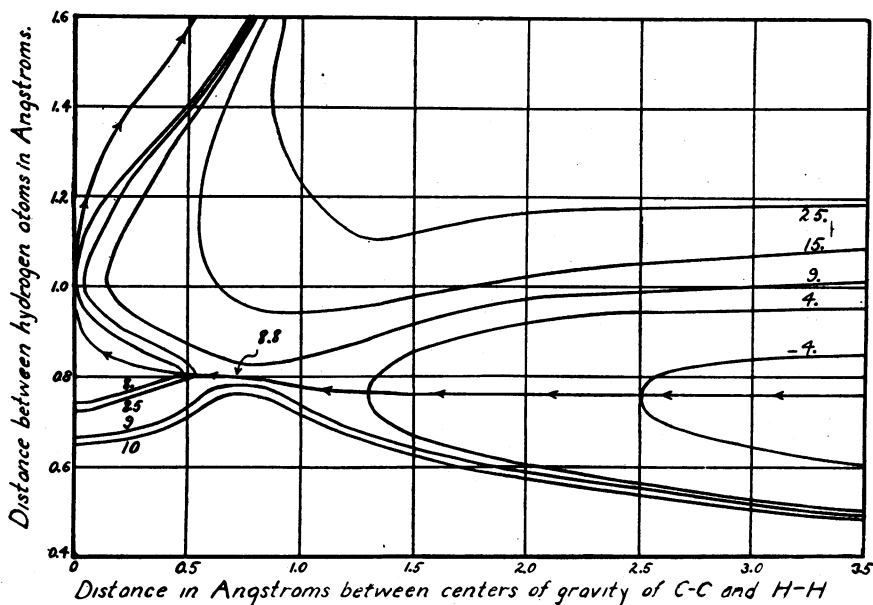

FIGURE 1

Energy contour lines in kg. cal. for the activated adsorption of H_2 on two carbon atoms 3.6 angstroms apart.

voltage. According to this theory the hydrogen ion approaches the metal surface permitting an electron to leak through an energy barrier to neutralize the ion. This point of view seems to account very well for many aspects of overvoltage. Now the nearer the ion approaches the surface the more readily an electron leaks through the thinner barrier. Thus the lighter isotopic ion having a higher zero point energy will come nearer the surface and so should be preferentially discharged. If it were not for the hydration of the ions we might expect this effect to be of considerable importance. It will, however, be practically nullified for an H_3O^+ ion. At the same time the hydrogen ion is being neutralized it is attaching

itself to a suitable atom in the surface if the surface is of a kind to provide such atoms. The second step in our process then ensues and for it the zero point energy for the oscillator, hydrogen atom-surface atom, plays a fundamental rôle.

Figure 1 is a potential energy surface taken from a paper by Sherman and Eyring[3] for the desorption of a hydrogen molecule from carbon. Such a potential surface is exactly the same for a molecule formed from either isotope of hydrogen or for a molecule formed from a mixture.

In all cases the reaction $2C—H \longrightarrow C—C + H_2$ corresponds to the system passing from a point to the left and higher up than any shown on the diagram down along the left edge, through the low point in the energy barrier (marked 8.8 kilo calories) and out along the valley paralleling the lower edge, finally yielding a hydrogen molecule. This is the reverse of the process indicated by the line with arrows in the diagram. If the molecule H^1H^1 is formed the system can finally reach an energy indicated as the zero of energy on the diagram and actually 6.2 kilo calories higher than the lowest potential in the trough of energy surrounded by the contour line -4. If the molecule H^1H^2 is formed the zero of energy is -0.8 kilo calories on the diagram. The state which the hydrogen molecule finally reaches of course has no effect on the activation energy in the electrolysis of water. A similar effect holds, however, for the hydrogen atoms attached to the surface, the different zero point energies for light and heavy isotopes being the important factors. The half quantum of vibration for CH^1 is about 4.2 kilo calories while for CH^2 it is about 3.1 kilo calories. Now the zero point energies for a system at the low point in the pass, the so-called activated state, will be very small in all cases. Thus we see that to form the molecule H^1H^2 by desorption from a carbon surface will require an activation energy of about 1.2 kilo calories more than to desorb H^1H^1. So that the latter should have a specific rate at room temperature approximately 6.3 times the latter.

The difference in activation energy for the two isotopes is much greater than the difference in the corresponding electrode voltages and the two effects are of course to be distinguished. The situation may be summarized by the statement that in reactions the heavier isotopes are slightly more inert. It should be interesting to determine whether the difference in zero point energy in step two is solely responsible for the observed isotopic separation. The zero point energy effect should permit separation by many reactions not involving electrolysis. In considering overvoltage connected with the electrolysis of gases step two should not be neglected.

The foregoing represents the theoretical approach to the problem of isotope separation as dependent on zero point energy in processes involving velocity of adsorption as one special case of the general influence of zero point energy in reaction velocity. The intimate connection between the

published data on separation by electrolysis and of desorption with the consequent necessity for different velocities of desorption, and therefore of adsorption, of isotopes at electrode surfaces was also realized by Professor Hugh S. Taylor who is arranging for an experimental test of the possibilities of separation by such processes.

[1] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).
[2] H. Eyring and M. Polanyi, *Z. physik. Chem.*, [B] **12**, 279 (1931).
[3] A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).
[4] R. W. Gurney, *Proc. Roy. Soc. (London)*, **A134**, 137 (1931).

THE REACTION OF HYDROGEN ATOMS WITH OXYGEN AND THE HYDROGEN CHLORINE REACTION
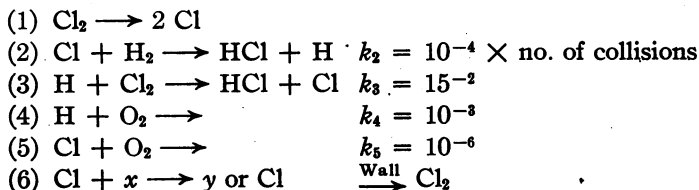
By John R. Bates

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN

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The rapidity with which the experimental facts connected with the photochemical union of hydrogen and chlorine change and have changed during the last century, always gives a discouraging outlook to any complete solution of the mechanism of the reaction. The results obtained during the last year, however, while still representing a comparative mobile condition, tend for the most part toward a greater simplification of the problem.

Notable among these results is the discovery in Bodenstein's laboratory[1,2] that the influence of water vapor on the reaction is not as given by the earlier work of Coehn and Jung. It is found that water vapor is without effect on the reaction. Thus is removed a difficulty which seemed to be increasingly impossible of explanation, in spite of a number of ingenious attempts.

At the symposium on photochemistry held by the Faraday Society[3] in 1931, Bodenstein pointed out that many of the facts of the reaction could be correlated in a very simple manner if we postulate the following mechanism:

(1) $Cl_2 \longrightarrow 2\ Cl$
(2) $Cl + H_2 \longrightarrow HCl + H$ $k_2 = 10^{-4} \times$ no. of collisions
(3) $H + Cl_2 \longrightarrow HCl + Cl$ $k_3 = 15^{-2}$
(4) $H + O_2 \longrightarrow$ $k_4 = 10^{-3}$
(5) $Cl + O_2 \longrightarrow$ $k_5 = 10^{-6}$
(6) $Cl + x \longrightarrow y$ or Cl $\xrightarrow{\text{Wall}} Cl_2$

From these may be derived the equations representing the experimental results of Thon,[4]