Theoretical Considerations Concerning the Separation of Isotopes

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The relative importance of effusion processes, the half quanta due to van der Waals forces, and half quanta associated with homopolar bonds is considered with respect to the question of the separation of isotopes. Specific reaction rate constants for various isotopic molecules in effusion processes have been calculated. It is shown that only in the neighborhood of liquid hydrogen temperatures or lower are the half quanta due to van der Waals forces important. Specific reaction rate constants involving the zero point energy of homopolar molecules have been calculated for various isotopic molecules, principally those in which a hydrogen atom is one constituent, at temperatures of 20°K, 90°K, and 273°K. The advantage of working at as low a temperature as possible is rendered apparent. Even at ordinary temperatures the differences in the constants are in general much greater than in the case of effusion or van der Waals processes. A general equation is derived relating the concentration of the light and heavy isotopes, valid for any one of the three processes considered.

RECENTLY theoretical discussions of the effect of zero point energy on reaction rates, with particular reference to the question of separating the hydrogen isotopes have been given.[1] This general question now possesses additional interest as a result of recent experiments.[2]

Lewis reports the obtaining of water of specific gravity 1.035, presumably by electrolysis. Taylor, Gould and Bleakney obtained a 5-fold increase in concentration of H^1-H^2 over that present in ordinary hydrogen by desorbing hydrogen from an active charcoal surface at liquid air temperatures. It is the purpose of this paper to consider the subject in greater detail and to present the results of some calculations which show maximum differences in specific reaction rate constants to be expected, at various temperatures, in reactions involving various isotopic molecules.

We shall first consider effusion processes. The rate at which a molecule of molecular weight M effuses through an orifice is proportional to its velocity component in the direction normal to the orifice. This in turn is inversely proportional to the square root of the molecular weight, as is shown by kinetic theory. The ratio of the specific rates of effusion of gaseous molecules of molecular weights M_1 and M_2 will, therefore, be proportional to $(M_2/M_1)^{\frac{1}{2}}$. This ratio is of course independent of temperature.

Consider a gas containing two isotopic molecules of concentration (X) and (Y) effusing through an orifice. One can think of the two processes as independent unimolecular reactions in the ordinary way and obtain for the relative concentration of the isotopes the expression $(Y_0)/(Y) = (X_0/X)^{(M_x/M_y)^{\frac{1}{2}}}$. The subscript 0 denotes the initial concentration. In column three of Table I is given the relative increase in concentration of the heavy isotope to be expected in the remaining gas when the pressure is reduced to the fraction of the initial pressure indicated in column two.

TABLE I.

Gas	Pressure drop	Relative increase in H^1-H^2
H^1-H^1	1/100	2.28
H^1-H^2	1/10	1.52
	1/5	1.34
$O^{16}-O^{16}$	1/100	1.15
$O^{16}-O^{18}$	1/10	1.07
	1/5	1.05
$N^{14}-N^{14}$	1/100	1.08
$N^{14}-N^{15}$	1/10	1.04
	1/5	1.03

[1] Cremer and Polanyi, Zeits. f. physik. Chemie **19B**, 443 (1932); Eyring, Proc. Nat. Acad. Sci. **19**, 78 (1933).

[2] Washburn and Urey, Proc. Nat. Acad. Sciences **18**, 496 (1932); G. N. Lewis, J. Am. Chem. Soc. **55**, 1297 (1933); H. S. Taylor, Gould and Bleakney, Phys. Rev. **43**, 496 (1933); Washburn, Smith and Frandsen, J. Chem. Phys. **1**, 288 (1933).

In the experiments of Taylor, Gould and Bleakney an initially adsorbed 5025 cc, desorbed to 35 cc, showed a 3-fold increase in the heavy isotope, while with 5715 cc adsorbed a reduction to 90 cc in a two stage process showed a 5-fold increase. It is seen from Table I that the results cannot be accounted for by an effusion process alone because the 5715 cc to 90 cc reduction should produce, at most, a 2-fold increase, in contrast to the 5-fold actually obtained. It is therefore clear that other factors must play an important rôle. If the molecules are not initially free but are escaping from a solid or liquid surface the forces with which they are held will further modify the specific rate for the two isotopes. To estimate the effect of the van der Waals forces in a liquid we shall use the empirical potential functions of Lennard Jones.[3]

For the potential energy between two hydrogen molecules as a function of the distance, r, between them, he gives

$$E = (48.9 \times 10^{-115})/13\tfrac{1}{3}r^{13\tfrac{1}{3}}$$

$$- (15.6 \times 10^{-45})/4r^4 \text{ ergs/molecule.}$$

One might object to the use of this function for this purpose on the grounds that it was designed to explain observed results on the basis of classical mechanics but a detailed consideration of the potential energy between hydrogen molecules using perturbation theory gives essentially the same results.[4]

Consider the removal to infinity of a hydrogen molecule initially at a distance r from a liquid hydrogen surface. Assume the molecules of the liquid are, on the average, at the corners of a cube, the size of which, calculated from the observed density of the liquid, is 3.6A. The van der Waals attraction of the molecule will be the sum of the attractions of the molecules in the liquid. The 196 nearest neighbors give the energy E presented in Table II, for distances, along the normal to the surface, equal to r. The contribution to the energy of the remaining molecules is small.

We fit the parabola $y - a = \tfrac{1}{2}k(x - b)^2$ to the values in Table II and use for the vibrational

frequency $\omega = (1/2\pi)(k/\mu)^{\frac{1}{2}}$, where we take for the reduced mass of the oscillator consisting of one molecule vibrating against the surface, the mass of the molecule. In this way we obtain for the oscillators H^1H^1 and H^1H^2 half quanta of 56.3 and 46.0 calories/mol, respectively. This gives a difference of 10.3 calories/mol as the difference between the half quanta so that, at the boiling point of liquid hydrogen, 20°K, the relative specific rates of desorption of H^1H^1 and H^1H^2 due to this energy alone is $e^{10.3/2 \times 20} = 1.29$.

TABLE II.

r (A)	3.20	3.40	3.60
E (ergs/mol)	-51.66×10^8	-53.96×10^8	-51.77×10^8

In considering the actual rate of escape from the surface this factor should probably also be multiplied by the factor arising from the difference in velocities for the effusion process discussed above.

Thus we see that the van der Waals forces in the evaporation of liquid hydrogen will materially increase the concentration of the heavier isotope in the residue.

We now make a rough estimate of the half quantum for van der Waals adsorption of a hydrogen molecule on charcoal at liquid air temperatures. For homopolar molecules the heat of dissociation, D, is approximately proportional to the force constant k for a wide variety of molecules as is shown by the fact that the constant a of the Morse equation varies but little from molecule to molecule. This same approximate proportionality holds for the van der Waals potential holding two molecules together. This is readily seen by a consideration of the empirical curves given by Lennard-Jones. For the evaporation process of any molecule held to a liquid or solid surface by van der Waals forces the force constant will remain about proportional to D for different surfaces and different molecules. A test of this assumption for the evaporation of liquid He, H_2, Ne, N_2 and A indicates that the force constant k does not rise quite as rapidly as the boiling point.

In the table k is the force constant for the oscillator molecule-surface. These values of k

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[3] Fowler, *Statistical Mechanics*, Chapter X, Cambridge Univ. Press, 1929.

[4] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

were calculated in the manner described for H_2, using the constants given by Lennard-Jones for the equation

$$E = \lambda r^{-n+1}/(n-1) - \mu r^{-m+1}/(m-1).$$

ΔH_v is the heat of vaporization and T_β the boiling point. The value of n used was $14\frac{1}{3}$ and of m used was 5.

For the evaporation of any molecule held to a liquid or solid surface we may expect Trouton's rule to hold, namely that the heat of vaporization is proportional to the absolute temperature at which the vapor pressure is atmospheric. Consequently we expect $\frac{1}{2}h\omega = (c/2\pi)(T/M)^{\frac{1}{2}}$ to hold roughly for all substances. If c is chosen to fit for liquid hydrogen the calculated half quanta for substances with higher boiling points will probably be too high. As before, M is the reduced mass. Thus the difference in the half quanta for H^1H^1 and H^1H^2 at liquid hydrogen temperatures is 10.3 calories while for the same molecules boiling from charcoal at liquid air temperatures a difference of about $10.3(90/20)^{\frac{1}{2}} = 21.85$ calories or less is to be expected for molecules held by van der Waals forces. This gives for the ratio of the specific reaction rates at 90°K the value 1.13, which is less than the difference due to rates of effusion. Because of the larger reduced masses van der Waals forces will play an even less important rôle for substances other than hydrogen.

It thus seems clear that Urey, Brickwedde and Murphy's[5] separation of the hydrogen isotopes at the triple point (insofar as it departs from an equilibrium process) was due to van der Waals forces, helped by differences in the effusion rates of the isotopes, while the results of Taylor, Gould and Bleakney[6] at liquid air temperatures can only be explained on the basis of surface forces with greater associated half quanta than those of the van der Waals type.

When the hydrogen molecules instead of being held by the long range polarization or van der Waals forces are dissociated and form homopolar bonds with atoms in the surface the corresponding half quanta are much larger. In Table III are

[5] Urey, Brickwedde and Murphy, Phys. Rev. **39**, 164 (1932).

[6] Taylor, Gould and Bleakney, Phys. Rev. **43**, 496 (1933).

TABLE III.

Gas	He	H₂	Ne	N₂	A
k	34	186	441	238	740
$k/\Delta H_v$	1.4	0.87	1.1	0.18	0.49
k/T_β	7.9	9.2	12.9	3.0	8.5

tabulated values for the extreme case where the surface atom and the adsorbed atom behave as isolated oscillators. The actual half quanta for surfaces will no doubt in general be smaller but the table should help in the selection of a desirable surface for separation of isotopes by either desorption or electrolysis.

The ratios of the factors $e^{E/RT}$ for light and heavy isotopes in columns 3, 4 and 5 give the relative specific rates at 20°, 90° and 273°K. The advantage of using low temperatures becomes strikingly obvious. Thus, for $C^{12} - H^1$ and $C^{12} - H^2$ these ratios are 1.3×10^{12}, 5.0×10^2, and 7.7 at 20, 90 and 273°K respectively. (Table IV.)

The calculations for electrolysis or desorption presuppose reaction processes with identical potential barriers for both isotopes. The chief difference in relative rates arises from the greater half quanta of the lighter isotope. Consider the case where hydrogen atoms are being desorbed from a solid surface to make hydrogen molecules. This can occur by two light atoms coming off together, or a light and heavy one, or finally by two heavy ones combining. If we represent the concentration of heavy isotope by y, and light ones by x, we have the two simultaneous equations,

$$-dx/dt = kx^2 + ksxy; \quad -dy/dt = ksxy + ks^2y^2. \quad (1)$$

The two equations become identical if we take $y = cx^s$ so that this relationship is maintained between light and heavy isotopes. Evaluating c by putting in the initial concentrations x_0 and y_0 we obtain

$$y/y_0 = (x/x_0)^s. \quad (2)$$

Of course $s = e^{-\Delta E/RT}$ where ΔE is the difference between the zero point energy for an oscillator composed of a surface atom and H^1 and for a second oscillator composed of a surface atom and H^2. Further, s is a proper fraction.

It is interesting to observe that (2) is the same relationship obtained for the separation by

TABLE IV.

Bond	$\frac{1}{2}h\nu$ (kg.cal.)	$e^{E/20R}$	$e^{E/90R}$	$e^{E/273R}$	Bond	$\frac{1}{2}h\nu$ (kg.cal.)	$e^{E/20R}$	$e^{E/90R}$	$e^{E/273R}$
H^1-H^1	6.2	7.2×10^{67}	1.2×10^{15}	$9.4\times10^{\cdot}$	$Ni-H^1$	2.3	5.7×10^{24}	3.2×10^{5}	6.5×10^{1}
H^1-H^2	5.4	5.9×10^{58}	1.2×10^{13}	2.0×10^{4}	$Ni-H^2$	1.6	4.5×10^{17}	8.4×10^{3}	2.0×10^{1}
H^2-H^2	4.4	9.9×10^{47}	4.6×10^{10}	3.3×10^{3}	$Au-H^1$	3.2	7.8×10^{34}	5.7×10^{7}	3.6×10^{2}
$O^{16}-H^1$	5.2	5.9×10^{56}	4.1×10^{12}	1.4×10^{4}	$Au-H^2$	2.3	5.4×10^{24}	3.1×10^{5}	6.5×10^{1}
$O^{16}-H^2$	3.8	2.1×10^{41}	1.5×10^{9}	1.1×10^{3}	$Zn-H^1$	2.3	1.1×10^{25}	3.7×10^{5}	6.8×10^{1}
$O^{17}-H^1$	5.2	4.7×10^{56}	3.9×10^{12}	1.4×10^{4}	$Zn-H^2$	1.6	7.0×10^{17}	9.2×10^{3}	2.0×10^{1}
$O^{17}-H^2$	3.8	1.5×10^{41}	1.4×10^{9}	1.0×10^{3}	$Hg-H^1$	2.0	1.7×10^{22}	8.7×10^{4}	4.3×10^{1}
$O^{18}-H^1$	5.2	3.9×10^{56}	3.8×10^{12}	1.4×10^{4}	$Hg-H^2$	1.4	5.2×10^{15}	3.1×10^{3}	1.4×10^{1}
$O^{18}-H^2$	3.8	1.1×10^{4J}	1.3×10^{9}	1.0×10^{3}	Hg^+-H^1	2.9	1.9×10^{31}	8.9×10^{6}	2.0×10^{2}
$C^{12}-H^1$	4.2	2.8×10^{45}	1.3×10^{10}	2.1×10^{3}	Hg^+-H^2	2.0	1.3×10^{22}	8.2×10^{4}	4.2×10^{1}
$C^{12}-H^2$	3.1	2.2×10^{33}	2.6×10^{7}	2.8×10^{2}	$O^{16}-O^{16}$	2.25	3.8×10^{24}	2.9×10^{5}	6.3×10^{1}
$C^{13}-H^1$	4.1	2.0×10^{45}	1.2×10^{10}	2.1×10^{3}	$O^{16}-O^{17}$	2.22	1.7×10^{24}	2.4×10^{5}	6.0×10^{1}
$C^{13}-H^2$	3.0	1.5×10^{33}	2.4×10^{7}	2.7×10^{2}	$O^{16}-O^{18}$	2.19	7.6×10^{23}	2.0×10^{5}	5.6×10^{1}
$Be-H^1$	3.0	4.6×10^{32}	1.8×10^{7}	2.5×10^{2}	$O^{17}-O^{18}$	2.15	3.2×10^{23}	1.7×10^{5}	5.3×10^{1}
$Be-H^2$	2.2	1.7×10^{24}	2.4×10^{5}	6.0×10^{1}	$O^{18}-O^{18}$	2.12	1.5×10^{23}	1.4×10^{5}	5.0×10^{1}
$Al-H^1$	2.4	1.2×10^{26}	6.3×10^{5}	8.2×10^{1}	$N^{14}-N^{14}$	3.35	4.0×10^{36}	1.4×10^{8}	4.8×10^{2}
$Al-H^2$	1.7	5.9×10^{18}	1.5×10^{4}	2.4×10^{1}	$N^{14}-N^{15}$	3.29	9.4×10^{35}	9.9×10^{7}	4.3×10^{2}
$Fe-H^1$	1.9	3.6×10^{20}	3.7×10^{4}	3.2×10^{1}	$N^{15}-N^{15}$	3.23	2.3×10^{35}	7.2×10^{7}	3.9×10^{2}
$Fe-H^2$	1.3	4.5×10^{14}	1.8×10^{3}	1.2×10^{1}	$Cl^{35}-Cl^{35}$	0.80	5.9×10^{8}	8.9×10^{1}	4.4
$Pt-H^1$	1.7	7.6×10^{18}	1.6×10^{4}	2.4×10^{1}	$Cl^{35}-Cl^{37}$	0.79	4.6×10^{8}	8.4×10^{1}	4.3
$Pt-H^2$	1.2	2.4×10^{13}	9.4×10^{2}	9.6	$Cl^{37}-Cl^{37}$	0.78	3.4×10^{8}	7.9×10^{1}	4.2
$Cu-H^1$	2.7	3.4×10^{29}	3.6×10^{6}	1.5×10^{2}					
$Cu-H^2$	1.9	1.1×10^{21}	4.8×10^{4}	3.5×10^{1}					

effusion or by van der Waals forces if s is interpreted, there also, as the ratio of the specific rates for the light and heavy isotopes. Thus the determination of the efficacy of separation by the three processes reduces to comparing the ratios of the specific reaction rates.

It is of course possible to distinguish experimentally the first order desorption of molecules held by van der Waals forces and the desorption of atoms which obey the Eq. (1). Eqs. (1) become after the substitution of (2)

$$\int_{x_0}^{x} \frac{dx}{x^2+[s(y_0/x_0^s)]x^{s+1}} = -kt,$$

and for y_0/x_0 very small this behaves for a considerable time as a typical second order reaction.

From Table II we see that the separation of other isotopes than those of hydrogen should at least be more readily attained by reactions at suitably low temperatures than by a straight diffusion process. The particular virtue of electrolysis is that, even though the activation energy (overvoltage) may be considerable, still, by applying a suitable potential, the reaction may be made to go at low temperatures. The same object may be accomplished by carrying out reactions photochemically. With this in mind Taylor and Gould are carrying out the hydrogen

and chlorine reaction at suitably low temperatures. Of course any other agent than light which will supply atoms at low temperatures would do equally well.

Many reactions which in a laboratory would proceed too slowly at ordinary temperatures to secure the desired separation may have occurred geologically where an entirely different time scale is available. Low temperature mineralizing and erosion processes immediately suggest themselves.

Since all chemical reactions having a positive temperature coefficient will go about half as fast, or less, at ordinary temperatures with the heavy as with the light hydrogen isotope it will be possible to single out such reactions in biological processes.

Separation of isotopes due to equilibrium differences have been frequently discussed and require no additional consideration here. In general such separations will be less efficient than the corresponding dynamic processes. The heavier isotope approaches equilibrium more slowly from both directions.

CONCLUSIONS

Detailed calculations of the rôle of zero point energy in the separation of isotopes by dynamic processes are given. Apparently only in the

neighborhood of liquid hydrogen temperatures are the half quanta due to van der Waals forces important. Processes which involve the breaking of homopolar bonds at moderate or low temperatures are far more efficient than effusion processes.

Any agents which provide atoms at low temperatures which then enter into subsequent reactions are particularly effective. Familiar examples are catalysts, light, electric discharges, and electrolysis.