

ture allowed to rise slowly. No change was apparent until the temperature -1.5° was reached, when the entire liquid layer began to decompose with the rapid evolution of hydrogen sulfide.

Within the temperature limits of this investigation, no other breaks were observed. It seems probable, therefore, that below and above -1.45° the liquid phases consist of equilibrium mixtures of various polysulfides, always with the possibility of the presence of dissolved sulfur. The solubility curve readily explains the results obtained by Rebs⁷ who poured alkali polysulfides corresponding to H_2S_2 , H_2S_3 and H_2S_5 , into cold conc. hydrochloric acid. He obtained a product that he considered to be H_2S_5 , although the analysis varied from $H_2S_{4.7}$ to $H_2S_{5.7}$. In the light of the foregoing experiments it is evident that Rebs obtained equilibrium mixtures of sulfur and polysulfides, the composition varying with the temperature of the reaction mixture. The free sulfur necessary for equilibrium could easily have been provided by decomposition of some of the polysulfides, which always occurs when the yellow oil is prepared.

It is of further interest to point out that the instability of hydrogen hexasulfide above -1.45° explains the necessity of keeping the reaction mixture cold when preparing the yellow oil.

Summary

1. Hydrogen disulfide and hydrogen trisulfide dissolve sulfur copiously. When these two liquids are saturated with sulfur at a given temperature the two resulting liquid phases have the same composition.

2. A solubility curve has been established by saturating hydrogen trisulfide with sulfur at temperatures ranging from -34.71° to $+55.3^{\circ}$.

3. The existence of a compound having the composition H_2S_5 has been established. This compound is stable below -1.45° .

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS] A STATISTICAL THEORY OF MONOMOLECULAR REACTIONS

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The change of specific reaction rate with the temperature can be represented fairly well for many reactions by an equation of the form, $k = s e^{-E/RT}$ where s is presumably a constant characteristic of the reaction in question and E , R and T have their usual significance. If we assume that only those molecules react which have acquired, through a particularly violent collision or otherwise, a certain "critical" amount of energy greatly in excess of the average energy per molecule, then the kinetic theory offers us a physical basis for the derivation of the equation above. A

⁷ Rebs, *Ann.*, **246**, 356 (1888).

number of writers have speculated upon this basis.¹ Arrhenius² showed that this equation is, if not a thermodynamic consequence, at least in agreement with thermodynamics. Marcelin³ attempted to derive from statistical mechanics an expression for the rate at which molecules become "activated" and obtained an expression similar to the one above, but his derivation is invalidated by an error which has been pointed out by Tolman.⁴ Dushman⁵ has suggested that not only the temperature coefficient but also the absolute rate of the reaction itself is given by the equation if we assume that $s = \nu = E/Nh$. Dushman has made a large number of calculations using this modified form of the equation, and has obtained fair agreement with experimental results but most of his calculations involve the necessity of assumption in regard to molecular diameter and number of effective collisions.

In the case of a monomolecular reaction in the gaseous phase where the rate of reaction is independent of the concentration, the kinetic theory appears, at first thought, inadequate to explain the mechanism underlying the reaction, since the rate of reaction must be independent of the number of collisions. This question, which was formerly an academic one, becomes of real interest since the work of Daniels⁶ and Johnston which furnishes us with reliable data upon the rate of an apparently bona fide monomolecular reaction in the gaseous phase.⁷

The fact that the various theories of radiation as a cause of chemical reactions have so far apparently failed of experimental verification in the case of the decomposition of nitrogen pentoxide, has led the author to the belief that the reaction could be explained upon the basis of the kinetic theory alone, and he has attempted a derivation of an expression from statistical mechanics with rather gratifying results. The fundamental postulate of this derivation is that, while molecules may, of course, receive energy by radiation, the greater part of the interchange of energy between molecules at moderate temperatures takes place by collision. Also, it appears that Dushman's assumption of the factor $s = \nu = E/Nh$ does have a theoretical justification, but the term s is found to be also a function of the temperature. With the complete expression finally obtained, the

¹ Compare Tolman, *THIS JOURNAL*, **43**, 269 (1921).

² Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

³ Marcelin, *Ann. phys.*, **3**, 120 (1915).

⁴ Tolman, *THIS JOURNAL*, **44**, 76 (1922).

⁵ Dushman, *ibid.*, **43**, 397 (1921).

⁶ Daniels, *ibid.*, **43**, 53 (1921).

⁷ The decomposition of phosphine appears to be a monomolecular reaction according to the work of Trautz and Bhandarkar [*Z. anorg. allgem. Chem.*, **106**, 95 (1919)] but the work was carried out under such experimental difficulties that the accuracy of the measurements is open to question. Radioactive decompositions present an entirely separate problem in monomolecular reactions since they are independent not only of concentration but also of temperature.

rates of reaction for the two monomolecular reactions for which accurate data are available, can be calculated with extraordinary success.

Marcelin³ appears to have made two assumptions in his derivation which are a start in the right direction. The first is that the activation of a molecule for any sort of a reaction can be represented as the acquirement of a certain critical energy in some one mode of motion or degree of freedom, which might, for example, be the oscillation of an atom in a molecule or of an electron within a single atom. The second assumption is that it is not the actual number of "activated" molecules present at any instant which determines the rate of reaction, but the rate at which molecules acquire this critical energy. The reasonableness of these assumptions becomes apparent if we consider evaporation of molecules from the surface of a solid or liquid. Obviously, only those molecules escape from the surface which have sufficient momentum in the direction normal to the surface. Furthermore, it is only the molecules on the surface which can escape. As soon as one of these molecules does attain the critical momentum upward, it does escape. The rate of evaporation then depends upon the rate at which the molecules in the surface acquire the critical energy. The same considerations will apply to any sort of monomolecular reaction.

Statistical considerations can apply to only those reactions in which the rate is slow enough so that no appreciable disturbance of statistical equilibrium takes place. When this condition is satisfied, we may then proceed to a consideration of statistical equilibrium as if the reaction were not taking place at all. Accordingly, we shall proceed to obtain an expression for the rate at which molecules acquire a given critical energy in the simpler cases with confidence that the result so obtained will be valid for all cases. This expression can be most easily obtained by finding the rate at which molecules having the critical energy or above, lose energy and pass to a condition where they possess less than the critical amount. We shall not in this article consider any cases where the critical energy is less than about 45 times the average kinetic energy per degree of freedom per molecule.

In the simplest case, that of a monatomic gas whose molecules possess only kinetic energy due to translational motion, Jeans⁴ shows that any molecule of relatively high velocity will, on the average, lose the major portion of its energy at the first collision. This means that all but a negligible fraction of the molecules possessing energy above the critical, will on the first collision pass below the critical value or cease to be "activated."

The rate, then, at which molecules cease to be activated will be given by the number of impacts per unit time of molecules having kinetic energy above the critical amount.

⁴ Jeans, "Dynamical Theory of Gases," Cambridge University Press, 1921, Chap. X.

Likewise, Langmuir⁹ has shown from practical considerations that a molecule of a crystal possessing a high kinetic energy loses the greater part of this energy on collision with the adjacent molecule. Volmer and Estermann¹⁰ have shown experimentally that at low pressure there is no appreciable reflection of the atoms of mercury vapor from the surface of liquid mercury with which it is in equilibrium. It is generally agreed that the "time of relaxation" for molecules or atoms moving independently with high kinetic energy in a condensed phase, is very short.⁹

Let us assume that the "activation" of a molecule undergoing a chemical change such as dissociation means that one of the atoms of the molecule has acquired a certain critical energy of oscillation in the molecule. Then this atom must, at either end of its oscillation, when its motion is checked undergo what amounts to a collision either with the rest of the molecule to which it belongs, or with an adjacent molecule. The rate at which impacts occur then becomes a question of frequency of vibration rather than of mean free path. The same sort of reasoning might be applied to an electron which was sharing in the partition of energy since it would be more liable to disturbance in certain portions of its orbit. We shall assume, however, a vibrating atom since we know that the atoms do take part to a considerable extent, at least in the partition of energy. If now we represent the number of molecules in which this particular atom possesses vibrational energy in excess of the critical amount as \bar{N} , and let ν be the average frequency of vibration, then the rate at which impacts occur and hence the number of molecules which lose the critical energy per unit time is given by the expression

$$dN = 2\nu\bar{N}^{11} \quad (1)$$

The distribution of kinetic energy among the individual molecules of a system in any particular mode of vibration is represented by the expression

$$dN = \frac{N}{\sqrt{\pi}} e^{-E/RT} d\sqrt{E/RT}^{12} \quad (2)$$

⁹ Langmuir, *THIS JOURNAL*, **38**, 2250 (1916).

¹⁰ Volmer and Estermann, *Z. Physik*, **7**, 1 (1921).

¹¹ Since, in general, two impacts occur per complete oscillation, the factor 2 appears in the expression.

¹² Jeans, *Ref. 8*, p. 87. Langmuir, *THIS JOURNAL*, **42**, 2188 (1920). The objection of Kraus, *ibid.*, **43**, 2527 (1921) that the distribution law cannot be applied to ions, does not appear to be well founded. The expression for the distribution of potential energy is not so simple unless the oscillations are simple harmonic, but since we are interested in the *transfer of energy by collisions*, apparently we are concerned only with the distribution of kinetic energy. It may be objected that the above distribution law cannot be applied unless we have complete equipartition of energy in the internal degrees of freedom of the molecule. As a matter of fact, equipartition is very nearly established at ordinary temperatures, and for large values of E the expression given by the quantum theory becomes identical with the one above, even where equipartition is not established.

This expression is valid for molecules, ions, or whatever component portions thereof are capable of independent motion and partake in the equipartition of energy. Hence

$$\bar{N} = \frac{N}{\sqrt{\pi}} \int_{E=E_0}^{E=\infty} e^{-E/RT} d\sqrt{E/RT} \quad (2)$$

The definite integral is obtained in the form of a series but since E_0 is large compared to RT we can discard all but the first term which is

$$\bar{N} = N \sqrt{\frac{RT}{E_0\pi}} e^{-E_0/RT} \quad (3)$$

The error in this approximate expression is less than $RT/2E_0$. Hence, the rate at which molecules cease to be activated is given by the expression

$$dN = 2\bar{\nu}N \sqrt{\frac{RT}{E_0\pi}} e^{-E_0/RT} \quad (4)$$

But at equilibrium this must equal the rate at which molecules become activated and, hence, must be the expression we are seeking.

We are now ready to apply the equation to the data obtained by Daniels and Johnston. Tolman¹ has applied the simple equation of Dushman to this reaction and obtained a calculated rate of reaction about five times the observed. If we assume with Dushman¹³ that $\bar{\nu} = E_0/Nh$ and that a molecule decomposes as soon as it attains the critical energy, we will have then

$$k = \frac{dN}{N} = \frac{1}{Nh} \frac{\sqrt{E_0RT}}{\sqrt{\pi}} e^{-E_0/RT} \quad (5)$$

It is first necessary to solve for the heat of activation. This is then substituted in the formula and the absolute rate of reaction obtained. The results are tabulated below.

Temp. ° K.	k calc.	k calc. by Tolman	Found
338	3.71×10^{-3}	19×10^{-3}	4.87×10^{-3}
298	2.54×10^{-5} ($E_0 = 24500$)	($E_0 = 25000$)	3.38×10^{-5}

It will be noted that this equation leads to a slightly different heat of activation than that obtained by Tolman. The agreement is most extraordinary and in view of the fact that a slight change in ratio of the rates of reaction at the two temperatures would cause a change in the value for the heat of activation and hence a relatively great change in the calculated rates of reaction, it is well within the experimental error.

¹³ Apparently the more exact expression would be $\bar{\nu} = \bar{E}/Nh$, where \bar{E} is an average value for all the molecules which possess more than the critical energy in the degree of freedom in question. Calculations from the distribution law show, however, that \bar{E} is approximately equal to E_0 .

¹⁴ Since the dissociation can occur presumably only by motion in one direction, only half the molecules that acquire the critical energy really become activated and the factor 2 falls out.

The methods of statistical mechanics are so general that they cause us to lose sight of the mechanism of a particular reaction. It might be well to try to picture how the result which we have obtained above, whereby the rate of reaction is independent of the number of collisions, actually comes about. The mechanism which is really postulated by our deductions is that the molecule decomposes when it acquires a certain configuration or distribution of energy in its internal degrees of freedom. Since the internal motions are oscillations, they have definite frequencies and hence the molecule proceeds from configuration to configuration with a definite rate. Collisions with other molecules come so frequently that the molecule is not allowed to fall into any condition of stationary oscillations, but the internal motions must be so well insulated against external collisions that a variation in the number occurring in a given time has no effect on the rate at which the molecule passes from one configuration to another. Since at 1 atmosphere and 298° K. probably 10^{14} collisions¹⁵ occur for every molecule that decomposes, this conclusion does not appear unreasonable.¹⁶

The assumption of statistical equilibrium in the internal degrees of freedom of the molecule may appear doubtful at first thought, but reflection shows that so far as statistical considerations are concerned a gas is hardly different from a solid or liquid.

As to the quantum relation, $\bar{\nu} = E_0/Nh$, we are still very much in the dark. Recent investigators have shown, however, that it may be nothing more mysterious than the existence of a fundamental relation in the mechanics of matter between the frequency and energy of an oscillation.¹⁷

The only other monomolecular reaction for which we have accurate data is the evaporation of a monatomic liquid.¹⁸ The number of molecules escaping from the surface per square centimeter per second is given by the expression

$$N \bar{\nu} \sqrt{\frac{RT}{E_0 \pi}} e^{-E_0/RT} \quad (6)$$

¹⁵ Since the number of collisions is proportional to the density it would not be possible to work at pressures low enough so that the number of collisions would be comparable to the number of molecules decomposing.

¹⁶ Langmuir [THIS JOURNAL, 42, 2201 (1920)] reasons that the number of violent collisions is not sufficient to account for a monomolecular reaction. Aside from the difficulty of calculating the number of *effective* collisions, it should be emphasized that the mechanism postulated above is that the dissociation of a molecule is not caused by a violent collision but by a series of collisions of only ordinary violence, fortuitously timed so as to accelerate the oscillation of some part of the molecule to the breaking point.

¹⁷ See Whittaker, *Proc. Roy. Soc. Edinburgh*, 42, 129 (1921).

¹⁸ The evaporation of a solid cannot be treated by the simple statistical method above because the liquid phase intervenes between the solid and the vapor. Polyatomic liquids also present a difficulty due to the fact that molecules may escape from the surface by activation in more than one degree of freedom.

where N is the number of molecules per square centimeter of surface. Here $E_0 = L - RT$ the internal energy of vaporization. The number of molecules condensing per second¹⁹ per square centimeter is given by the expression $n\sqrt{\frac{RT}{2\pi M}}$ where n is the number of molecules per cubic centimeter of vapor and M is the gram molecular weight. Equating these two expressions

$$N\bar{\nu}\sqrt{\frac{RT}{E_0\pi}}e^{-E_0/RT} = n\sqrt{\frac{RT}{2\pi M}} \quad (7)$$

Solving for n

$$n = N\bar{\nu}\sqrt{\frac{2M}{E_0}}e^{-E_0/RT}{}^{20} \quad (8)$$

Menzies' data²¹ on the vapor pressure of mercury afford a second critical test of our equation. The internal energy of vaporization can be calculated only approximately from the vapor-pressure data, and the value obtained is 14,000 cal. Placing as before $\bar{\nu} = E_0/Nh$, we obtain for 25°, $n = 2.57 \times 10^{14}$, whereas Menzies obtained experimentally $n = 0.65 \times 10^{14}$, a discrepancy which is less than the experimental error of any data at present available.

Hildebrand's improvement²² on Trouton's rule consists in comparing the entropy of vaporization of substances at temperatures where the molecular vapor densities are equal. Thus we have

$$n_1 = N_1\nu_1\sqrt{\frac{2M_1}{E_1}}e^{-E_1/RT_1} = N_2\nu_2\sqrt{\frac{2M_2}{E_2}}e^{-E_2/RT_2} \quad (9)$$

The logic of this comparison is at once obvious, but in order that the relation holds it requires that

$$\frac{E_1}{E_2} = \left(\frac{V_1}{V_2}\right)^{\frac{4}{3}} \frac{M_2}{M_1} = \left(\frac{d_2}{d_1}\right)^{\frac{4}{3}} \frac{M_1}{M_2} \quad (10)$$

where V is the molecular volume and d the density. This relation appears rather curious but an even more interesting relation can be obtained from this equation.

If we take logarithms of both sides of Equation 7 and multiply through by $-R$ we obtain

$$R \ln \frac{\sqrt{E\pi}}{N\bar{\nu}\sqrt{RT}} + \frac{E}{T} = R \ln \frac{1}{n} \sqrt{\frac{2\pi M}{RT}} \quad (11)$$

Adding $R \ln \frac{2\pi M(RT)^{2/5}}{N^3 h^3} e^{3/2}$ to both sides of the equation we obtain finally

$$R \ln \frac{2M(\pi RT)^{3/5} e^{3/2}}{N\sqrt{E}h^2 N^2} + \frac{L}{T} = R \ln \frac{(2\pi MRT)^{3/5}}{N^3 h^3} \frac{V}{N} e^{5/2} \quad (12)$$

¹⁹ Ref. 8, p. 121. Ref. 9.

²⁰ This expression can be valid only at low pressures.

²¹ Menzies, *THIS JOURNAL*, **41**, 1783 (1919).

²² Hildebrand, *ibid.*, **37**, 970 (1915).

The right-hand side of Equation 12 is the expression for the entropy of a monatomic vapor.²³ The second term is the entropy of vaporization; hence, the first term must be the entropy of the liquid metal. The difference in the entropies of 2 metals at a given temperature then would be represented by the equation

$$S_2 - S_1 = R \ln \frac{M_2 N_1 \sqrt{E_1}}{M_1 N_2 \sqrt{E_2}}$$

But from Equation 10

$$\frac{N_1 \sqrt{E_1}}{N_2 \sqrt{E_2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Hence

$$S_2 - S_1 = R \ln \left(\frac{M_2}{M_1} \right)^{\frac{3}{2}}$$

The meaning of this equation is that if the entropies of two metals are compared at a given temperature the difference between the entropies will be equal to $3/2 R$ times the logarithm of the ratio of the atomic weights. A similar relation has been shown experimentally to hold for monatomic gases²⁴ and for solids where the constraints operating on the atoms are of the same order.

The failure of such a relation to hold for the metals appears to be due to the great difference in the constraints on the atoms in the different metals. This difference in constraints must largely disappear when the metals are melted.

The validity of the relation depends entirely, of course, on the validity of the relation (10), $\frac{E_1}{E_2} \left(\frac{d_2}{d_1} \right)^{\frac{4}{3}} \left(\frac{M_1}{M_2} \right)^{\frac{1}{3}}$. It appears obvious that this relation cannot hold for all the metals. On the other hand, it is highly probable that it holds with considerable accuracy for the metals of a group, as mercury, cadmium and zinc. There are no data on heats of vaporization available of sufficient accuracy to test this relation, although work is in progress along this line in this Laboratory.

Summary

An equation has been derived from kinetic theory for the rate of a monomolecular reaction.

²³ The general form of the expression was first given by Gibbs ("Elementary Principles of Statistical Mechanics," "Yale Bicentennial Publications," 1914, p. 170). Tetrode [*Ann. Physik*, **38**, 434 (1912)] introduced the term h as a natural unit of action. The entropy of mercury vapor calculated by the expression at 298° K. and 1 atmosphere is 42.0. G. N. Lewis [THIS JOURNAL, **44**, 1008 (1922)] has calculated by ultimate rational units 41.5, and from experimental data 41.3. It seems probable that with more accurate measurements of the quantities involved, calculations by this expression and from ultimate rational units will lead to the same value.

²⁴ Tolman, THIS JOURNAL, **42**, 1185 (1920). Latimer, *ibid.*, **43**, 818 (1921).

In the two cases where data are available, the equation gives results which are probably as accurate as the data themselves.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]
OBSERVATIONS ON THE RARE EARTHS. XIV. THE PREPARATION AND PROPERTIES OF METALLIC LANTHANUM

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One phase of the various researches on the rare earths carried on in this Laboratory is represented in a systematic study of the metallurgy and properties of the rare-earth metals. Very little is known of most of these metals and many of them, particularly those of the yttrium group, have never yet been isolated.

Lanthanum has been prepared in some quantity and studied by Muthmann and Weiss.² Most of the present accepted properties of the metal are those given by these workers. We have prepared lanthanum metal by the electrolysis of the chloride and have redetermined several of its properties. Some 3 kg. of pure lanthanum trioxide which showed no absorption bands of the other earths was obtained by a fractionation of the double magnesium nitrates and double ammonium nitrates and served as our starting material. A filtered solution of the chloride derived from this material was evaporated slowly in porcelain by direct flame until the thick sirupy liquid solidified to a crystalline mass when poured upon a cold surface. By exercising care in the extent of the evaporation no basic salt was formed. This solidified mass was then ground up and dried for several days at 85°. It was found that at this temperature basic salt was not formed and most of the water of crystallization was removed. Final dehydration was then easily and quickly carried out in an atmosphere of dry hydrogen chloride. The temperature was first kept at approximately 125° for 2 or 3 hours and then brought up to 300° for final dehydration.

The Electrolysis

The Cell.—It was necessary to have the cell sufficiently small to conserve material and at the same time large enough to afford good current efficiency. After repeated trials the cell finally selected was that of a slightly tapering shape 8 cm. deep and of an average diameter of 5 cm. A cylindrical graphite anode 2.5 cm. in diameter was found to give best results with this type of cell. The cell, of course, was the cathode and

¹ Part of this paper was presented by R. G. Stevens to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Master of Science.

² Muthmann and Weiss, *Ann.*, **331**, 1 (1904).