The Absolute Rate of a Chemical Reaction

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Krishnamurti[1] investigated the Raman spectra of a number of inorganic halides in the solid state at room temperature. Those substances with heteropolar binding showed no Raman spectra whereas homopolar substances such as the mercuric halides showed strong Raman lines. Zinc chloride and cadmium iodide, substances of intermediate polarity, whose crystal structure is of the layer lattice type showed weak Raman lines. Our data would classify zinc bromide in the intermediate group with zinc chloride and cadmium iodide, the higher electrical conductivity of the zinc bromide being offset by its lower melting point.

Krishnamurti[1] found a frequency shift for zinc chloride of 234 cm^{-1}, which is in satisfactory agreement with the higher frequency line found by us. The frequency shifts of 297 and 396 cm^{-1} found from concentrated aqueous solutions of zinc chloride by Hibben[2] are probably due to complex ions or molecules.[3, 4] Furthermore, Braune and Engelbrecht[5] have shown that the displaced frequencies of the mercuric halides are nearly the same for the fused salt as for the salt at room temperature. Grassman[6] and Thatte and Ganesan[7] obtained similar results for a number of nitrates. The fact that the Raman frequencies persist some hundred degrees above the melting point indicates that the frequencies found here are not due to vibrations in the crystal lattice but are rather due to oscillations in the zinc halide grouping.

The results for both zinc chloride and zinc bromide do not indicate a linear type of molecule. The determination of the angle between the valence bonds and strength of bonds awaits additional data.

We failed to observe Raman lines from fused LiBr, PbCl$_2$, PbBr$_2$ and CdCl$_2$, but the experimental conditions for obtaining these lines were not as satisfactory as with the zinc salts.

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February, 27, 1935.

[1] Krishnamurti, Ind. J. Phys. 5, 113 (1930).
[2] Hibben, Proc. Nat. Acad. Sci. 18, 532 (1932).
[3] Damaschun, Zeits. f. physik. Chemie B16, 92 (1932).
[4] Braune and Engelbrecht, Zeits. f. physik. Chemie B11, 416 (1931).
[5] Braune and Engelbrecht, Zeits. f. physik. Chemie B19, 303 (1932).
[6] Grassman, Zeits. f. Physik 77, 616 (1932).
[7] Thatte and Ganesan, Ind. J. Phys. 8, 341 (1934).

The Absolute Rate of a Chemical Reaction

Various writers[1, 2, 3] have attempted to formulate the factors determining the absolute rate of a chemical reaction. To a first approximation the task is not difficult. There are two methods of approach. One method is to calculate the number of favorable collisions from kinetic theory. The other is to treat the colliding molecule as a complex and apply the laws of statistical mechanics and chemical equilibrium for what they are worth. The two methods correspond at every point. Thus, the heat of activation in the latter treatment becomes the factor which determines the number of collisions of sufficient violence in the former method. The collision radius in the kinetic theory determines the moment of inertia and rotational entropy of the complex in the thermodynamic treatment. The greater the entropy of the complex, the greater must be the probability of reaction. By an arbitrary choice of collision radii, the "steric" factor may often be made unity, but this does not really give us any more information than we had before. Both methods involve uncertainties due to the lack of exact knowledge of force constants, collision radii, etc.

Recently Eyring[4] has proposed to treat the subject by a method which is essentially the second method mentioned above. His method is not, therefore, novel, nor does it produce any results new to statistical mechanics. What he does propose that is new is to calculate the contours of the potential surface by wave mechanics so that the various uncertainties mentioned above may disappear. It may even be possible to calculate the rate of reflection at a barrier. This latter quantity may be described as a true steric factor.

One may await results to see how well it will succeed. Presumably no one would claim that it is now possible to calculate the energy of any but the simplest chemical bonds with any precision by wave mechanics. Certainly a survey of the amount of work required to reach a satisfactory value for the heat of dissociation of the hydrogen molecule does not inspire one with confidence. The method of Heitler and London may be a better approximation in the case of a reactive complex than a stable molecule; it would be very fortunate if this is the case. It is, of course, possible to adapt calculations to experimental data, but in doing this one may produce agreement ·by changing one factor when some other factor is really at fault.

Nevertheless, the writer has believed for a long time that it should be possible to determine all the constants of a reaction rate from measurements at a single temperature.

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February 27, 1935.

[1] W. H. Rodebush, J. Am. Chem. Soc. 45, 606 (1923); J. Chem. Phys. 1, 440 (1933).
[2] M. Polanyi and E. Wigner, Zeits. f. physik. Chemie (Haber band), 439 (1928).
[3] O. K. Rice and H. Gershinowitz, J. Chem. Phys. 2, 853 (1934).
[4] Eyring, J. Chem. Phys. 3, 107 (1935).

The Raman Spectrum of Deuterium

A number of observers have studied the emission spectra of mixtures of hydrogen and deuterium. The Fulcher bands for HD and D$_2$ have been photographed.[1] In the extreme ultraviolet Jeppesen,[2] and Beutler and Mie,[3] have obtained emission spectra from hydrogen-deuterium mixtures and have ascribed several bands to HD. From these data on HD, Urey and Teal[4] have calculated molecular constants for the molecule D$_2$ in the ground state. No experimental data for this molecule in this state appear to have been obtained.

We have obtained Raman spectra of gaseous deuterium (99.5 percent D$_2$) at a pressure of 2.5 atmos., using Hg 2537 as an exciting line. 24- to 48-hour exposures were made. Two rotation lines and the Q branch of the vibration line were obtained. Their frequencies and mean deviations from

TABLE I. *Observed and calculated Raman frequencies of D_2.*

v	J	ν obs. cm^{-1}	ν calc. cm^{-1}	Difference	I calc.
$0 \to 0$	$0 \to 2$	179.6 ± 0.5	179.1	0.5	
	$1 \to 3$	298.3 ± 1.3	297.4	0.9	
$0 \to 1$	$0 \to 0$		2996.7	-7.2	0.00*
	$1 \to 1$		2994.7	-5.2	0.90
	$2 \to 2$	2989.5 ± 1.3	2991.2	-1.7	1.21
	$3 \to 3$		2986.2	3.3	0.33
	$4 \to 4$		2974.7	14.8	0.26

means in measuring plates are given in Table I, together with frequencies calculated from the equation of Urey and Teal, for the rotation-vibration energy levels of the molecule in the ground state. Using a formula given by Placzek[5] and due to Mannenbeck, we have calculated the relative intensities I of four of the strongest lines in the vibrational Q branch. The result gives 2990.0 cm^{-1} for the position of the center of gravity of the Q branch, and this is in agreement with the observed frequency.

The constants of Urey and Teal are therefore confirmed. This result is important in connection with the use of deuterium to establish the structure of hydrogen-containing molecules.[6] In such cases $M-D$ distances are assumed equal to $M-H$ distances, where M is any atom. The greatest deviation from this assumption would probably occur in D_2; and since no deviation is found in this case the assumption appears to be justified. Moreover the force constant for D_2 is the same as that for H_2, and this suggests that $M-D$ force constants are equal to those for $M-H$.

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March 2, 1935.

[1] M. F. Ashley, Phys. Rev. 43, 770 (1930); G. H. Dieke and R. W. Blue, Nature 133, 611 (1934); Phys. Rev. 47, 261 (1935).
[2] C. R. Jeppesen, Phys. Rev. 45, 480 (1934); 44, 165 (1933).
[3] H. Beutler and K. Mie, Naturwiss. 22, 418 (1934); K. Mie, Zeits. f. Physik 91, 475 (1934); H. Beutler, Zeits. f. physik. Chemie B27, 287 (1934).
[4] H. C. Urey and G. K. Teal, Rev. Mod. Phys. 7, 34, (1935). Table XV, p. 80. A complete set of references is given in this review.
[5] G. Placzek, *Rayleigh-Streuung und Raman-Effekt* (Leipzig, 1934) Eqs. (15), (15a), p. 343.
* F. Rasetti reports a line ν_{10}^{00} for hydrogen. Phys. Rev. 34, 367, (1929). The matter is worth further investigation.
[6] For example the structure of NH₃: Barnes, Benedict and Lewis, Phys. Rev. 45, 347 (1934).

A Transition in Potassium Superoxide

During the study of the magnetic properties[1] of potassium superoxide, KO_2, I noticed that on cooling in liquid air the substance changes from a deep orange to a light cream color. In order to see whether or not this change in color accompanies a transition from one form to another, and if so to determine the transition temperature, the following experiments were carried out.

Samples of the superoxide and of sodium chloride were put in a glass tube 7 mm in diameter, each in a layer 2 cm deep, with the two junctions of a differential thermocouple at the centers of the two layers, and the junction of another thermocouple (for measuring the temperature) at the center of one of the layers. The tube was sealed from the atmosphere by a plug of cotton followed by a layer of picien. The tube was enclosed in a copper jacket about 5 mm thick,

in order to insure a uniform heat transfer between the cell constants and the surroundings. Mercury was added as a further aid to this end and the whole was enclosed in a test tube. The thermocouples were single junction and were made of No. 32 copper and constantan wire joined with silver solder. The differential thermocouple was connected directly to a Leeds and Northrup Type R galvanometer which had a period of 5.5 sec. and a sensitivity of 2.7 mm/m per mv. The galvanometer scale was 60 cm from the instrument. No damping resistance was found necessary with this instrument. This differential thermocouple was used only as a means of observing differences of temperature between the oxide and the chloride. The actual temperature of the oxide was measured by means of the other thermocouple which was used in conjunction with a Leeds and Northrup Type K potentiometer. This thermocouple was calibrated by comparison with nine fixed points.

Warming curves were obtained from liquid air temperature to the temperature of melting ice. The cell was first cooled in liquid air for about an hour, the air was then removed from the enclosing Dewar flask, a cotton plug was inserted into the mouth of the flask to prevent irregular heating due to convection, and the cell was allowed to rise to room temperature. The most uniform curves were obtained when the time of warming over the temperature range studied was between 4 and 5 hours.

Cooling curves were obtained by enclosing the cell in an unsilvered Dewar flask and cooling by immersing this flask in liquid air. The flask that was used allowed the temperature of the cell to fall from room temperature to liquid air temperature in about 4 hours.

The warming curves and cooling curves all showed a pronounced break, corresponding to a transition at the temperature $-75.5° \pm 0.5°$C. (No break in this region was shown by control curves obtained by replacing the superoxide in the cell by sodium chloride.) Observation of the color change showed that it occurs at the same temperature, to within about $\pm 15°$.

The experimental method is not sufficiently delicate to distinguish between a true polymorphic transition and a gradual transition;[2] if the transition is of the latter type, it is reasonably sharp, extending over a temperature range not greater than three or four degrees.

The normal superoxide ion is in the state $^2\Pi$, and the separation of the two levels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ is probably about the same as for NO, 121 cm^{-1}. It is interesting to note that this energy value is equal to kT at the temperature $T = 213°$A, only 15° from the observed transition temperature; though until more definite evidence is obtained the suggestion that the transition of the solid substance is related to the electronic transition of the molecules must be considered as speculative.

The author is grateful to Professor Linus Pauling for his interest in the investigation.

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[1] E. W. Neuman, J. Chem. Phys. 2, 31 (1934).
[2] Linus Pauling, Phys. Rev. 36, 430 (1930).
[3] Now at Carroll College, Capitol Hill, Helena, Montana.