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−53°C. The rate for this process is approximately 30 times as fast as that for the corresponding concentration of cupric ion in $H_2O$ at 25°C. Since the magnetism of the Na solutions is very much smaller than that for the cupric solutions, a further comparison upon the basis of magnetism (such as for equal values of the square of the magnetic moments) would be even more striking.

[1] Farkas and Sachsse, Zeits. f. physik. Chemie **B23**, 1 (1933); **B24** 429 (1933).

[2] Wigner, Zeits. f. physik. Chemie **B23**, 28 (1933).

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## On the Probability Formulation of Chemical Reaction Kinetics

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February 16, 1948

CHEMICAL kinetics has been usually described by kinematic differential equations. Recently, Erofeyev[1] started a phenomenological formulation from the probability concept. The fact that a constant probability, independent of the time for a molecule to undergo reaction, will lead to a first-order kinetic equation is well known. However, it is interesting to see what form of the probability function will give a kinetic equation of zero or higher order.

Let $\bar{p}(t)$ be the average probability per unit time in which a molecule undergoes reaction, then the average probability that a molecule would survive from reaction over a finite period of time $t$ is[1]

$$Q(t) = \exp\left(-\int_0^t \bar{p}(t)dt\right). \tag{1}$$

For the transformation of molecules of a single chemical species the kinematic equation of kinetic order $n$ is

$$-\dot{c}(t) = k_n c(t)^n,$$

where $c$ is the concentration of the molecules. Dividing through by $c$ and integrating yields

$$Q(t) = c(t)/c(0) = \exp\left(-k_n \int^t c(t)^{n-1}dt\right). \tag{2}$$

Therefore,

$$\bar{p}(t) = k_n c(t)^{n-1} \tag{3}$$

by comparing (2) and (1).

Similar considerations for a bimolecular reaction between two different molecules $A$ and $B$, i.e.,

$$-\dot{c}_A(t) = -\dot{c}_B(t) = k_2 c_A c_B,$$

give the following result:

$$\left.\begin{array}{l} Q_A(t) = \exp\left(-\int_0^t \bar{p}_A(t)dt\right), \\[2mm] Q_B(t) = \exp\left(-\int_0^t \bar{p}_B(t)dt\right), \end{array}\right\} \tag{4}$$

with

$$\bar{p}_A(t) = k_2 c_B(t) \quad \text{and} \quad \bar{p}_B(t) = k_2 c_A(t). \tag{5}$$

It can be shown that the functions (3) and (5) are the unique solution for the probability functions defined in (1) and (4) which satisfy the corresponding kinematic equations. The form of these probability functions for reactions of second and higher orders are in accord with the collision mechanism of chemical reactions.

Furthermore, if the probability functions for the molecules of different energies be put in the form

$$p_i(E_i, t) = f(E_i)p(t),$$

then

$$\bar{p}(t) = 2\pi^{-\frac{1}{2}}(kT)^{-\frac{3}{2}}p(t)\int_0^\infty f(E_i)E_i^{\frac{1}{2}}\exp(-E_i/kT)dE_i.$$

Further, the assumption that

$$f(E_i) = \begin{cases} 0 \text{ for } E_i < E_0, \\ 1 \text{ for } E_i \geq E_0, \end{cases}$$

leads to the following temperature dependence of the probability function,

$$kT^2 \frac{\partial \ln \bar{p}}{\partial T} = \frac{\int_{E_0}^\infty E_i^{\frac{3}{2}}\exp\left(-\frac{E_i}{kT}\right)dE_i}{\int_{E_0}^\infty E_i^{\frac{1}{2}}\exp\left(-\frac{E_i}{kT}\right)dE_i} - \frac{3}{2}kT. \tag{6}$$

For a first-order reaction, $\bar{p}$ is identical to the rate constant $k_1$, and such a temperature dependence of $k_1$ has been first derived by Tolman.[2]

It is hereby shown that the generalized kinetic equation (1) is a partially integrated form of the usual kinematic equation and it is therefore equivalent to the latter. For cases where the reaction probability function can be formulated *a priori*, the present formulation will give the reaction kinetics directly without solving the differential equations.

[1] B. V. Erofeyev, Comptes Rendus U.R.S.S. **52**, 511 (1946).

[2] R. C. Tolman, J. Am. Chem. Soc. **42**, 2506 (1920).

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## Erratum: Absorption Spectrum of Carbon Dioxide from 14 to 16 Microns

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DR. FRANK MATOSSI kindly pointed out to the author an error on page 812 of the above paper. The half-width in wave numbers should be equal to the collision frequency divided by $2\pi$ times the velocity of light.[1] Since the value of 0.17 $cm^{-1}$ obtained appears to be close to the correct value at atmospheric pressure,[2] the kinetic theory diameter seems to be too small by a factor of about $\sqrt{2\pi}$, which would account for the compensating error. Born[3] estimates the ratio of the optical diameter to the kinetic theory diameter to be 3.0 for carbon dioxide, 2.2 for nitrogen, and 2.3 for oxygen, resulting in an effective optical diameter of 2.6 times the kinetic theory value.

[1] M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), p. 437; H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 37 (1936).

[2] Dr. Arthur Adel, in a communication to the author, has given a probable value of 0.15 to 0.18 $cm^{-1}$, based on the procedure described in Rev. Mod. Phys. **16**, 236 (1944).

[3] Reference 1, p. 441.