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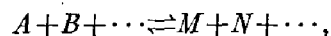
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Chemical Reactions near Equilibrium

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IN seeming contradiction to usual deductions from thermodynamics, it has been shown by De Donder¹ on the basis of his affinity function, by Prigogine² on the basis of the Chapman-Enskog model, and by Manes, Hofer, and Weller³ using purely mathematical methods, that the rate of a chemical reaction close to equilibrium is directly proportional to the free energy difference between reactants and products. This relation may be shown to be a consequence of the theory of absolute reaction rates, also.

If one has the generalized reaction



$$\Delta F_f^\ddagger = \Delta F_f^{\ddagger 0} + RT \ln Q_f^\ddagger = \Delta F_f^{\ddagger 0} + RT \ln \frac{a^\ddagger}{a_A a_B \dots}$$

$$\Delta F_r^\ddagger = \Delta F_r^{\ddagger 0} + RT \ln Q_r^\ddagger = \Delta F_r^{\ddagger 0} + RT \ln \frac{a^\ddagger}{a_M a_N \dots},$$

where ΔF_f^\ddagger is the free energy of activation of the forward reaction at any concentration, ΔF_r^\ddagger is the free energy of activation of the reverse reaction at any concentration, $\Delta F_f^{\ddagger 0}$ is the standard free energy of activation of the forward reaction, and $\Delta F_r^{\ddagger 0}$ is the standard free energy of activation for the reverse reaction. a_i is the activity of the i th component and a^\ddagger is the activity of the activated complex.

We may now write the expressions for the rate constants of the forward and reverse reactions as

$$\begin{aligned} k_f &= \kappa_f \frac{kT}{h} \exp\left(-\frac{\Delta F_f^{\ddagger 0}}{RT}\right); & k_r &= \kappa_r \frac{kT}{h} \exp\left(-\frac{\Delta F_r^{\ddagger 0}}{RT}\right); \\ &= \kappa_f \frac{kT}{h} Q_f^\ddagger \exp\left(-\frac{\Delta F_f^\ddagger}{RT}\right); & &= \kappa_r \frac{kT}{h} Q_r^\ddagger \exp\left(-\frac{\Delta F_r^\ddagger}{RT}\right). \end{aligned}$$

The expression for the rate of this reaction becomes

$$\begin{aligned} \frac{da_A}{dt} = \frac{da_B}{dt} = \dots = -\frac{da_M}{dt} = -\frac{da_N}{dt} = \dots \\ = k_f a_A a_B \dots - k_r a_M a_N \dots. \end{aligned}$$

If we assume that $\kappa_f = \kappa_r$

$$\begin{aligned} \frac{da_A}{dt} &= \kappa \frac{kT}{h} a^\ddagger \left[\exp\left(-\frac{\Delta F_f^\ddagger}{RT}\right) - \exp\left(-\frac{\Delta F_r^\ddagger}{RT}\right) \right] \\ &= \kappa \frac{kT}{h} a^\ddagger \sum_{n=0}^{\infty} \frac{1}{n!} \left[\left(-\frac{\Delta F_f^\ddagger}{RT}\right)^n - \left(-\frac{\Delta F_r^\ddagger}{RT}\right)^n \right]. \end{aligned}$$

If the reaction is close enough to equilibrium, $\Delta F_f^\ddagger/RT \ll 1$, $\Delta F_r^\ddagger/RT \ll 1$, and

$$\begin{aligned} \frac{da_A}{dt} &\simeq \kappa \frac{kT}{h} \frac{a^\ddagger}{RT} (\Delta F_r^\ddagger - \Delta F_f^\ddagger) \\ &\simeq \frac{\kappa a^\ddagger}{hN} \Delta F, \end{aligned}$$

where $\Delta F = \Delta F_r^\ddagger - \Delta F_f^\ddagger$ and N is Avogadro's number. This approximation also becomes better as the temperature becomes higher.

Near equilibrium, a^\ddagger will be approximately constant and the rate becomes directly proportional to the free energy change.

It is to be noted that this development indicates such behavior only in the limit. Some experimental results in the literature support this contention. This development also indicates that attempts to apply this treatment to the kinetics of reactions not very close to equilibrium will not be successful.

The most useful form of the absolute reaction rate theory involves the Gibbs free energy. However, as Manes *et al.*, show, the mathematical analysis can be carried out for any thermodynamic state function. So long as the conditions on the reaction are appropriate, any state function may be used in the absolute reaction rate theory to obtain results analogous to those of Manes.

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¹ Th. De Donder, *L'affinite* (Gauthier-Villars, Paris, France, 1927).

² I. Prigogine, *Etude thermodynamique des phenomenes irreversibles* (Desoer, Leige, Belgium, 1947).

³ Manes, Hofer, and Weller, *J. Chem. Phys.* **18**, 1355 (1950).