

$$K^* = \frac{F_a^*}{F_n} e^{-\Delta E_a/kT}$$

$$= e^{\Delta S_a^*/k} e^{-\Delta E_a/kT}$$

$$= e^{-\Delta F_a^*/kT}$$

- $m$  = mass of activated complex,
  - $\bar{p}$  = mean momentum of activated complex normal to the barrier,
  - $\kappa$  = transmission coefficient, the probability that once having crossed the barrier, the complex will not return, usually about unity,
  - $F_a^*$  = partition function of activated complex, omitting one translational degree of freedom,
  - $F_n$  = partition function of normal state,
  - $\Delta E_a$  = energy of activation,<sup>a</sup>
  - $\Delta F_a$  = free energy of activation,
  - $\Delta S_a$  = entropy of activation,
- and other symbols have their usual meanings.

Equation (1) is the fundamental equation for any rate process, whether it be a chemical reaction, flow, or diffusion, i.e., for any process in

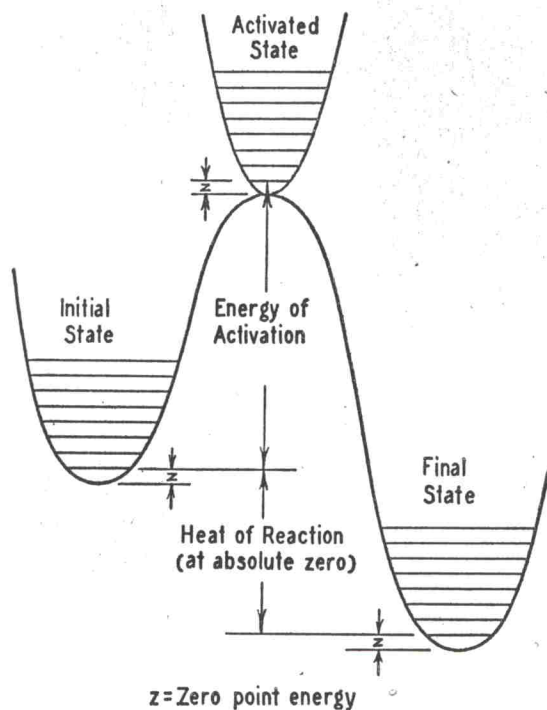


FIG. 1. Energy profile of the path of a reacting system.

which the slow step is passage over a potential barrier. This equation supersedes in generality the older idea of collision frequency, although

<sup>a</sup> Throughout this article the same symbol will be used for energy per mole or per molecule, the particular one in question being distinguished by the value of the gas constant used with it.

Eyring has shown that they are equivalent for simple bimolecular reactions. Fig. 1 shows some of the energy relations in a rate process, and shows clearly that the rate of an exothermic reaction can have no relation to the heat or the free energy of the reaction. For practical purposes the contribution of the zero point energies to the activation energy can often be ignored.

### Application of the Theory of Reaction Rates to Flow

The development to be presented in this section follows quite closely that given by Eyring.<sup>1</sup> As stated in the introductory paragraph, flow will be considered as a unimolecular process in which the elementary process is the passing of a molecule from one equilibrium position to another over a potential barrier. The activation energy of this process takes the form of providing a hole for the molecule to flow into (or possibly of providing some extra space so that it may slip past its neighbors). If no velocity gradient exists in the liquid the energy profile of the flow process will be as shown by the full line in Fig. 2. A molecule will diffuse equally often from right to left as from left to right, and no net flow will occur. We will have for diffusion then

$$k_1 = \frac{kT}{h} \frac{F_a^*}{F_n} e^{-\Delta E_a/kT}$$

This is Eq. (1) with  $\kappa$ , the transmission coefficient, omitted. Since  $\kappa$  is usually about unity it will be omitted hereafter.

If, however, a velocity gradient is set up in the liquid by a force acting in the direction left to right in Fig. 2, there will be a decrease in the activation energy for a flow process in the direction left to right, and an equal increase in the direction right to left, so that the forward rate will be greater than the backward rate and a net flow results. Thus we have

$$k_f = \frac{kT}{h} \frac{F_a^*}{F_n} e^{-(\Delta E_a - \frac{1}{2} f \lambda_2 \lambda_3 \lambda) / kT}$$

$$= k_1 e^{f \lambda_2 \lambda_3 \lambda / 2kT}$$

$$k_b = \frac{kT}{h} \frac{F_a^*}{F_n} e^{-(\Delta E_a + \frac{1}{2} f \lambda_2 \lambda_3 \lambda) / kT}$$

$$= k_1 e^{-f \lambda_2 \lambda_3 \lambda / 2kT}$$

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