

Interpretation of the Activation Energy

The Arrhenius activation energy E_a is a phenomenological quantity defined in terms of the slope of an Arrhenius plot [$\ln k(T)$ versus $1/T$] as

$$E_a = -k_B \frac{d \ln k(T)}{d(1/T)} \quad (1)$$

$$= k_B T^2 \frac{1}{k(T)} \frac{dk(T)}{dT} \quad (2)$$

where $k(T)$ is a rate constant and k_B is Boltzmann's constant. When E_a is a constant (independent of T), integration of eqn. (1) leads to the Arrhenius form of the rate constant

$$k(T) = A \exp(-E_a/k_B T) \quad (3)$$

The Arrhenius activation energy is often interpreted approximately as the energetic threshold E_0 for reaction but it may be either larger or smaller than E_0 . The Arrhenius activation energy for an elementary bimolecular gas-phase reaction step occurring at equilibrium does have a simple interpretation that was first given by Tolman (1). It is the average total energy (relative translational plus internal) of all reacting pairs of reactants minus the average total energy of all pairs of reactants. Although this is an elegant and useful result it is not as well known as it should be; e.g., it is not mentioned in most physical chemistry and kinetics textbooks, and some books which do mention the result give a proof and discussion which involve only relative translational energy E_{rel} (e.g., (2)) or only internal energy E_{int} (e.g., (3)). Although several complete derivations, including both E_{rel} and E_{int} , have been given (e.g., 1, 4-6), it is instructive to rederive the result (7) using the language of modern collision theory (8-11), i.e., using state-to-state reaction cross-sections. The purpose of this article is to present such a derivation in the hope that it will lead to a better appreciation of the result.

Review of Collision Theory: Definitions

The reader is referred to articles by Widom (12) and Boyd (13) for discussions of equilibrium rate constants and to the textbook of Gardiner (10) for the way equilibrium rate constants are expressed in terms of state-to-state cross-sections. We summarize the results here in a convenient notation for the proof which follows. Consider the reaction of molecule A in state i with molecule B in state j to give molecule C in state k and molecule D in state l . (The special case of atoms is also included, and the extension to more than two products will be obvious.) Let $\langle g(A_i) \rangle_i^T$ denote an average of any function $g(A_i)$ of states i of A over a Boltzmann distribution $P_{A_i}(T)$ of states i

$$\langle g(A_i) \rangle_i^T = \sum_i P_{A_i}(T) g(A_i) \quad (4)$$

$$= (Z_{A_{int}})^{-1} \sum_i d_{A_i} \exp(-E_{A_i}/k_B T) g(A_i) \quad (5)$$

where d_{A_i} is the degeneracy, E_{A_i} is the internal energy of A, and $Z_{A_{int}}$ is the internal partition function of A

$$Z_{A_{int}} = \sum_i d_{A_i} \exp(-E_{A_i}/k_B T) \quad (6)$$

Similarly

$$\langle g(B_j) \rangle_j^T = \sum_j P_{B_j}(T) g(B_j) \quad (7)$$

Let α denote the set (i, j) of pairs of quantum states of A and B and let $\langle g(\alpha) \rangle_\alpha^T$ denote an average over a Boltzmann dis-

tribution of such pairs of specified states of reactants

$$\langle g(\alpha) \rangle_\alpha^T = \langle \langle g(A_i, B_j) \rangle_j^T \rangle_i^T \quad (8)$$

$$= \frac{\sum_\alpha g(\alpha) \exp(-E_\alpha/k_B T)}{\sum_\alpha \exp(-E_\alpha/k_B T)} \quad (9)$$

where the pair's internal energy E_α is the sum of E_{A_i} and E_{B_j} and the term labelled α must be included $d_{A_i} d_{B_j}$ times in the sum of eqn. (9) because we have not included any degeneracy factors here.

Let $\langle g(V_R) \rangle_{V_R}^T$ denote an average of a function $g(V_R)$ of initial relative speed V_R over a Maxwell-Boltzmann distribution $P(V_R, T)$ of relative speeds

$$\langle g(V_R) \rangle_{V_R}^T = \int_0^\infty P(V_R, T) g(V_R) dV_R \quad (10)$$

$$= 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty g(V_R) V_R^2 \exp(-\mu V_R^2/2k_B T) dV_R \quad (11)$$

where μ is the reduced mass for relative motion

$$\mu = m_A m_B / (m_A + m_B) \quad (12)$$

By $g(E_{rel})$ we denote the same quantity as $g(V_R)$ but now considered as a function of E_{rel}

$$E_{rel} = \mu V_R^2 / 2 \quad (13)$$

Then by these definitions

$$\langle g(V_R) \rangle_{V_R}^T = \langle g(E_{rel}) \rangle_{E_{rel}}^T \quad (14)$$

$$= \int_0^\infty P(E_{rel}, T) g(E_{rel}) dE_{rel} \quad (15)$$

$$= 2 \left(\frac{1}{\pi} \right)^{1/2} \left(\frac{1}{k_B T} \right)^{3/2} \int_0^\infty g(E_{rel}) E_{rel}^{1/2} \exp(-E_{rel}/k_B T) dE_{rel} \quad (16)$$

Let $\sigma(A_i, B_j, E_{rel} \rightarrow C_k, D_l)$ be the state-to-state reaction cross-section for a fixed initial relative translational energy E_{rel} and let $\sigma(\alpha, E_{rel})$ be its sum over states of the products

$$\sigma(\alpha, E_{rel}) = \sum_k \sum_l \sigma(A_i, B_j, E_{rel} \rightarrow C_k, D_l) \quad (17)$$

The state-to-state, fixed-velocity rate constant $k(\alpha, V_R)$ is simply the product $V_R \sigma(\alpha, V_R)$. Then the equilibrium rate constant $k(T)$ is $V_R \sigma(\alpha, V_R)$ averaged over Boltzmann distributions of initial internal states α and initial relative velocities V_R

$$k(T) = \langle \langle V_R \sigma(\alpha, E_{rel}) \rangle_\alpha^T \rangle_{E_{rel}}^T \quad (18)$$

$$= \langle V_R \sigma(T, E_{rel}) \rangle_{E_{rel}}^T \quad (19)$$

where $\sigma(T, E_{rel})$ is sometimes called the excitation function (14) and is defined by

$$\sigma(T, E_{rel}) = \langle \sigma(\alpha, E_{rel}) \rangle_\alpha^T \quad (20)$$

It is the reaction cross-section for a fixed E_{rel} but averaged over initial internal states at temperature T . The corresponding rate constant $k(T, E_{rel})$ is simply $V_R \sigma(T, E_{rel})$. By using eqns. (13) and (16), equation (19) can be written more explicitly

$$k(T) = \left(\frac{1}{\pi \mu} \right)^{1/2} \left(\frac{2}{k_B T} \right)^{3/2} \int_0^\infty \sigma(T, E_{rel}) E_{rel} \exp(-E_{rel}/k_B T) dE_{rel} \quad (21)$$

Derivation of Tolman's Result

Substituting (21) into (2) yields

$$E_a = -\frac{3}{2}k_B T + \frac{k_B T^2 \frac{d}{dT} \int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (22)$$

$$= -\frac{3}{2}k_B T + \text{(I)} + \text{(II)} \quad (23)$$

where

$$\text{(I)} = \frac{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}}^2 \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (24)$$

and

$$\text{(II)} = k_B T^2 \frac{\int_0^\infty \frac{d\sigma(T, E_{\text{rel}})}{dT} E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (25)$$

First consider the average value of E_{rel} for all A,B pairs. This is given by

$$\langle E_{\text{rel}} \rangle_{E_{\text{rel}}}^T = \int_0^\infty P(E_{\text{rel}}, T) E_{\text{rel}} dE_{\text{rel}} \quad (26)$$

$$= \frac{\int_0^\infty E_{\text{rel}}^{3/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty E_{\text{rel}}^{1/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (27)$$

$$= \frac{3}{2} k_B T \quad (28)$$

Next consider the average value of E_{rel} for all reactive A,B collisions. This is given by an average like eqns. (26)–(28) except the additional weighting factor $k(T, E_{\text{rel}})$ must be added to account for the distribution of relative translational energies at which reaction occurs

$$\langle E_{\text{rel}} \rangle_{\text{collisions}}^T = \frac{\int_0^\infty k(T, E_{\text{rel}}) E_{\text{rel}}^{3/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty k(T, E_{\text{rel}}) E_{\text{rel}}^{1/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (29)$$

$$= \frac{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}}^2 \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty \sigma(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (30)$$

$$= \text{(I)} \quad (31)$$

Substituting (28) and (31) into (23) yields

$$E_a = \langle E_{\text{rel}} \rangle_{\text{collisions}}^T - \langle E_{\text{rel}} \rangle_{E_{\text{rel}}}^T + \text{(II)} \quad (32)$$

Thus if term (II) were zero [e.g., if $\sigma(\alpha, E_{\text{rel}})$ were independent of α], E_a would be just the average E_{rel} of reacting pairs minus the average E_{rel} of all pairs.

Next consider term (II). Using eqns. (14)–(16) and (21) we rewrite this as

$$\text{(II)} = k_B T^2 \frac{\left\langle V_R \frac{d\sigma(T, E_{\text{rel}})}{dT} \right\rangle_{E_{\text{rel}}}^T}{k(T)} \quad (33)$$

The derivative can be evaluated using eqns. (20) and (9)

$$\frac{d\sigma(T, E_{\text{rel}})}{dT} = \frac{\sum_{\alpha} (E_{\alpha}/k_B T^2) \sigma(\alpha, E_{\text{rel}}) \exp(-E_{\alpha}/k_B T)}{\sum_{\alpha} \exp(-E_{\alpha}/k_B T)}$$

$$= \frac{\sum_{\alpha} \sigma(\alpha, E_{\text{rel}}) \exp(-E_{\alpha}/k_B T)}{\left[\sum_{\alpha} \exp(-E_{\alpha}/k_B T) \right]} \sum_{\alpha} \frac{E_{\alpha}}{k_B T^2} \exp(-E_{\alpha}/k_B T) \quad (34)$$

Therefore

$$k_B T^2 \frac{d\sigma(T, E_{\text{rel}})}{dT} = \langle E_{\alpha} \sigma(\alpha, E_{\text{rel}}) \rangle_{\alpha}^T - \sigma(T, E_{\text{rel}}) \langle E_{\alpha} \rangle_{\alpha}^T \quad (35)$$

and

$$\text{(II)} = \frac{\langle \langle E_{\alpha} V_R \sigma(\alpha, E_{\text{rel}}) \rangle_{\alpha}^T \rangle_{E_{\text{rel}}}^T}{k(T)} - \langle E_{\alpha} \rangle_{\alpha}^T \frac{\langle V_R \sigma(T, E_{\text{rel}}) \rangle_{E_{\text{rel}}}^T}{k(T)} \quad (24)$$

Using the two definitions (18) and (19) of $k(T)$ then yields

$$\text{(II)} = \frac{\langle \langle E_{\alpha} V_R \sigma(\alpha, E_{\text{rel}}) \rangle_{\alpha}^T \rangle_{E_{\text{rel}}}^T}{\langle \langle V_R \sigma(\alpha, E_{\text{rel}}) \rangle_{\alpha}^T \rangle_{E_{\text{rel}}}^T} - \langle E_{\alpha} \rangle_{\alpha}^T \quad (36)$$

which is the average internal energy of pairs that react minus the average internal energy of all pairs of reagents. This, combined with eqn. (32), yields

$$E_a = \langle E_{\text{rel}} + E_{\alpha} \rangle_{\text{collisions}}^T - \langle E_{\text{rel}} \rangle_{E_{\text{rel}}}^T - \langle E_{\alpha} \rangle_{\alpha}^T \quad (37)$$

which completes the proof.

Discussion

The Tolman interpretation of the Arrhenius activation energy allows us to interpret the rate of change of the equilibrium reaction rate with temperature in terms of the distribution of reaction energies when the reaction proceeds at equilibrium at a given temperature. Experimentally, one measures the so-called phenomenological or steady-state rate constant, not necessarily the equilibrium rate constant (13). But for typical atom-transfer and metathesis reactions with activation energy characterized by a reaction cross-section an order of magnitude (or more) smaller than the collision cross-section, the measured rate constant is expected to equal the equilibrium rate constant within experimental error (15, 16). One example where nonequilibrium effects may be important (and hence Tolman's interpretation may not apply to the measured rate constants) is dissociation of diatomic molecules in shock-tubes (17). The derivation of Tolman's result did not actually require equilibrium. It merely required what Boyd (13) calls "local equilibrium" of reactants, in particular a Maxwellian distribution of relative velocities and an equilibrium distribution of the internal states of reactants but not equilibrium of reactant concentrations with product concentrations. Snider (18) has shown that when the state-to-state reaction cross-sections are very small compared to the state-to-state cross-sections governing transitions between reactant states, then the steady-state rate constant is equal to the one-way flux given by eqn. (18). The conditions under which this local equilibrium assumption is valid have been further discussed in Boyd's review (13).

Tolman (1) originally stated the result a different way. His result is equivalent to saying that, at equilibrium, E_a is the average total energy of reacting pairs minus the average total energy of colliding pairs plus $1/2 k_B T$. The version of the theorem used here was compared to Tolman's version by Fowler and Guggenheim (4). The comparison requires the recognition that while the average E_{rel} for all pairs at equilibrium is given by eqns. (26)–(28), pairs with high E_{rel} collide more often and the average energy of colliding pairs at equilibrium is given by

$$\langle E_{\text{rel}} \rangle_{\text{colliding pairs}}^T = \frac{\int_0^\infty k_{\text{col}}(T, E_{\text{rel}}) E_{\text{rel}}^{3/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty k_{\text{col}}(T, E_{\text{rel}}) E_{\text{rel}}^{1/2} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (38)$$

where $k_{\text{col}}(T, E_{\text{rel}})$ is the equilibrium rate constant for collisions. Writing this as $V_R \sigma_{\text{col}}(T, E_{\text{rel}})$ where $\sigma_{\text{col}}(T, E_{\text{rel}})$ is the collision cross-section yields

$$\langle E_{\text{rel}} \rangle_{\text{colliding pairs}}^T = \frac{\int_0^\infty \sigma_{\text{col}}(T, E_{\text{rel}}) E_{\text{rel}}^2 \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}}{\int_0^\infty \sigma_{\text{col}}(T, E_{\text{rel}}) E_{\text{rel}} \exp(-E_{\text{rel}}/k_B T) dE_{\text{rel}}} \quad (39)$$

In the special case where $\sigma_{\text{col}}(T, E_{\text{rel}})$ is independent of E_{rel} (e.g., if it equals πD^2 where D is the hard-sphere collision-diameter so that $\langle k_{\text{col}}(T, E_{\text{rel}}) \rangle_{E_{\text{rel}}}^T$ becomes the familiar hard-sphere collision rate constant $(8\pi kT/\mu)^{1/2} D^2$ (10b)) then $\langle E_{\text{rel}} \rangle_{\text{colliding pairs}}^T$ is $2k_B T$, which exceeds E_{rel} for all pairs by the

$1/2 k_B T$ in Tolman's statement. This has sometimes been misstated in the literature (19). Thus Tolman's statement involves an approximation for the collision rate. The version of the theorem proved here does not involve any such assumption and is completely general.

Many chemists consider the Arrhenius form of the rate constant as just a useful functional form for fitting experimental data. It is hoped that the derivation presented here will lead to a greater appreciation for the Tolman interpretation of the Arrhenius energy of activation.

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