How are Arrhenius frequency factor and rates of activation and deactivation related?

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Abstract: This project is to establish the relationship between Arrhenius frequency factor and the rates of activation and deactivation.

In the following paragraphs, we will derive the mathematical relationship between Arrhenius frequency factor for the overall reaction and the rates of activation and deactivation. We will illustrate the derivation using a bimolecular reaction; however, the idea is valid for any elementary reaction.

The bimolecular reaction

$$A + B \rightarrow C \qquad\qquad \text{rate} = k\,[A]\,[B]$$

is considered by "activated complex theory".

According to activated complex model, the reactants are getting over into an unsteady activated complex on the reaction pathway

$$A + B \leftrightarrow AB^{\ddagger} \rightarrow C \qquad\qquad \text{rate} = k_3\,[AB^{\ddagger}]$$

It can be shown that

$$k\,[A]\,[B] = k_3\,[AB^{\ddagger}] \quad \dots (1.1)$$

In this equation, k is the bimolecular rate constant for conversion of A and B to C and k_3 is the unimolecular rate constant for decomposition of the activated complex $AB^{\ddagger}$ to form C.

The dependence of the reaction rate on the concentrations of reacting substances is given by the **Law of Mass Action**. This law states that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at any constant temperature at any given time.

According to law of mass action,

$$\text{Rate of activation } (v_1) = k_1\,[A]\,[B] \qquad \dots (1.2)$$
$$\text{Rate of deactivation } (v_2) = k_2\,[AB^{\ddagger}] \qquad \dots (1.3)$$
$$\text{Rate of decomposition } (v_3) = k_3\,[AB^{\ddagger}] \qquad \dots (1.4)$$

Further, the ratio of Eq. (1.2) to Eq. (1.3) yields

$$v_1/v_2 = (k_1\,k_3/\,k_2\,k) \dots (1.5)$$

since k_1, k_2, k_3 and k are constants at constant temperature; (v_1/v_2) should also be constant at constant temperature.

The change in $[AB^{\ddagger}]$ over time is given by the equation

$$d\,[AB^{\ddagger}]/dt = k_1\,[A]\,[B] - k_2\,[AB^{\ddagger}] - k_3\,[AB^{\ddagger}]$$

Since $AB^{\ddagger}$ is short lived intermediate, we can apply to $AB^{\ddagger}$ the steady state principle. We thus obtain

$$d\,[AB^{\ddagger}]/dt = k_1\,[A]\,[B] - k_2\,[AB^{\ddagger}] - k_3\,[AB^{\ddagger}] = 0$$
$$k_1\,[A]\,[B] = [AB^{\ddagger}]\,(k_2 + k_3) \dots (1.5)$$

The Eqs. (1.1) and (1.5) are combined and are expressed as per Eq. (1.6):

$$k\,(k_2 + k_3) = k_3\,k_1 \dots (1.6)$$

Taking logarithms and then differentiating with respect to temperature, Eq. (1.6) yields

$$d\ln k/dT + d\ln(k_2 + k_3)/dT = d\ln k_3/dT + d\ln k_1/dT$$

or equivalently

$$d\,(k_2 + k_3)/dT = (k_2 + k_3)\,[d\ln k_3/dT + d\ln k_1/dT - d\ln k/dT]$$

or equivalently

$$dk_2/dT + dk_3/dT = (k_2 + k_3)\,[d\ln k_3/dT + d\ln k_1/dT - d\ln k/dT]$$

or equivalently

$$k_2\,(d\ln k_2/dT) + k_3\,(d\ln k_3/dT) = (k_2 + k_3)\,[d\ln k_3/dT + d\ln k_1/dT - d\ln k/dT] \qquad \dots (1.7)$$

Arrhenius (1889) first pointed out that the variation of rate constant with temperature can be represented by an equation similar to that used for equilibrium constant, namely,

$$d\ln k'' /dT = E'' / RT^2$$

In this equation k'' is the reaction rate constant, T the absolute temperature, R the gas constant in calories and E'' a quantity characteristic of the reaction with the dimension of energy. E'' is known as the energy of activation. From this it follows that

$$d\ln k_1/dT = E_1/RT^2 \qquad\qquad d\ln k_2/dT = E_2/RT^2$$
$$d\ln k_3/dT = E_3/RT^2 \qquad\qquad d\ln k/dT = E_a/RT^2$$

where: E_1, E_2, E_3 and E_a indicate the activation energies of the reactions involving k_1, k_2, k_3 and k respectively. Substitution of these values in Eq. (1.7) gives

$$k_2 E_2 + k_3 E_3 = (k_2 + k_3)(E_3 + E_1 - E_a)$$

or equivalently

$$(k_2 + k_3)E_a = k_2 (E_3 + E_1 - E_2) + k_3 E_1 \qquad \dots (1.8)$$

Inserting $(k_2 + k_3)$ from Eq. (1.6) into Eq. (1.8), we thus obtain

$$E_a (k_1 k_3/k) = k_2 (E_3 + E_1 - E_2) + E_1 k_3$$

or equivalently

$$E_a (k_3/k) = (k_2/k_1)(E_3 + E_1 - E_2) + E_1 (k_3/k_1)$$

or equivalently

$$E_a (k_3/k) = (v_2/v_1)(k_3/k)(E_3 + E_1 - E_2) + E_1 (k_3/k_1) \quad \dots (1.9)$$

on rearrangement this yields for the rate constant of the overall reaction

$$k = (k_1/E_1)[E_a - (v_2/v_1)(E_3 + E_1 - E_2)] \qquad\qquad \dots (1.10)$$

The Arrhenius equation gives "the dependence of the rate constant k of overall reaction on the temperature T (in absolute temperature kelvin) and activation energy E_a ", as shown below:

$$k = A\, e^{-E_a/RT}$$

where A is the pre-exponential factor or simply the Arrhenius frequency factor for the overall reaction.
this, on substitution into Eq. (1.10), finally gives

$$A = (k_1/E_1)\, e^{E_a/RT}[E_a - (v_2/v_1)(E_3 + E_1 - E_2)]$$

or equivalently

$$A = (P_1 Z_1/E_1)\, e^{(E_a - E_1)/RT}[E_a - (v_2/v_1)(E_3 + E_1 - E_2)]$$

or equivalently

$$A = (v_2/v_1)\, e^{(E_a - E_1)/RT}[E_a (P_1 Z_1/E_1)(v_1/v_2) - (P_1 Z_1/E_1)(E_3 + E_1 - E_2)] \dots (1.11)$$

Conclusion: Relying on steady state principle, we thus can establish the relationship between Arrhenius frequency factor for the overall reaction and the rates of activation and deactivation. Equation (1.11) is valid only if the reaction intermediate forms slowly and reacts readily so its concentration stays low.

References:
1. Eyring, H.; Journal of Chemical Physics, 1935, 3, 107-115
2. Samuel H. Maron and Carl F. Prutton, Principles of physical chemistry: "**Kinetics of Homogeneous Reactions**", fourth edition, Oxford & IBH Publishing Co. Pvt. Ltd.
3. Laidler, K. J., Chemical Kinetics: "**Composite Reactions**", In, McGraw-Hill Book Company, Inc., New York, 1950
4. Laidler, K.; King, C, "**Development of transition-state theory**". The Journal of physical chemistry 1983, 87, (15), 2657
5. Arrhenius, J. Phys. Chem., 4, 226 (1889)
6. Laidler, K. J. (1993) The World of Physical Chemistry, Oxford University Press
7. Eric V. Anslyn, Dennis A. Doughtery., "**Transition State Theory and Related Topics**". In Modern Physical Organic Chemistry University Science Books: 2006; pp 365–373

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