

CH1201 : General Physical Chemistry

Satvik Saha, 19MS154

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Note: All logarithms are natural unless specified otherwise.

Problem 1 Is the activation energy E_a dependent on temperature? Qualitatively draw an E_a versus temperature plot, i.e. represent how E_a changes with reaction temperature.

Solution The activation energy represents the extra energy required by reactant molecules to reach an ‘activated complex’, a state where the formation and breaking of bonds along with restructuring of the molecule takes place. Thus, it is the difference between the energy of such an activated complex E_X and the average energy of the reactant molecules E_A .

The activation energy for the forward reaction $E_{a,1}$ is thus given by $E_X - E_A$, and that of the backward reaction $E_{a,-1}$ is given by $E_X - E_B$, where E_B is the average energy of the products. The heat of the reaction $\Delta H = E_B - E_A = E_{a,1} - E_{a,-1}$ is given by the Van’t Hoff equation

$$\frac{d \log K}{dT} = \frac{\Delta H}{RT^2}.$$

Here, the equilibrium constant $K = k/k_{-1}$ is the ratio of the rate constants for the forward and backward reactions. Separating the forward reaction, we have the relation

$$E_a = RT^2 \frac{d \log k}{dT}.$$

Integration and rearrangement yields the Arrhenius equation $k = Ae^{-E_a/RT}$, or

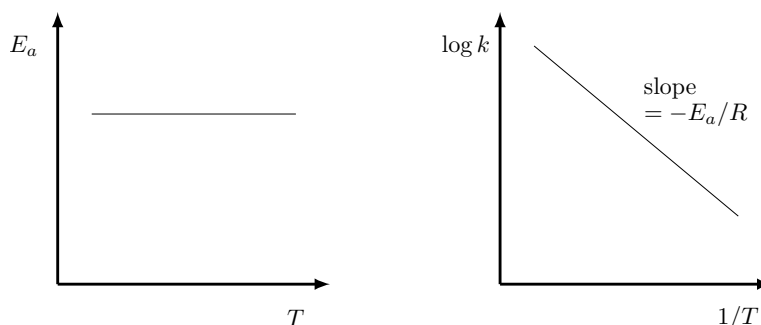
$$\log k = -\frac{E_a}{RT} + \log A.$$

Another approach is to interpret E_a in terms of the Gibbs energy of activation, given by the relations $\Delta G^\ddagger = -RT \log k = \Delta H^\ddagger - T\Delta S^\ddagger$, where ΔH^\ddagger is the enthalpy of activation and ΔS^\ddagger is the entropy of activation for the forward reaction. Rearranging, we obtain the Eyring equation

$$\log k = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}.$$

Comparing this with the Arrhenius equation gives $E_a = \Delta H^\ddagger + RT$.

For typical reaction temperatures, the activation energy E_a is assumed to be independent of temperature. Empirically, a plot of $\log k$ vs $1/T$ is generally a straight line, with constant slope E_a/R . Although some reactions do not show such a linear trend, this is generally corrected by introducing a pre-exponential factor to the Arrhenius equation, such as $k = AT^m e^{-E_a/RT}$ keeping E_a constant.



More precisely, the activation energy of a reaction may be regarded as the minimum amount of energy required in the collision between reactant molecules, for the the initiation of the reaction. Increasing the reaction temperature does increase the *average kinetic energy* of the reactant, however this does not change the energy threshold, merely the *number of molecules* which have that energy. Hence, the impact is purely on the kinetics of the reaction.

Problem 2 For a chemical reaction, the rate constant at 25 °C is doubled when the temperature is raised to 45 °C. Determine the activation energy in kJ mol⁻¹.

Solution We use the Arrhenius equation,

$$k = Ae^{-E_a/RT}.$$

Considering two different temperature, $T_1 = 298$ K and $T_2 = 318$ K, we divide and take logarithms, obtaining

$$\log \frac{k_2}{k_1} = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right].$$

Rearranging, and using $k_2/k_1 = 2$, we have

$$E_a = \frac{T_1 T_2}{T_2 - T_1} R \log 2 = \frac{298 \times 318}{318 - 298} \times 8.314 \times \log 2 = 27.3 \text{ kJ mol}^{-1}.$$

Problem 3 For a 10 °C rise in temperature, the rate constant doubles for reaction I and triples for reaction II. If both reactions have the same pre-exponential factor, what is the ratio of their activation energies?

Solution We again use the relation from the previous problem, setting the initial and final temperatures the same for both reactions. Thus,

$$E_a \propto \log \frac{k_f}{k_i}.$$

Thus, the ratio of activation energies (I over II) is simply $\log 2 / \log 3 \approx 0.631$.

Problem 4 Explain mathematically how the value of the Michaelis-Menten constant k_m can be obtained for an enzyme catalyzed reaction. What factors affect k_m ?

Solution Consider a general enzyme catalyzed reaction, with substrate S, enzyme E and products P.



Here, $[ES]^*$ represents an intermediate complex. Since the amount of enzyme is much less than the amount of substrate, we apply a steady state assumption on the intermediate complex, claiming that its concentration becomes constant over time. Thus,

$$\frac{d[ES]^*}{dt} = k_1[E][S] - k_2[ES]^* - k_3[ES]^* = 0.$$

$$[ES]^* = \frac{k_1}{k_2 + k_3} [E][S].$$

Now, the concentration of the free enzyme can be obtained using conservation as $[E] = [E]_0 - [ES]^*$. Plugging this into the relation for $[ES]^*$, and setting $(k_2 + k_3)/k_1 = k_m$ yields

$$k_m [ES]^* = ([E]_0 - [ES]^*) [S] \implies [ES]^* = \frac{[E]_0 [S]}{k_m + [S]}.$$

The rate of the reaction is governed by the rate of formation of the product, i.e. $R = k_3 [ES]^*$. Thus,

$$R = \frac{k_3 [E]_0 [S]}{k_m + [S]}.$$

This reaches its maximum values when $[S] \gg k_m$, i.e. $R_{max} = k_3[E]_0$. We thus call k_3 the turnover rate, i.e. the rate of conversion of substrate molecules per molecule of enzyme.

For experimentally determining k_m , we use the reciprocal of the previous relation to obtain

$$\frac{1}{R} = \frac{k_m}{k_3[E]_0[S]} + \frac{1}{k_3[E]_0} = \frac{k_m}{R_{max}} \left(\frac{1}{[S]} \right) + \frac{1}{R_{max}}.$$

Thus, by varying the concentration of substrate, we obtain a plot of $1/R$ versus $1/[S]$ called a Lineweaver-Burk plot. Clearly, this has a y -intercept of $c = 1/R_{max}$ and slope $m = k_m/R_{max}$. The ratio m/c thus yields the Michaelis-Menten constant k_m .

The factors which affect k_m are pH, temperature, ionic strength and the nature of the substrate.

Problem 5 How does the Michaelis-Menten equation explain why the rate of an enzyme catalyzed reaction is proportional to the amount of enzyme?

Solution We use the previously derived Michaelis-Menten equation,

$$R = \frac{k_3[E]_0[S]}{k_m + [S]}.$$

Note that when the amount of substrate is very large (as it generally is), $R \rightarrow k_3[E]_0$. Thus, $R \propto [E]_0$, and is mostly independent of $[S]$.

Essentially, when a large amount of substrate relative to the enzyme is present, the rate of formation of the intermediate is limited by the amount of free enzyme present. Note that the total amount of enzyme (free or bound in the intermediate complex) is conserved. Thus, the rate of formation of the product, which is directly proportional to the amount of intermediate, is also proportional to the amount of enzyme supplied.

Problem 6 For an enzyme catalyzed reaction, the Lineweaver-Burk plot resulted in a slope and intercept values of $3.5 \times 10^{-2} \text{ s}$ and $5 \times 10^4 \text{ mol}^{-1} \text{ l s}$ respectively. Estimate k_m and the turnover number when the initial concentration of the enzyme is $2.5 \times 10^{-9} \text{ mol l}^{-1}$.

Solution We simply use $k_m = \text{slope}/\text{intercept}$ to obtain

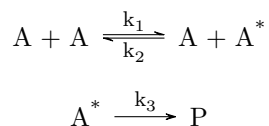
$$k_m = \frac{3.5 \times 10^{-2}}{5 \times 10^4} = 7 \times 10^{-7} \text{ mol l}^{-1}.$$

Note that the intercept is simply $1/R_{max}$. Now, the turnover number k_3 is given by

$$k_3 = \frac{R_{max}}{[E]_0} = \frac{1}{5 \times 10^4 \times 2.5 \times 10^{-9}} = 8000 \text{ s}^{-1}.$$

Problem 7 In the Lindemann mechanism of unimolecular reactions, what is the observed order at low concentration?

Solution The Lindemann mechanism posits the following steps.



Here, A^* is the activated reactant and P is the decomposition product(s). Since activated molecules are short lived, we impose a steady state condition on them.

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_2[A][A^*] - k_3[A^*] = 0.$$

$$[A^*] = \frac{k_1[A]^2}{k_3 + k_2[A]}.$$

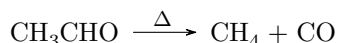
The rate of the reaction is again governed by the formation of the product, i.e. $R = k_3[A^*]$. Hence,

$$R = \frac{k_1 k_3 [A]^2}{k_3 + k_2 [A]}.$$

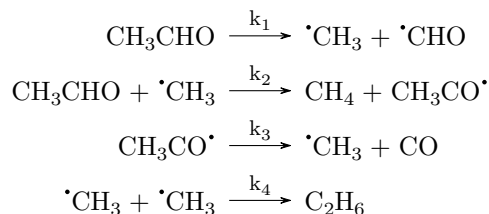
Now, when $[A]$ is very low, we make the approximation $k_3 \gg k_2[A]$. This means that the rate of deactivation is very low, because of fewer collisions. Thus, the denominator in the rate law tends to k_3 , giving $R = k_1[A]^2$. This behaviour is second order with respect to the concentration of the reactant $[A]$.

Problem 8 Give the kinetics of the thermal decomposition of CH_3CHO .

Solution We propose that the thermal decomposition of CH_3CHO takes place via a chain reaction.



The initiation and propagation steps involve the synthesis of intermediate radicals.



Applying the steady state assumption on the intermediates,

$$\frac{d[\cdot\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] + k_3[\text{CH}_3\text{CO}\cdot] - 2k_4[\cdot\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] - k_3[\text{CH}_3\text{CO}\cdot] = 0$$

Adding these together,

$$k_1[\text{CH}_3\text{CHO}] = 2k_4[\cdot\text{CH}_3]^2 \quad \implies \quad [\cdot\text{CH}_3] = \sqrt{\frac{k_1}{2k_4}[\text{CH}_3\text{CHO}]}.$$

Hence, the rate of the reaction is given by the rate of formation of methane, i.e.

$$R = \frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3\text{CHO}][\cdot\text{CH}_3] = \sqrt{\frac{k_2^2 k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{3/2}.$$

Thus, the rate of the reaction is of 3/2 order with respect to the concentration of acetaldehyde.

Problem 9 On irradiation of propionaldehyde at 30°C with light of wavelength 3020 \AA , the quantum yield for the production of CO is observed to be 0.54. If the incident light intensity is 15000 erg/s , calculate the rate of CO formation. What is the light intensity in Einstein per second?

Solution A wavelength of 3020 \AA corresponds to an energy of $E = hc/\lambda = 6.58 \times 10^{-19} \text{ J}$ per photon. Now, using $1 \text{ erg} = 10^{-7} \text{ J}$, the given light intensity is $I = 1.5 \times 10^{-3} \text{ J s}^{-1}$. This corresponds to $n = I/E = 2.28 \times 10^{15}$ photons per second, i.e. $N = n/N_A = 3.79 \times 10^{-9} \text{ mol photons per second}$. Thus, the rate of production of CO is simply $\phi n = 1.23 \times 10^{15}$ molecules per second, or $\phi N = 2.04 \times 10^{-9} \text{ mol s}^{-1}$.

The energy of 1 mol of photons here is $N_A E = 3.96 \times 10^5 \text{ J}$. Thus, the given light intensity corresponds to $I/(N_A E) = 3.79 \times 10^{-9} \text{ Einstein/s}$.