

Module 6 : Reaction Kinetics and Dynamics

Lecture 29 : Temperature Dependence of Reaction Rates

Objectives

In this Lecture you will learn to do the following

- Give examples of temperature dependence of reaction rate constants (k).
- Define the activated complex.
- Outline Arrhenius theory of temperature dependence of k.
- Rationalize the temperature dependence of molecular speeds and molecular energies through appropriate distribution functions.
- Summarize other theories for temperature dependence of k.

29.1 Introduction

Temperature dependence of physical and chemical parameters is of great interests to chemists and predicting correct temperature dependence is a test as well as a challenge for framing suitable theories. In thermodynamics, temperature dependence of heat capacities and enthalpies was used in calculating equilibrium constants at different temperatures. The departure of real gas behaviour from the ideal gas behaviour is expressed through the temperature dependent virial coefficients.

In chemical kinetics, it was observed that for many reactions, increasing the temperature by 10°C, doubled the rates. In rate processes, the temperature dependence is quite striking. In this lecture, we will consider preliminary attempts at explaining this temperature dependence and take up the detailed explanations in later lectures. A knowledge of the distribution of molecular speeds at a given temperature and the population of energy levels is essential in understanding the temperature dependent rate processes and these aspects will also be outlined here.

The most common analysis of temperature dependence of reaction rates over a small temperature range of a few tens of degrees Celsius has been through the Arrhenius equation given below.

$$k = A e^{-E_a / RT} \quad (29.1)$$

Where A is the pre exponential factor (commonly referred to as the frequency factor) and E_a is the energy of activation. The absolute temperature is denoted by T and R is the gas constant. The rationalization of the Arrhenius equation was given by Van't Hoff, who noted that the equilibrium constant K_c for a reaction like



depends on temperature according to the Gibbs Helmholtz equation (lecture 21)

$$\left(\frac{\partial \ln K_c}{\partial T} \right)_p = \frac{\Delta U^0}{RT^2} \quad (29.3)$$

Where ΔU^0 is the standard internal energy change for the reaction. Since

$$K_c = k_1 / k_{-1} = \{ [C] [D] / [A] [B] \}_{eq} \quad (29.4)$$

$$\partial \ln K_c / \partial T = \partial \ln k_1 / \partial T - \partial \ln k_{-1} / \partial T = \Delta U^0 / RT^2 = E_1 / RT^2 - E_{-1} / RT^2 \quad (29.5)$$

When $\Delta U^0 = E_1 - E_{-1}$ and the central observation is that the forward and reverse rates are influenced by different activation energies Eq (29.5) can be split into two separate equations

$$d \ln k_1 / dT = E_1 / RT^2 \text{ and } d \ln k_{-1} / dt = E_{-1} / RT^2 \quad (29.6)$$

and eq (29.6) readily integrates to give the Arrhenius equation for the forward and backward reactions

$$k_1 = A_1 e^{-E_1 / RT}, k_{-1} = A_{-1} e^{-E_{-1} / RT} \quad (29.7)$$

The activation energies are graphically shown in Fig 29.1

Figure 29.1 Energy as a function of the reaction coordinate (RC).

Activation energies for the forward and reverse reactions. The reaction coordinate (RC) represents a variable or a parameter that changes as we go from reactants to the products. In a reaction like $F_2 \rightarrow 2F$, RC is the distance between the fluorine atoms. Before the reaction, $RC = \text{bond distance in } F_2$ and when the reaction is over, $RC = \infty$. In a reaction, such as $H_A + H_B H_C \rightarrow H_A H_B + H_C$, $RC = r_{BC} - r_{AB}$.

In the course of the reaction, RC goes from large negative values to large positive values. The important region of interest is around the high values of the energy where the reaction "occurs".

Even though Arrhenius equation seems to imply that A and E are independent of temperature, kineticists have all along been aware of a more complex temperature dependence. Some of the equations that have been used are

$$k = AT^m \quad (29.8)$$

$$k = A e^{DT} \quad (29.9)$$

$$k = AT^m e^{-B/T} \quad (29.10)$$

$$k = AT^m e^{-(B - DT^* T) / T} \quad (29.11)$$

The temperature dependence of k in eq (29.11) is determined by the temperature dependence of the three parameters m , B and D .

Let us interpret the graph of Fig. 29.1. When the reactants collide in the normal course of their motion, they do not necessarily react and remain as reactants. Certain collisions which occur with sufficient energy (the activation energy) to enable the bond breaking (in the reactants) and the bond making (in the products) steps so that the reaction goes in the forward direction.

There is a minimum or threshold energy for this process which has been referred to as the activation energy. This explanation does not imply that all reactions have a positive activation energy. Reactions such as precipitation reactions seem to occur "instantly", i.e., as soon as the reactants approach one another within a certain distance, the reaction is complete. These are called diffusion controlled reactions. There are some reactions for which the activation energy is negative !

Example 1

The rate constant for the aqueous transformation of thiourea to ammonium thiocyanate is measured at 90°C, 120°C and 130°C. Obtain the Arrhenius parameters for this reaction.

Solution :

The values of k and temperature are shown in the first two rows of Table 29.1. The first step is converting °C into Kelvins. Since $\ln k = \ln A - E_a / RT$ ($\ln = \log_e$), $\ln k$ plotted against $1/T$ should yield a straight line with slope = $-E_a / R$ and intercept = $\ln A$. If there are departures from Arrhenius like behaviour, the graph will depart from a straight line. Plot the graph and verify that you get a straight line. Assuming that you have verified that, let us get values of E_a and A in a simpler way.

Table 29.1 Temperature dependence of k for the reaction thiourea \rightarrow ammonium thiocyanate.

Temp / °C	k / s^{-1}	$\ln (k / s^{-1})$	Temp / K	$\{ 1 / T \} K^{-1}$	$10^3 K / T$
90	4.53×10^{-8}	-16.910	363.15	0.00275	2.754
110	59.3×10^{-8}	- 14.338	383.15	0.00261	2.610
120	197×10^{-8}	-13.137	393.15	0.00254	2.544
130	613×10^{-8}	-12.002	403.15	0.00248	2.480

Let k_1 correspond to $T_1 = 363.15$ K and k_2 correspond to $T_2 = 403.15$ K.

$$\ln k_2 - \ln k_1 = +12.002 - 16.910 = - 4.902 \quad (29.12)$$

$$= (- E_a / R) (1 / T_1 - 1 / T_2) = -(E_a / R) (0.002754 - 0.002480) = -0.000274 E_a / R \quad (29.13)$$

Taking R as $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$E_a = 8.314 \times 4.902 / 0.000274 = 148 \times 10^3 \text{ kJ mol.} \quad (29.14)$$

Substituting the values of E_a in Arrhenius equation, we get the value of A

$$\ln A = \ln k + E_a / RT = - 13.137 + 148 / (8.314 \times 393.15)$$

$$= 8.8 \times 10^{13} \text{ s}^{-1} \quad (29.15)$$

Note that when \ln of k was taken, k was taken dimensionless (as we are interested in the difference between $\ln k$ values). E_a and RT have to be in the same units in the calculations.

29.2 The Maxwell Boltzmann Distribution of Molecular Speeds

We have already commented that molecules have to collide with sufficient speeds so that the reaction occurs. Where does this sufficient energy come from? At a given temperature, not all molecules have the same speeds. During intermolecular collisions, these speeds change too. If we represent a molecular velocity by \vec{v} , it has three independent components v_x , v_y and v_z in the three directions x , y and z . Let us consider monoatomic gas of molecular mass m . The probability $F(v_x, v_y, v_z)$ that a given molecule will have velocity components lying between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$ is written as

$$F(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z \quad (29.16)$$

F is written as a product of three f s because v_x , v_y and v_z are independent and since nature does not distinguish between x , y and z (unless directional fields like gravitational or electromagnetic are present), the form of f is the same in the three directions. Again, since there is no distinction between positive and negative x , f depends on $|v_x|$ or v_x^2 . We can rephrase (29.16) as

$$F(v_x^2, v_y^2, v_z^2) = f(v_x^2) f(v_y^2) f(v_z^2) \quad (29.17)$$

The only function that satisfies an equation like eq (29.17) is an exponential function since $e^{x^2 + y^2 + z^2} = e^{x^2} e^{y^2} e^{z^2}$ and so we conclude that $f(v_x^2)$ may be written as

$$f(v_x^2) = C e^{\pm b v_x^2} \rightarrow C e^{-b v_x^2} \quad (29.18)$$

We take only the negative exponent (C and b are positive) because a positive exponent implies that very large velocities have very high probabilities. This scenario is highly unlikely. To evaluate C , we invoke the physical argument that the velocity has to lie somewhere between $-\infty$ to $+\infty$ and that the total probability is one, i.e.,

$$\int_{-\infty}^{\infty} f(v_x^2) dv_x = C \int_{-\infty}^{\infty} e^{-b v_x^2} dv_x = 1 \quad (29.19)$$

The above integral is a standard integral $\int_0^{\infty} e^{-ax^2} dx = 1/2 (\pi/a)^{1/2}$. Thus eq (29.19) becomes

$$C \int_{-\infty}^{\infty} e^{-b v_x^2} dv_x = C (\pi/b)^{1/2}. \quad (29.20)$$

But since we want the right side to be unity, $C (\pi/b)^{1/2} = 1$ or $C = (b/\pi)^{1/2}$ and

$$f(v_x) = (b/\pi)^{1/2} e^{-b v_x^2} \quad (29.21)$$

From a probability distribution such as $f(x)$, average quantities can be easily determined. The averages of v_x and v_x^2 are given by

$$\langle v_x \rangle = (b/\pi)^{1/2} \int_{-\infty}^{\infty} v_x e^{-bv_x^2} dv_x = 0 \quad (29.22)$$

$$\langle v_x^2 \rangle = (b/\pi)^{1/2} \int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2} dv_x = 1/2b \quad (29.23)$$

In eqs (29.22) and (29.23), averages are denoted by $\langle \rangle$. We have also used another standard integral,

$$\int_0^{\infty} x^2 e^{-ax^2} dx = (1/4) (\pi/a^3)^{1/2}$$

The integral in eq (29.22) is zero because the value of the integrand for positive v_x is equal and opposite to its value at $-v_x$ and thus the area corresponding to the integral on the left of $v_x = 0$ is equal and opposite in sign to the area on the right. This is a special case of a general result that the integral of the product of an even function and an odd function of x is zero over a symmetric interval around zero.

To evaluate eq (29.23), we take the help of the kinetic theory of gases. Do look up the derivation. The pressure of a gas is given in terms of the mean square velocity (speed) as

$$p = (1/3) (N/V) m \langle v^2 \rangle \quad (29.24)$$

Where N/V = number of molecules of the gas / volume = the density of the gas. But $N = n N_A$ where n = number of moles and N_A the Avogadro number. Since $pV = nRT$, we have

$$pV = (1/3) Nm \langle v^2 \rangle = 1/3 n N_A m \langle v^2 \rangle = nRT \quad (29.25)$$

$$\langle v^2 \rangle = 3 RT / mN_A = 3 k_B T / m \quad (29.26)$$

Where $k_B = R / N_A$ is the Boltzmann constant, 1.38×10^{-23} J / K. Since $\langle v^2 \rangle = 3 k_B T / m$, we have $\langle v_x^2 \rangle = k_B T / m$ and substituting this in eq (29.23), we get

$$b = m / 2 k_B T \quad (29.27)$$

Equations (29.21) and (29.17), now become

$$f(v_x) = (m/2\pi k_B T)^{1/2} e^{-mv_x^2/2k_B T} \quad (29.28)$$

$$f(v_x, v_y, v_z) = (m/2\pi k_B T)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_B T} \quad (29.29)$$

This is the Maxwell - Boltzmann distribution of molecular speeds. $F(v_x, v_y, v_z) dv_x, dv_y, dv_z$ gives the probability of finding an arbitrary molecule with a velocity (v_x, v_y, v_z) in the corresponding volume element. A more appealing interpretation of the same is that it is the fraction (of the total molecules) of molecules having velocities (v_x, v_y, v_z) .

Analogous to the radial probability distribution, we can now estimate the probability of finding a particle in a spherical shell of volume $4\pi v^2 dv$. This probability in such a spherical shell is given by

$$4\pi(m/2\pi kT)^{3/2} v^2 \left[e^{-mv^2/k_B T} \right] dv \quad (29.30)$$

The plot of this function at two temperature is given in Fig 29.2.

Fig 29.2 The Maxwell - Boltzmann velocity distribution at low and high temperatures.

The ordinate gives the probability of finding molecules with velocity v in a spherical shell of radius v in a unit interval dv .

Having described the velocity distribution, we can now interpret Arrhenius's equation for temperature dependence of reaction rates. Only a fraction of collisions are with molecular velocities that correspond to sufficient energy E_a (activation energy). When the temperature is raised, the fraction of molecules with high velocities (or large energies) is raised, and so we get a larger value of the rate constant.

29.3 The Boltzmann Distribution of energies

The dependence of the probability of the earlier section on molecular speed can be re-expressed alternatively in terms of kinetic energy $K.E = 1/2 m v^2$. The probability $p(v^2) = P(K.E) = e^{-K.E/k_B T}$. The

gas molecules in an ideal gas possess only kinetic energies and the dependence of the probability on v^2 and on K.E are equivalent. However, in a general case, molecules possess both kinetic and potential energies (PEs) and the total energy $E = K.E + P.E$. Boltzmann generalised Maxwell's result for only KEs to include all energies and the probability distribution for energies, $P(E)$, is called the Boltzmann distribution and is given by,

$$P(E) \propto e^{-E/k_B T} \quad (29.31)$$

This also has to be normalized such that the sum of $P(E)$ s for all energies should be 1. Boltzmann, and Gibbs in particular, developed very general methods for deriving equations such as eq. (29.31) and here, we have merely stated the equation and given some justification for it.

As the energies of all microscopic systems are quantized into levels E_i , we should indeed be looking for the probability of finding a given system with energy E_i and this is given by

$$P(E_i) = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \quad (29.32)$$

The denominator in the above equation is a factor that ensures that $\sum_i P(E_i) = 1$ and it is called the partition function Q .

$$Q = \sum_i e^{-\beta E_i}, P(E_i) = e^{-\beta E_i} / Q \quad (29.33)$$

Here, $\beta = 1/k_B T$ and is called the Boltzmann factor.

Once we know the probability distribution for energy, we can calculate thermodynamic properties like the energy, entropy, free energies and heat capacities, which are all average quantities. To calculate $P(E)$ s we need the energy levels of a system. The energy "levels" of a system can be built up from the molecular energy levels and intermolecular forces. We will consider the simpler problem of molecular energy levels which are pictorially shown in the figure 29.3.

Figure 29.3 Molecular energy levels and the Boltzmann distribution.

You have already studied molecular energy levels in the spectroscopy section (Module 3). The electronic

energy levels are widely separated. In each electronic level, there are several vibrational levels and for each vibrational level, there are several rotational states. This is a simplified and useful model to start with. The total energy is a sum of all these energies and is given by

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} + E_{\text{others}} \quad (29.34)$$

The term E_{others} includes nuclear spin energy levels and interactions between the first four. Assuming the first four to be independent and neglecting the last term, the molecular partition function (i.e., a sum over the molecular energy states) is given by

$$q = \sum_{\text{el}} e^{-(E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}) / k_B T} = \sum_{\text{el}} e^{-\beta E_{\text{el}}} \sum_{\text{vib}} e^{-\beta E_{\text{vib}}} \sum_{\text{rot}} e^{-\beta E_{\text{rot}}} \sum_{\text{trans}} e^{-\beta E_{\text{trans}}} \quad (29.34)$$

$$\text{or } q = q_{\text{el}} q_{\text{vib}} q_{\text{rot}} q_{\text{trans}}, \text{ where } \beta = 1/k_B T \quad (29.35)$$

The molecular partition q function is written as the product of electronic, vibrational, rotational and translational partition functions.

The partition function is a sum over states (of course with the Boltzmann factor β multiplying the energy in the exponent) and is a number. Larger the value of q , larger the number of states which are available for the molecular system to occupy. Since $E_{\text{el}} > E_{\text{vib}} > E_{\text{rot}} > E_{\text{trans}}$, there are far too many translational states available compared to the rotational, vibrational and electronic states. q_{el} is very nearly unity, q_{vib} and q_{rot} are in the range of 1 to 100 while q_{trans} can be much in excess of 10^{10} . We shall calculate the values of these q s and indicate how these q s and the molecular velocity distribution functions are useful in calculating the rate constants.

Example 29.2

Using the standard formulae for the translational, rotational and vibrational energy levels, calculate the molecular translational, vibrational and rotational partition functions.

Solution

a) The translational partition function, q_{trans} .

A molecule confined inside a box of length L has the translational energy levels given by $E_{\text{trans}} = h^2 / 8 mL^2 (n_x^2 + n_y^2 + n_z^2)$ where n_x , n_y and n_z are the quantum numbers in the three directions.

$$q_{\text{trans}} = \sum_{n_x, n_y, n_z} e^{-E_{\text{trans}} / k_B T} = \sum_{n_x} e^{-a n_x^2} \sum_{n_y} e^{-a n_y^2} \sum_{n_z} e^{-a n_z^2} \quad (29.36)$$

$$q_{\text{trans}} = q_x q_y q_z, \text{ the product of translational partition functions in the three directions.} \quad (29.37)$$

Since the levels are very closely spaced, we can replace the sum by an integral

$$q_x = \int_1^{\infty} e^{-\left(\frac{h^2 n_x^2}{8mL^2}\right) / k_B T} dn_x \approx \int_0^{\infty} e^{-a n_x^2} dn_x, \quad a = \frac{h^2}{8mL^2 k_B T} \quad (29.38)$$

using eq 29.20, this becomes

$$q_x = 1/2 \left(\pi / a \right)^{1/2} = \frac{1}{2} \frac{\sqrt{\pi 8 m k_B T}}{h} L \quad (29.39)$$

Multiplying q_x , q_y and q_z , we have, using $V = \text{volume of the box} = L^3$

$$q_{\text{trans}} = [2 \pi m k_B T / h^2]^{3/2} V \quad (29.40)$$

This is usually a very large number (10^{20}) for volumes of 1 cm^3 . This means that such a large number of translational states are accessible for occupation by the molecules of a gas.

b) The rotational energy levels.

$$E_{\text{rot}} = \bar{B} J (J + 1) \text{ where } \bar{B} = h^2 / 8 \pi^2 I \quad (29.41)$$

In the summation, $q_{\text{rot}} = \sum_j (2J+1) e^{-E_{\text{rot},j}/k_B T}$, we can do an explicit summation if only a few terms contribute. The factor $(2J+1)$ for each term accounts for the degeneracy of a rotational state J . The partition function is a sum over states. If energy E_J is degenerate with $(2J + 1)$ states corresponding to it, the Boltzmann factor $e^{-E_{\text{rot},j}/k_B T}$ has to be multiplied by $(2J+ 1)$ to account for all these states. If the rotational energy levels are placed very close to one another, we can integrate similar to what we did in (a) above to get.

$$\begin{aligned} q_{\text{rot}} &= \int_0^{\infty} e^{-\bar{B}J(J+1)/k_B T} (2J + 1) dJ \quad (29.42) \\ &= \int_0^{\infty} e^{-a x} dx \text{ where } a = \bar{B} / k_B T \text{ and } x = J^2 + J, dx = (2J + 1) dJ \end{aligned}$$

$$q_{\text{rot}} = 1/a = k_B T / \bar{B} \quad (29.43)$$

c) The vibrational energy levels

$$E_{\nu} = (\nu + 1/2) h \nu \text{ where } \nu \text{ is the vibrational frequency and } \nu \text{ is the vibrational quantum numbers.}$$

In this case, it is easy to sum the geometric series shown below

$$\begin{aligned} q_{\text{vib}} &= \sum_{\nu=0}^{\infty} e^{-(\nu+1/2)h\nu/k_B T} \quad (29.44) \\ &= e^{-h\nu/2k_B T} (1 + e^{-h\nu/k_B T} + e^{-2h\nu/k_B T} + \dots) \\ &= e^{-h\nu/2k_B T} (1 + x + x^2 + x^3 \dots) \\ &= e^{-h\nu/2k_B T} [1 / (1-x)] \text{ where } x = e^{-h\nu/k_B T} \text{ which is less than 1} \end{aligned}$$

$$\frac{1}{1 - e^{-h\nu/k_B T}} \text{ if the zero of energy scale is at } h\nu/2k_B T. \quad (29.45)$$

Example 29.3

Find the electronic partition of H_2 at 300 K.

Solution

The lowest electronic energy level of H_2 is near - 32 eV and the next level is about 5 eV higher. Taking - 32 eV as the zero (or reference value of energy),

$$q_e = e^0 + e^{-5 \text{ eV} / kT} + \dots \quad (29.46)$$

At 300 K, $k_B T = 0.02\text{eV}$ and $q_e = 1 + e^{-200} + \dots$

Where all terms other than the first are nearly 0. This implies that $q_e = 1$. The physical meaning of this is that only the ground electronic state is generally accessible at room temperature.

Example 29.4

Express the partition function (Q) of a collection of N molecules in terms of the molecular partition function q .

Solution

Assuming molecules to be independent, the total energy E of molecules is a sum of individual molecular energies E_i and

$$Q = \sum_{\text{all possible } E_s} e^{-\beta E} = \sum_{\text{all } i} e^{-\beta E_i^{(1)}} \sum_{\text{all } i} e^{-\beta E_i^{(2)}} \dots \sum_{\text{all } i} e^{-\beta E_i^{(N)}} \\ = q \, q \dots \dots \dots q = q^N \quad (29.47)$$

Here $\varepsilon_i^{(1)}, \varepsilon_i^{(2)} \dots \varepsilon_i^{(N)}$ are energies of individual molecules 1, 2,N, and a sum of all E_s can only come from summing over all ε_i s. Gibbs postulated that $Q = q^N / N!$ (29.48)

The $N!$ in the denominator is due to the indistinguishability of the tiny molecules (or other quantum particles in a collection).

Example 29.5

Show that the average energy $\langle E \rangle$ of the system above is given by $-\partial \ln Q / \partial \beta$

Solution :

In the collection of N molecules, how many molecules (n_i) have the energy E_i ? This has to be $N e^{-\beta E_i} / Q$ using eq (29.32). This is because the fraction of molecules n_i / N having the energy E_i is $e^{-\beta E_i} / Q$ which is the same as the probability of finding a molecule with energy E_i in the collection. The average energy is obtained by multiplying E_i with its probability and summing over all i . i.e.,

$$\langle E \rangle = \sum E_i P_i = \sum E_i e^{-\beta E_i} / Q = - \sum \frac{1}{Q} \frac{\partial}{\partial \beta} e^{-\beta E_i} = - \frac{1}{Q} \frac{\partial}{\partial \beta} \sum e^{-\beta E_i} \quad (29.49)$$

$$= - \frac{1}{Q} \frac{\partial Q}{\partial \beta} = - \frac{\partial \ln Q}{\partial \beta} \quad (29.50)$$

Other thermodynamic functions from the partition function we have already seen that $P_i = e^{-\beta E_i} / q$ and that the average energy $U = -\partial \ln q / \partial \beta$. This average energy is not the absolute value (since the thermodynamic functions U, S, A and G have no absolute value, their value has to be measured with respect to a standard or a reference value. Let the standard value of U be $U(0)$. Then U is given by

$$U = U(0) - \partial \ln Q / \partial \beta = U(0) + \sum E_i P_i; P_i = e^{-\beta E_i} / q \quad (29.51)$$

We next obtain entropy. The standard procedure is to use the Boltzmann formula $S = k_B \ln W$ where W is the number of ways of achieving a given configuration or a given distribution of energies of molecules. We will use a shorter path to S by noting that the formula for entropy of mixing, $S = -N k_B \sum x_i \ln x_i$ can be generalized by replacing x_i s by P_i s, the probabilities of the states of a distribution.

$$S = -k_B N \sum P_i \ln P_i = -k_B N \sum (n_i / N) \ln (n_i / N) \quad (29.52)$$

$$\text{Using } \ln P_i = -\beta E_i - \ln q \quad (29.53)$$

$$S = -Nk_B \left(-\beta \sum P_i E_i - \sum P_i \ln q \right) \quad (29.54)$$

$$= k_B \beta \sum P_i E_i + Nk_B \ln q \quad (29.55)$$

$$= k_B \beta (U - U(0)) + Nk_B \ln q \quad (29.56)$$

$$= [U - U(0)]/T + k \ln Q \quad (29.57)$$

Where Q, the partition function for N molecules is written as q^N for distinguishable molecules. For indistinguishable molecules, $Q = q^N / N!$

Rewriting (29.57), we get the Helmholtz free energy.

$$TS - [U - U(0)] = kT \ln Q$$

$$\text{or } A - A(0) = [U - U(0)] - TS = -kT \ln Q \quad (29.58)$$

Just as U is measured relative to U(0), A is measured relative to A(0). As $T \rightarrow 0$, $U(0) = A(0)$.

To obtain the thermodynamic functions, enthalpy (H) and the Gibbs free energy (G), we need to express pressure in terms of the partition function. From thermodynamics, we know that $\left(\frac{\partial A}{\partial V} \right)_T = -P$. Using this in

eq (29.58), we get

$$P = -\left(\frac{\partial A}{\partial V} \right)_T = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (29.59)$$

Enthalpy $H = U + PV$ or $H - H(0) = U - U(0) + PV$, or

$$H - H(0) = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_V + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (29.60)$$

Similarly, $G - G(0) = H - H(0) - TS$ or $A - A(0) + PV$, or

$$G - G(0) = -kT \ln Q + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (29.61)$$

$$\text{For an ideal gas, } PV = nRT, \quad Q = q^N / N! \quad (29.62)$$

Substituting these values in (29.61), we get

$$G - G(0) = -nRT \ln (q/N)$$

where $N = \text{number of molecules} = \text{number of moles} \times \text{Avogadro number}$, i.e. nN_A . Defining the molar partition as q_m / q_n in units of mol^{-1} , we have the final expression.

$$G - G(0) = -nRT \ln (q_m / N_A) \quad (29.63)$$

This is a very central expression which is useful for the calculation of equilibrium constants in terms of partition functions.

Consider the reaction



To obtain the equilibrium constant K, we need ΔG^0 , the standard free energy change for the reaction, which is given by

$$\Delta G^0 = -RT \ln K = cG_{C,m}^0 - bG_{B,m}^0 - aG_{A,m}^0 \quad (29.65)$$

Where

$$G_{A,m}^0 = G_{A,m}^0(0) - RT \ln \left(\frac{q_{A,m}^0}{N_A} \right) \quad (29.66)$$

is the standard molar free energy of A (subscript m refers to molar and superscript 0 refers to the

$$G_{A,m}^0$$

standard state of 1 bar pressure). We can write similar relations for $G_{B,m}^0$ and $G_{C,m}^0$ and equation (29.65) becomes

$$\Delta G^0 = cG_{C,m}^0(0) - aG_{A,m}^0(0) - bG_{B,m}^0(0) - cRT \ln(q_{C,m}^0/N_A) - bRT \ln(q_{B,m}^0/N_A) + aRT \ln(q_{A,m}^0/N_A) \quad (29.66)$$

We know that at $T = 0$, $U(0) = H(0) = A(0) = G(0)$ and the first three terms of eq (29.65) can be combined to give

$$\Delta_r G^0 = \Delta_r U^0 = cU_{C,m}^0(0) - bU_{B,m}^0(0) - aU_{A,m}^0(0) \quad (29.67)$$

The last three terms of eq (29.66) can be combined and using (29.67) and $\Delta G^0 = -RT \ln K$,

$$K = \frac{(q_{C,m}^0/N_A)^c}{(q_{A,m}^0)^a (q_{B,m}^0)^b} e^{-\Delta_r U^0/RT} \quad (29.68)$$

This is an expression for the equilibrium constant for reaction (29.64) in terms of the partition functions of reactants and products and the reference values of their energies U^0 . This can be very easily generalized to reaction of all stoichiometry.

29.4 Problems

29.1) The rate constants for the decomposition of acetaldehyde are $0.343 \text{ M}^{-1} \text{ s}^{-1}$ and $0.789 \text{ M}^{-1} \text{ s}^{-1}$ at 70 K and 81 K respectively. Find the preexponential factor and the activation energy.

29.2) Using the following information, find E_a and A (in $\text{M}^{-1} \text{ s}^{-1}$ where $\text{M} = \text{mol / lit}$)

T in K	300	350	400	450
$k / (10^7 \text{ M}^{-1} \text{ s}^{-1})$	0.79	3.0	8.0	17

At what temperature is the rate constant at 300 K doubled?

29.3) The rate constant for a first order reaction is 4.53×10^8 and $5.93 \times 10^9 \text{ s}^{-1}$ at 363 K and 383 K respectively. Find E_a and A (now in s^{-1}).

29.4) Bromination of propanone in acidic medium gave the following data. Find A and E_a .

T / K	293	297	300	302
$k(10^{-6} \text{ M}^{-1} \text{ s}^{-1})$	1.16	2.02	5.59	8.60

29.5) For the Maxwell - Boltzmann distribution of molecular speeds, at what speed is $F(v)$ maximum?

29.6) At $T = 300 \text{ K}$, for what v ($v = v_{\text{max}}$) is $F(v)$ maximum? What should be the increase in T so that the new $F(v_{\text{max}})$ (at the higher T) has half the value of $F(v_{\text{max}})$ at 300 K?

29.7) The ground state of Na is a doublet (two states with the same energy). Assuming this to be the zero of

energy and assuming that the next higher energy to be $2 e V$ higher than this state, calculate q_e

29.8) The bond length r_e of O_2 is 1.2 \AA . The moment of inertia I is $m r_e^2 / 2$ where m of O is $16 * 1.66 * 10^{-27} \text{ kg}$. Calculate B and the rotational partition function at 300 K.

29.9) The vibrational frequency of ICI is 384 cm^{-1} . What is its vibrational partition function at 300 K? What is the fraction of molecules in the ground state ($v = 0$) and the first excited state $v = 1$?

29.10) Calculate the translational partition function of N_2 at 300 K. For volume, use the molar volume at 300 K.

Recap

In this Lecture you have learnt the following.

Summary

In the present lecture, the temperature dependence of reaction rates was the focus of interest. Arrhenius equation accounted for the increase in reaction rates with increasing temperature with considerable success. It postulated an energy of activation which was the minimum energy needed for the reactants to cross over to the products. Temperature dependence of reaction rates was used to estimate the activation energy using the Arrhenius plot.

The reaction coordinate is a parameter or an indicator indicating the extent of passage from the reactant to the product. Since the activation energy plays a critical role in reaction rates (except in diffusion limited reactions where in just bringing the reactants "close to one another" completes the reaction) we need to find out where this "extra" energy comes from. Additional energy may either come from collisions with molecules with great speeds or from some of the molecules which have excess internal energy which can be transferred to the reacting molecules. This led us naturally to the velocity distribution and energy distribution among molecules. We presented approximate derivations of the Maxwell Boltzmann distribution of molecular speeds and the Boltzmann distribution of energies.

The energy distributions are expressed in terms of partition functions which measure the number of available states with each state i weighted by the Boltzmann factor, $\exp(-E_i / k_B T)$. Since the total molecular energy can be written as a sum over electronic, vibrational, rotational and translation energies, the total partition function was expressed as the product of electronic, rotational, vibrational and translational partition functions. Separate expressions were obtained for these partition functions; their estimates were given and the partition function for a collection of molecules and the average energy of a system was obtained in terms of molecular partition functions.