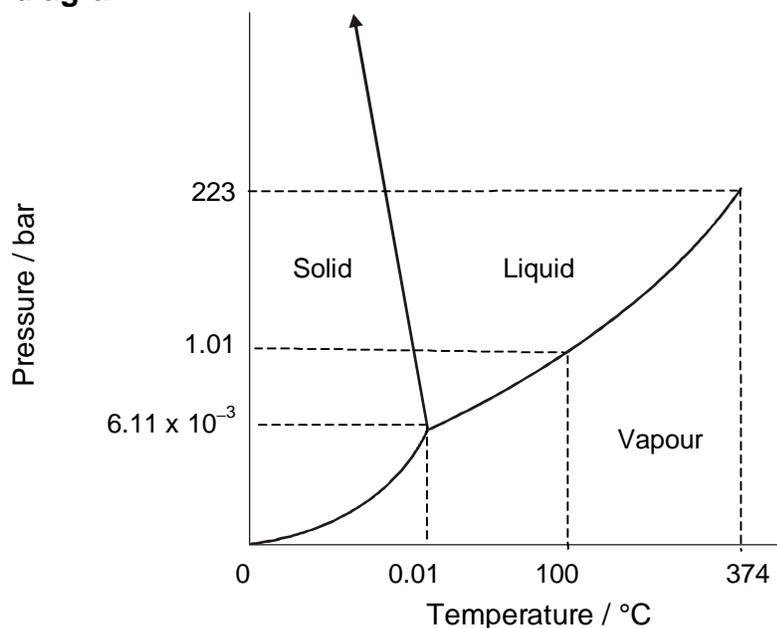


Theoretical Problems

Problem 1 Water

Water, the commonest substance around us, is an excellent system to understand many concepts of thermodynamics. It exists in three different phases: solid (ice), liquid and vapour. [At high pressures, different solid phases of ice exist, but we do not consider them here.] The phase diagram for water, which gives the pressure versus temperature curves for its different phases in equilibrium, is shown below :

A. Phase diagram



Phase diagram of water (not to scale)

- At what temperature and pressure do all the three phases of water coexist in equilibrium?
- What is the effect of decrease of pressure on boiling point of water and melting point of ice, as seen from the phase diagram?
- The liquid-vapour coexistence curve ends at the point $P_c = 223$ bar and $T_c = 374^\circ\text{C}$. What is the significance of this point?
- What is the phase of water at $T = 300$ K, $P = 12.0$ bar; $T = 270$ K, $P = 1.00$ bar?

- e. Below what value of pressure will ice, when heated isobarically, sublime to vapour?
- f. At a certain temperature and pressure on the liquid-vapour co-existence line, the molar volumes of water in the two phases are

$$\bar{V}_\ell = 3.15 \times 10^{-5} \text{ m}^3 \quad \bar{V}_v = 15.8 \times 10^{-5} \text{ m}^3$$

For 1.00 mole of water in a 0.100 litre vessel at this temperature and pressure, determine the volume fractions in liquid and vapour phases.

B. Clausius – Clapeyron equation

- a. Explain your answer to part **A. b** above on the basis of the Clapeyron equation.
- b. Autoclaves used for medical sterilisation need to have a temperature of 120°C of boiling water to kill most bacteria. Estimate the pressure required for the purpose. The molar enthalpy change of vaporisation of water is 40.66 kJ mol⁻¹ at the normal boiling point. Indicate the assumptions made in your estimate.
- c. The molar enthalpy change of fusion at normal freezing point (273.15 K) is 6008 J mol⁻¹. Estimate the pressure at which water and ice are in equilibrium at – 0.200°C. Density of ice = 917 kg m⁻³ and density of water = 1000 kg m⁻³. Indicate the assumptions made in your estimate.

C. Irreversible condensation

- a. Consider 28.5 g of supercooled (liquid) water at –12.0°C and 1.00 bar. Does this state lie on the P - T plane of the phase diagram?
- b. This metastable state suddenly freezes to ice at the same temperature and pressure. Treat the metastable state as an equilibrium state and calculate the heat released in the process. Molar heat capacities, assumed constant, are :

$$\bar{C}_{p(\text{ice})} = 76.1 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\bar{C}_{p(\text{liquid water})} = 37.15 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta\bar{H}_{(\text{fusion})} = -333.5 \text{ J g}^{-1}$$

- c. Determine the total entropy change of the universe in the process and assure yourself that the answer is consistent with the Second Law of Thermodynamics. Take the surroundings to be at -12.0°C .

Problem 2 van der Waals gases

The ideal gas equation $PV = nRT$ implies that the compressibility factor

$$Z = \frac{PV}{nRT} = 1$$

However, the compressibility factor is known to deviate from 1 for real gases. In order to account for the behavior of real gases, van der Waals proposed the following equation of state :

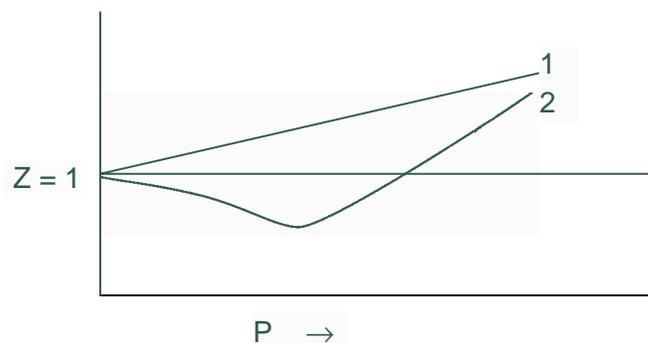
$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

where a and b are constants, characteristic of the gas. The constant a is a measure of the intermolecular force and b that of the size of the molecules.

- a. Show on the basis of van der Waals equation that
- i. at sufficiently high temperatures, Z is greater than unity for all pressures. At high temperatures and low pressures, Z approaches the value for an ideal gas.
 - ii. at lower temperatures, Z can be less than unity.
 - iii. for $a = 0$, Z increases linearly with pressure.
- b. At a certain temperature, the variation of Z with P for He and N_2 is shown schematically in the following figure.

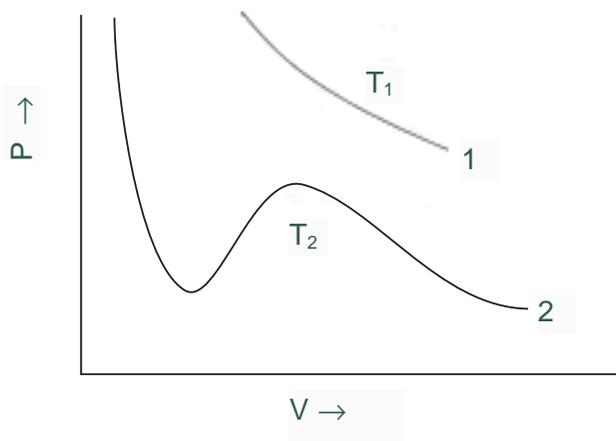
For He, $a = 3.46 \times 10^{-2} \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 2.38 \times 10^{-2} \text{ Lmol}^{-1}$

For N_2 , $a = 1.37 \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 3.87 \times 10^{-2} \text{ Lmol}^{-1}$



Identify the graph corresponding to He and N₂.

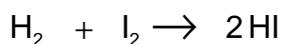
- c. Two P-V isotherms of a van der Waals gas are shown below schematically. Identify the one that corresponds to a temperature lower than the critical temperature (T_c) of the gas.



- d. For a given P , the three roots of van der Waals equation in V coincide at a certain temperature $T = T_c$. Determine T_c in terms of a and b , and use the result to show that N₂ is liquefied more readily than He.
- e. Determine the work done by 1 mol of N₂ gas when it expands reversibly and isothermally at 300 K from 1.00 L to 10.0 L, treating it as a van der Waals gas.

Problem 3 Rates and reaction mechanisms

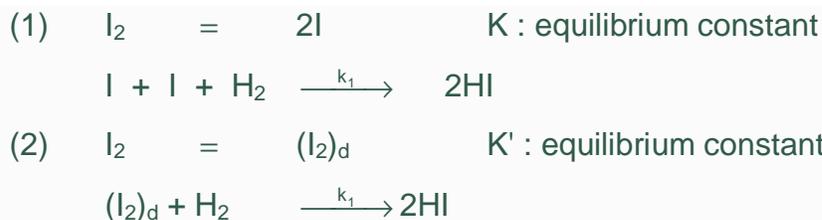
The observed rate law for a chemical reaction can arise from several different mechanisms. For the reaction



the observed rate law is

$$-\frac{d[\text{H}_2]}{dt} = k [\text{H}_2] [\text{I}_2]$$

For a long time it was believed that the above reaction took place as it was written down; that is, it was a bimolecular elementary reaction. It is now considered that several mechanisms compete. Below a certain temperature, two alternative mechanisms have been proposed :



where $(\text{I}_2)_d$ represents a dissociative state of I_2 . The first step in each mechanism is fast and the second slow.

- a. Show that both mechanisms are consistent with the observed rate law.
- b. The values of the rate constant k for the reaction at two different temperatures are given in the table :

T(K)	k ($\text{L mol}^{-1} \text{s}^{-1}$)
373.15	8.74×10^{-15}
473.15	9.53×10^{-10}

- i. Determine the activation energy E_a .
- ii. The bond dissociation energy of I_2 is 151 kJ mol^{-1} . Justify why the second step in each mechanism is rate determining.
- c. The change in internal energy (ΔU) for the reaction is -8.2 kJ mol^{-1} . Determine the activation energy for the reverse reaction.
- d. The activation energy for a reaction can even be negative. An example is the gas phase recombination of iodine atoms in the presence of argon:



whose activation energy is about -6 kJ mol^{-1} .

One of the proposed mechanisms of this reaction is :



where IAr is a very loosely bound species.

- i. Assume that the second step is rate determining and obtain the rate law for the reaction.
- ii. Give a possible explanation of why the activation energy for the iodine recombination is negative.

Problem 4 Enzyme catalysis

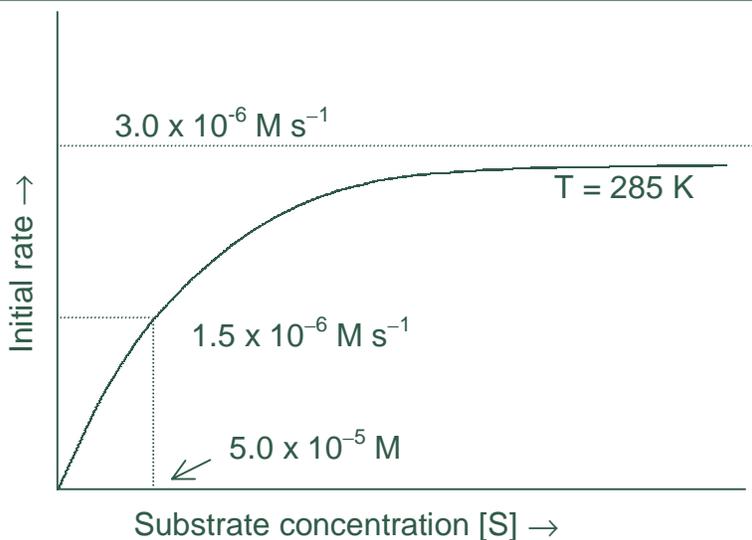
Enzymes play a key role in many chemical reactions in living systems. Some enzyme-catalysed reactions are described in a simple way by the Michaelis-Menten mechanism, as given below.



where E stands for the enzyme, S stands for the substrate on which it acts and P, the end product of the reaction. k_1 and k_1' are the forward and backward rate constants for the first step and k_2 the forward rate constant for the second step.

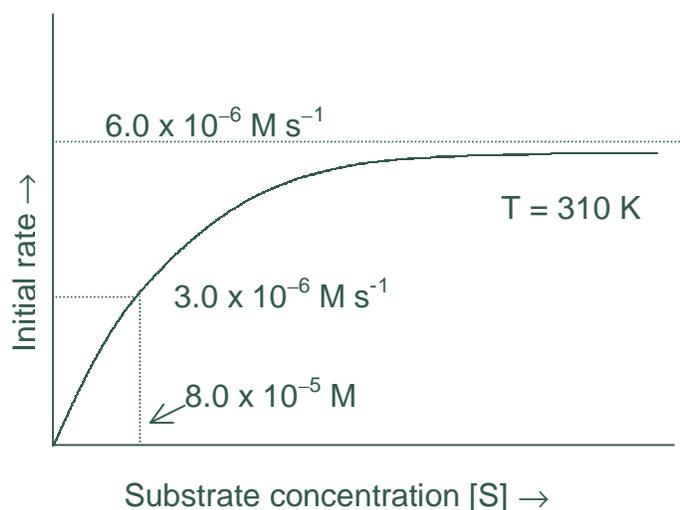
Ignore the backward rate for the second step. Also assume that the enzyme equilibrates with its substrate very quickly.

- a. In an experiment, the initial rate (of formation of P) is determined for different concentrations of the substrate, keeping the total concentration of enzyme fixed at $1.5 \times 10^{-9} \text{ M}$. The following graph is obtained.



- i. The graph is linear for small $[S]$ and it approaches a constant value for large $[S]$. Show that these features are consistent with the Michaelis-Menten mechanism. (Use steady state approximation for the intermediate step.)
 - ii. Determine the rate constant k_2 for the second step.
 - iii. Predict the initial rate on the basis of the Michaelis-Menten mechanism for the substrate concentration $[S] = 1.0 \times 10^{-4} \text{ M}$.
 - iv. Determine the equilibrium constant for the formation of the enzyme - substrate complex ES.
- b. The experiment above studied at 285 K is repeated for the same total enzyme concentration at a different temperature (310 K), and a similar graph is obtained, as shown below.

Determine the activation energy for the conversion of ES to E and P.

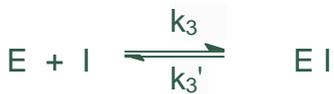
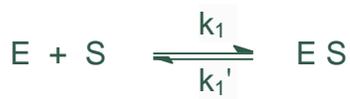


- c. One interesting application of the ideas above is the way enzyme catalysed reactions inactivate antibiotics. The antibiotic penicillin is, for example, inactivated by the enzyme penicillinase secreted by certain bacteria. This enzyme has a single active site. Suppose, for simplicity, that the rate constants obtained in a above apply to this reaction. Suppose further that a dose of $3.0 \mu\text{mol}$ of the antibiotic triggers the release of $2.0 \times 10^{-6} \mu\text{mol}$ of the enzyme in a 1.00 mL bacterial suspension.
- i. Determine the fraction of the enzyme that binds with the substrate (penicillin) in the early stage of the reaction.
 - ii. Determine the time required to inactivate 50% of the antibiotic dose.
- d. To control the inactivation of penicillin, suppose a substance is introduced which has a similar structure to penicillin and is able to occupy the enzyme site, but is otherwise completely unreactive. This naturally inhibits the enzyme-catalysed reaction. The degree of inhibition i is defined by

$$i = 1 - \frac{r}{r_0}$$

where r and r_0 are the initial rates of reaction with and without the inhibitor respectively.

Consider again the Michaelis-Menten type of mechanism to describe the situation :



- i. Show that the degree of inhibition decreases with increase in concentration of the substrate (for constant concentration of the inhibitor), and the inhibitor ceases to be effective for large substrate concentrations. (This is known as *competitive inhibition*.)
- ii. For low substrate concentration of penicillin, determine the concentration of the inhibitor that reduces the rate of the inactivation of penicillin by a factor of 4. The dissociation constant of enzyme-inhibitor complex is given to be 5.0×10^{-5} .

Problem 5 Schrödinger equation

The simplest Schrödinger equation, describing a free particle confined to move in a one-dimensional 'rigid box' brings out a most basic fact: quantization arises due to boundary conditions on the wave function.

- a. An electron of mass m is confined to move in a line along the x -axis from $x = 0$ to $x = L$. Between the two ends it experiences no force.
 - i. Write down the (time-independent) Schrödinger equation for the wave function ψ of an electron.
 - ii. Which of the following are possible wave functions of an electron in one-dimensional rigid box :

$$e^{-kx}$$

$$\cos \frac{n\pi x}{L}$$

$$\sin kx$$

$$\sin \frac{n\pi x}{L}$$

where k is any real number and n is a positive integer ?

- iii. For the acceptable wave functions of the electron in (ii) above, show that the energies are given by

$$E_n = \frac{h^2 n^2}{8mL^2}$$

- iv. Plot schematically the wave function of the electron in the ground and the first two excited states. What is the number of nodes (in the region between $x = 0$ to L) of the wave function with energy E_n ?
- v. Normalize the ground state wave function of the electron.
(The integral of the square of the modulus of a normalized wave function over all space is unity.)
- b. An interesting example of this one-dimensional model in chemistry is the motion of an electron in a conjugated system of single and double bonds. The molecule 1,3-butadiene has four π electrons assumed to move freely in a line consisting of three carbon-carbon bonds, each of approximately the same length (1.4×10^{-10} m), with an additional length of 1.4×10^{-10} m at each end. Using the aufbau principle, determine a scheme to fill the electrons in the available energy levels. Calculate the lowest excitation energy of the system.
- c. 'Boundary conditions' on wave functions result in quantization of not only energy but also other physical quantities, such as angular momentum. The wave function corresponding to the value $h\lambda/2\pi$ for the z-component of angular momentum (L_z) is:
- $$\psi(\phi) = e^{i\lambda\phi},$$
- where ϕ is the (azimuthal) angle in the x-y plane measured relative to the x-axis. Use the condition that this function is single valued at every point in space and show that this implies that λ is quantized. Give the quantized values of angular momentum projection along the z-axis.