

Department of Chemistry  
Indian Institute of Technology Madras  
CY1001 - Physical Chemistry - Assignment 2 - 15 Marks  
Uploaded on 7th June 2021  
Last date of submission: 14th June 2021 (see page 3)

Questions 1-8 carry 15 marks.

1. **(1 mark)**: For an ideal monatomic gas, the expression for the Helmholtz free energy obtained from statistical thermodynamics, is given by

$$A = -NkT \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{2\pi mkT}{h^2} \right) + 1 \right]$$

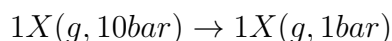
Use the appropriate fundamental equation to derive the ideal gas equation of state,  $pV = NkT$ .

2. **(2 marks)**: Given that enthalpy  $H(T, p)$  is a (state) function of two independent variables, temperature  $T$  pressure  $p$ , use the appropriate fundamental equation and Maxwell relation to show that

$$TdS = C_p dT - \alpha TV dp,$$

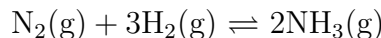
where  $C_p$  is the heat capacity at constant pressure and  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$  is the coefficient of thermal expansion, both of which are measurable quantities.

3. **(2 marks)**: A system consists of one mole of ideal gas that undergoes the following change in state:



- (a) What is the value of  $\Delta S_{sys}$  and  $\Delta S_{surr}$  if the expansion is isothermal and reversible and occurs at 298 K?
- (b) For the same change in pressure in an isolated system, what is the value of  $\Delta S_{sys}$  and  $\Delta S_{surr}$  if the gas expands into a larger evacuated container so that the final pressure is 1 bar.

4. **(2 marks)**: At 400 K, the reaction



has  $\Delta_r G^0 = -11.92 \text{ kJ/mol}$ . Starting with a mixture of 1.0 moles of  $\text{N}_2$ , 3.0 moles of  $\text{H}_2$  in the presence of a catalyst at a total pressure of 10.0 bar, calculate the number of moles of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  in the mixture at equilibrium. Take  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ .

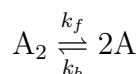
5. **(2 marks)** : You are given the following information regarding water (MW =18): Normal Melting point  $T_m = 273.15 \text{ K}$ ; Normal Boiling Point  $T_b = 373.15 \text{ K}$ ;  $\Delta_{fus} H_m = 6.0 \text{ kJ/mol}$ ;  $\Delta_{vap} H_m = 45.0 \text{ kJ/mol}$ ; Density of ice  $\rho_s = 0.9 \text{ g/cc}$ ; Density of water  $\rho_l = 1.0 \text{ g/cc}$ . Assume the enthalpies of fusion and vaporization to be independent of temperature in the range of interest. Use  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ .

(a) Calculate the slope of the solid-liquid coexistence line  $dP/dT$  in bar/K at 273.15K.

(b) Calculate the vapor pressure of liquid water at 273.16 K.

6. **(1 mark)**: Find  $P$ ,  $C$  and  $F$  for a system consisting of liquid ethanol and liquid methanol in equilibrium with a vapor mixture of ethanol and methanol. For this system, what can be a good choice of independent variables to describe the system.

7. **(2.5 marks)**: Consider a trimolecular reaction in equilibrium



(a) Write the Lindemann mechanism for this reaction and derive an expression for  $\frac{d[\text{A}_2]}{dt}$ .

(b) Determine the order of the reaction at low-pressure region for both forward and reverse reactions.

8. **(2.5 marks)**: (a) The transition state theory (TST) quantifies the temperature ( $T$ ) dependence of the effective rate constant  $k$  of a bimolecular reaction,

$\text{A} + \text{B} \xrightarrow{k} \text{P}$ . Based on the TST, plot the variation of  $\ln(k/T)$  with  $1/T$ , and show how  $\Delta S^\ddagger$ , the entropy of activation, can be determined from the plot.

(b) The rate constant for a certain unimolecular reaction in gas phase is  $2.5 \times 10^{-2} \text{ s}^{-1}$  at  $727^\circ\text{C}$ . If the activation energy is  $83.14 \text{ kJmol}^{-1}$ , calculate the entropy of activation at this temperature.

# Information about Assignment 2 submission

From course coordinator (artiATsmail.iitm.ac.in)

**Opening date and time:** Download from Moodle on 7th June 2021 after 2:00 pm.

**Closing date and time :** Submit by 14th June 2021, 5:00 pm.

**Please check the Batch number assigned to you and follow one of the six links provided below for submission\*.**

## **Batch I**

<https://forms.gle/iaECgUnWvP1QzWsr7>

## **Batch II**

<https://forms.gle/ruQpxg2iheKLbNRC9>

## **Batch III**

<https://forms.gle/vSKwGggfxLYYfTzp8>

## **Batch IV**

<https://forms.gle/e8SsSYShxwR48ssS8>

## **Batch V**

<https://forms.gle/tx543nNFux29Ghnc9>

## **Batch VI**

<https://forms.gle/QavbKo8XSkA41wB16>

**\*Only one submission is allowed. Access these links using your IITM mail id.**