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:

$$1X(g, 10bar) \rightarrow 1X(g, 1bar)$$

(a) What is the value of ΔS_{sys} and ΔS_{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 ΔS_{sys} and ΔS_{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

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

has $\Delta_r G^0 = -11.92$ kJ/mol. Starting with a mixture of 1.0 moles of N_2, 3.0 moles of H_2 in the presence of a catalyst at a total pressure of 10.0 bar, calculate the number of moles of N_2, H_2 and NH_3 in the mixture at equilibrium. Take $R = 8.314$ JK^{-1} mol^{-1}.

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

$$A_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2A$$

(a) Write the Lindemann mechanism for this reaction and derive an expression for $\frac{d[A_2]}{dt}$.
(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, $A + B \xrightarrow{k} P$. 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 2.5×10^{-2} s^{-1} at 727^oC. If the activation energy is 83.14 $kJmol^{-1}$, 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 smail id.**