

THE OPEN UNIVERSITY OF SRI LANKA
B. Sc. Degree Programme — Level 4
Assignment II (Test)— 2010/2011
(Part I/ 1-7- Thermodynamics)
CHU 2124/CHE 4124 — Physical Chemistry I



(1½ hours)

22nd October 2010

4.00 p.m. — 5.30 p.m.

Gas constant (R)	=	8.314 J K ⁻¹ mol ⁻¹
Avogadro constant (N _A)	=	6.023×10 ²³ mol ⁻¹
Faraday constant (F)	=	96,500 C mol ⁻¹
Planck constant (h)	=	6.63×10 ⁻³⁴ J s
Velocity of light (c)	=	3.0×10 ⁸ m s ⁻¹
Standard atmospheric pressure	=	10 ⁵ Pa (N m ⁻²)
Log _e (X)	=	2.303 Log ₁₀ (X)

Registration Number: -----

Signature (staff):-----

The paper has two parts, A and B;

Part A consists of **seven (7)** MCQ questions.

Part B consists of **04 (four)** Structured Questions for which answers must be written in the SPACE provided

Mobile phones are **NOT** allowed; **switch off** and leave them outside.

Part – A (21%)

- Choose the correct answer to each of these questions (1-7) and mark your answer with a cross ["X"] in the *relevant box in the question paper itself*.
- Any answer with more than **one** "X" marked will be considered as an *incorrect* answer.
- Each correct answer will score **03(three)** marks.
- Use a **PEN** (not a PENCIL) in answering.
- The use of a *non-programmable* electronic calculator is permitted.
- Logarithm tables will be provided on request.

Please write your **Registration number, Name, and Address** clearly in the space provided; see **last page** of this question paper.

1. The SI unit of Ebullioscopic constant is

kg K⁻¹

K g mol⁻¹

K kg mol⁻¹

kg m³ mol⁻¹

K kg⁻¹ mol

2. Identify one set of properties which comprise entirely of **path properties**.

U, H

q, w

S, G

G, w

q, H

3. Which of the following equations can be applied for an ideal gas under reversible, adiabatic conditions?

P.T = constant

TV^{γ-1} = constant

T/V = constant

P^γV = constant

T^{γ-1}V = constant

4. The equation $\Delta S = nC_{v,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$ will apply for a change of state from state

A(V₁, T₁) to B(V₂, T₂) only for

an ideal gas at constant pressure

an ideal gas at constant volume

for any homogeneous system under all conditions.

for an ideal gas under all conditions but for any other homogeneous system only at constant volume

an ideal gas under all conditions.

5. Which of the following descriptions will most correctly describe the process of freezing of liquid water to solid ice at its freezing point?

Reversible, isothermal process

Reversible, isochoric process

Isobaric, isothermal Process

Irreversible, Isochoric process

Univariant Phase transformation

6. The thermodynamic equilibrium constant, K, for a reaction at 127 °C is 20. The Gibbs free energy change for this reaction at this temperature (in kJ mol⁻¹) is most likely to be

-10.0

10.0

-4.3

4.3

-3.2

7. The following statements are related to the **Helmholtz free energy function, A**

- (i) $dA_{V,T} > 0$ for a spontaneous process
- (ii) $A = U - TS$
- (iii) A is a thermodynamic function

Of these, the correct statement/s is/are

(i) only

(ii) only

iii) only

(ii) and (iii) only

(i) and (ii) only

Part – B (79%)

1.(a) Under what conditions and to what kind of systems can the following thermodynamically deducible equations apply?

(i) $w = nRT \ln\left(\frac{V_1}{V_2}\right)$

(ii) $q = \Delta H$

(iii) $TS = H - G$

(iv) $\Delta S = \frac{\Delta H}{T}$

(v) $\Delta G = 0$

(20 marks)

(b) Consider the equation $dS = nC_{V,m} \frac{dT}{T}$

(the symbols used have their usual meanings)

This equation is applicable for any homogeneous system accompanying an **isochoric change in temperature**

(i) What is meant by “isochoric change in temperature”?

(ii) Assuming $C_{V,m}$ to be a function of T and is of the form, $C_{V,m} = 3T - 2T^2 + 4T^3$, derive an expression for the total change in entropy, ΔS , when the temperature changes from T_1 to T_2 .

(24 marks)

2. (a) (i) The **Clapeyron** equation is given by the equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Identify the three (3) symbols on the right hand side of this equation.

(ii) Derive the integrated form of this equation [called the **Clausius–Clapeyron** equation].
(State the assumptions required in deriving this equation)

(22 marks)

(iii) It is found that the vapour pressure of a liquid is increased ten fold when the temperature is increased from 300 to 400 K. Using the equation derived in (ii) above, calculate the mean molar enthalpy of evaporation (in units of kJ mol^{-1}) (assumed to remain constant in the above temperature range)

(10 marks)

3 (a) (i) Define molality;

(ii) Using appropriate symbols, write down the relationship between depression of freezing point, molality and cryoscopic constant.

(10 marks)

(b) An unknown non volatile compound, Y, is suspected to be either Biphenyl or Napthalene. It was decided to confirm this by carrying out an experiment to determine the molar mass of Y involving depression of freezing point of a solvent X

A solution was prepared by dissolving 1.00 g of Y in 55.00 cm^3 of X; the freezing point of this solution was found to be $79.0 \text{ }^\circ\text{C}$.

The following data with respect to X is given

density = 0.9 g cm^3 ;

freezing point $80 \text{ }^\circ\text{C}$;

cryoscopic constant = $6.40 \text{ K kg mol}^{-1}$

By carrying out an appropriate calculation, identify Y.

[Relative Atomic Mass: H = 1.0; C = 12.0; O = 16.0]

(30 marks)

4. (a) $dH = VdP + TdS$
 $dG = VdP - SdT$
 $dC = L dK - J dM$

are all fundamental thermodynamic equations applicable for a closed system under certain conditions. Apply the Euler Criterion (condition for exact differential equations) for the above equations and write down the three (3) Maxwell type Relationships.

(09 marks)

(b) Define using relevant mathematical expressions

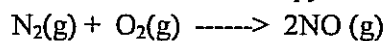
(i) the Joule- Thompson coefficient

(ii) the isobaric thermal capacity.

Indicate to what type of system/s the concept of thermal capacity can be applied.

(15 marks)

(c) Calculate the standard entropy of formation of NO(g)



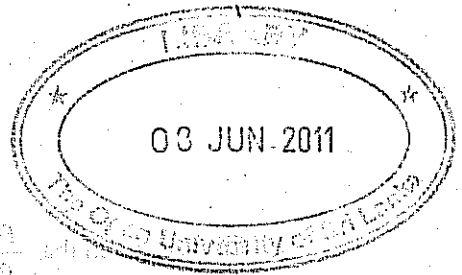
Standard Molar Entropies (in $\text{J mol}^{-1} \text{K}^{-1}$) are as follows

$$\text{N}_2(\text{g}) = 190$$

$$\text{O}_2(\text{g}) = 200$$

$$\text{NO}(\text{g}) = 210$$

(18 marks)



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Answer Guide – Assignment II

1.(a) (i) $w = nRT \ln \left(\frac{V_1}{V_2} \right)$ - Isothermal, Reversible, Ideal Gas

(ii) $q = \Delta H$ - constant pressure

(iii) $TS = H - G$ all conditions

(iv) $\Delta S = \frac{\Delta H}{T}$ Univariant Phase Transformation [or at constant T and P]

(v) $\Delta G = 0$ Reversible, constant P and constant T

(b) (i) Isochoric change in temperature means change in temperature taking place at constant volume

(ii) $\int dS = n \int C_{V,m} \frac{dT}{T} = n \int [3T - 2T^2 + 4T^3] \frac{dT}{T}$;

$$\Delta S = [S_2 - S_1] = n \left[3T - 2T^2/2 + 4T^3/3 \right]_{T_1}^{T_2}$$

$$\Delta S = n[3(T_2 - T_1) - (T_2^2 - T_1^2) + 4/3(T_2^3 - T_1^3)]$$

2. (a) (i) $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$

ΔH - Change in Enthalpy; T - absolute temperature; ΔV - Change in volume

(ii) Assumptions: Considering one of the phases is a gas, the volume of the gas is very much greater than that of the other phase such that ΔV is approximately equal to the volume of gas (V_g) and that the gas is ideal so that we can apply $PV = nRT$; assume ΔH is a constant.

Based on the above assumptions, we can write $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{TnRT/P}$;

$$\int \frac{dP}{P} = \frac{\Delta H}{nR} \int \frac{1}{T^2}; \text{ on integration, we get } \ln P = -\frac{\Delta H}{nR} \left(\frac{1}{T} \right) + C$$

We can eliminate C by applying limits for P (P_1 to P_2) and T (T_1 to T_2) and obtain

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H}{nR} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(iii) It is given that $\frac{P_2}{P_1} = 10$; $T_1 = 300 \text{ K}$ and $T_2 = 400 \text{ K}$; $n = 1$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$\text{Applying, } \ln \frac{P_2}{P_1} = -\frac{\Delta H}{nR} \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

$$\ln 10 = -\frac{\Delta H}{8.314} \left(\frac{1}{400} - \frac{1}{300} \right)$$

We can get ΔH (mean molar enthalpy of evaporation) = 23 kJ mol^{-1}

3 (a) (i) Molality is defined as number of moles of solute per kilogram of solvent (m)

$$(ii) \Delta T = k_f m$$

$$(b) \Delta T = 80 - 79 = 1 \text{ }^\circ\text{C}; k_f = 6.40 \text{ K kg mol}^{-1}$$

$$\text{volume of solvent} = 55 \text{ cm}^3; \text{ density of solvent} = 0.9 \text{ g cm}^{-3}$$

$$\text{mass (in kg) of solvent} = (0.9 \times 55)/1000 = 49.5 \times 10^{-3}$$

$$m = \frac{\frac{1}{M}}{\text{mass (in kg) of solvent}} = \frac{10^3}{49.5M}$$

$$\text{Applying } \Delta T = k_f m, \text{ we have } 1 = 6.40 \times \frac{10^3}{49.5M}$$

$$M = \frac{6400}{49.5} = 129.3 \text{ g mol}^{-1}$$

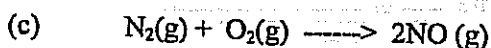
Comparing the values of molar mass of Biphenyl ($\text{C}_{12}\text{H}_{10} = 154$) and Naphthalene ($\text{C}_{10}\text{H}_8 = 128$), we can say, Y is Naphthalene

$$4. (a) \left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S; \quad \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T; \quad \left(\frac{\partial L}{\partial M} \right)_K = - \left(\frac{\partial V}{\partial K} \right)_M$$

$$(b) (i) \text{ the Joule-Thompson coefficient is } \mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

$$(ii) \text{ the isobaric thermal capacity is } C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

The concept of thermal capacity can be applied to any homogeneous system where no phase transformation takes place.



$$\text{Products} = 2 \times 210 = 420 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{Reactants} = 200 - 190 = 10 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S \text{ (for two moles of NO)} = 420 - 10 = 410$$

$$\text{Standard entropy of formation of N} = 410/2 = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$