

SECTION A

Question 1

- (a) State the expression for isothermal compressibility.
- (b) Show, in 5 lines or less, that, $\left(\frac{\partial E}{\partial P}\right)_T = C_V \left(\frac{\partial T}{\partial P}\right)_T$. [Note: Proof more than 5 lines will not be graded]
- (c) A sample of hydrogen is confined to a cylinder fitted with a piston of 5 cm^2 cross-sectional area. The gas occupies 500 cm^3 at 298 K and 2 atm . Assuming that the gas behaves ideally, calculate the change in entropy of the gas when the piston is drawn to the point of a quasi-static state.

Question 2

- (a) Write the Clapeyron equation in (i) differential form and (ii) integrated form
- (b) In 3 lines or less, state the practical importance of Hess' law.
- (c) A Carnot engine operating between 1000°C and 25°C produces work that is entirely used to run a refrigerating machine operating between 0°C and 25°C . Calculate the percentage of the heat absorbed by the engine to that absorbed by the refrigerator assuming both devices operate ideally.

SECTION B

Question 3

- (a) If the Gibbs energy varies with temperature according to $G/T = a + b/T + c/T^2$
How will the enthalpy and entropy vary with temperature?
- (b) At 298.15 K and a particular pressure, a real gas has a fugacity coefficient ϕ of 2.00 . At this pressure, what is the difference in the chemical potential of this gas and ideal gas?
- (c) For uranium hexafluoride the vapor pressure (in Pa) for solid and liquid are given by

SECTION A

(1)(a) Using the fundamental relation, $E=f(T,V)$ and the first law of thermodynamics, derive an expression for the relationship between C_p and C_v (the heat capacity of a gas at constant pressure and volume respectively).

(b) Is this relationship valid for real gases? Why?

(c)(i) Derive an expression for the work done in the isothermal expansion of a mole of a perfect gas from an initial pressure P_1 to a new pressure P_2 .

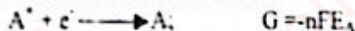
(ii) Calculate the maximum work obtainable in the isothermal expansion of 32g of oxygen gas from 760mm Hg pressure to 76mm Hg at 273K?

(Assume that oxygen behaves as an ideal gas; $R = 8.314$)

(2)(a) Write down expressions in terms of ΔG that predicts (i) spontaneity

(ii) non-spontaneity (iii) equilibrium for a reaction.

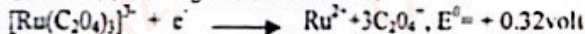
(b) Consider the half cell reactions



where E_A and E_B represent the electrode potentials of A and B respectively.

What is the relationship between E_A and E_B if B were to displace A from a solution containing A^{+} ?

(c) Given the following half-cell reactions:



Calculate the free energy change ΔG° for the reaction:



and predict the feasibility of the reaction. (IF = 96500 Coulombs)

SECTION B

3.(a)(i) Write an equation to express the molar free energy of a pure ideal gas in terms of pressure.

(ii) Write a second equation to express the chemical potential of a component of an ideal gas mixture.

(iii) Write a third equation to express the chemical potential of a component of a real gas mixture.

SECTION A

1(a) Write down a mathematical expression for the first law of thermodynamics.

(b) Use the above expression and the fundamental relation: $H = E + PV$ to show that:

$$\Delta E = (q)_V$$

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$$\Delta H = (q)_P$$

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(c) (i) Using the expressions in (b) above, derive Kirchhoff's equations for the variations of ΔE and ΔH with temperature.

(ii) State one importance of ΔH_0 .

(d) Write down any four thermodynamic criteria for perfect gas behaviour.

(e) Calculate the maximum work obtained in the isothermal expansion of 10g of hydrogen gas from 1 atmosphere to 0.1 atmosphere at 10°C . (Assume that hydrogen behaves as a perfect gas.)

2(a) (i) State the second law of thermodynamics.

(ii) Illustrate the law with any three examples.

(b)(i) State and prove Carnot's theorem.

(ii) Calculate the efficiency of a heat engine operated between 200°C and 400°C .

(iii) From the fundamental relation:

$$G = H - TS,$$

Derive Gibb's - Helmholtz equation.

(iv) Use this equation and the relation:

$$\Delta G = -RT \ln K$$

To show how ΔH can be deduced from a variation of K with temperature.

3(a)(i) Define chemical Thermodynamics.

(ii) Thermodynamics repose on two principal notions: energy and entropy.

SECTION A

QUESTION ONE

- State the zeroth law of thermodynamics
- With the present scale of absolute temperature, T , the zero of the Celsius scale is defined as 273.15 K exactly. Suppose we were to define an absolute scale, T' , such that the zero of the Celsius scale was at 300 K', exactly. If the boiling point of water on the Celsius scale is 100 °C, what would be the boiling point of water on the T' scale?
- Ammonium chloride when dissolved in water at constant temperature leads to cooling sensation. Explain this phenomenon in terms of the enthalpy change of the system and its surrounding
- For the allotropic change represented by the equation: $C(\text{graphite}) \rightarrow C(\text{diamond})$; $\Delta H = +1.9 \text{ kJ}$. If 6.0 g of diamond and 6.0 g of graphite is burnt completely in separate experiments, in which of reactions will the heat liberated will be higher and by how much?

QUESTION TWO

- State the second law of thermodynamics
- For each of the following processes, predict the entropy changes occurring during the process. Briefly justify your answers.
 - 1 mole of calcium carbonate decomposes completely into calcium oxide and carbon dioxide upon heating.
 - 1 mole of water is frozen rapidly at -5°C and a pressure of 1 atmosphere.

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$$\Delta E = (q)_V$$

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(d) Write down any four thermodynamic criteria for perfect gas behaviour.

(e) Calculate the maximum work obtained in the isothermal expansion of 10g of gas from 1 atmosphere to 0.1 atmosphere at 10°C . (Assume that hydrogen behaves as a perfect gas.)

2(a) (i) State the second law of thermodynamics.

(ii) Illustrate the law with any three examples.

(b)(i) State and prove Carnot's theorem.

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Derive Gibbs' - Helmholtz equation.

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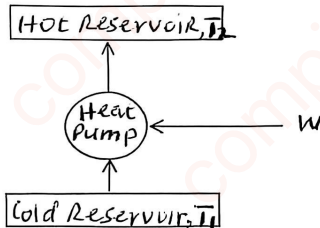
3(a)(i) Define chemical Thermodynamics.

(ii) Thermodynamics rests on two principal motions: energy and entropy.

4. (a) (i) One mole of an ideal monatomic gas is allowed to expand adiabatically and reversibly from 21.4 L mol^{-1} at 1 bar and 5°C to a volume 42.8 L mol^{-1} . Calculate;
- the final pressure and temperature.
 - the work done in the adiabatic expansion
- (b) Two blocks of the same metal are the same size but at different temperatures, T_1 and T_2 . These blocks of metal are brought together and allowed to come to the same temperature. Show that the entropy of change is given by $\Delta S = C_p \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$ if C_p is constant. How does this equation show that the change is spontaneous?
- (c) Theoretically how high in ft. could a gallon of gasoline lift an automobile weighing 2800 lb against the force of gravity, if it is assumed that the cylinder temperature is 2200 K and the exit temperature is 1200 K? (Density of gasoline = 0.80 g cm^{-3} ; 1 lb = 453.6 g; 1 ft = 30.48 cm; 1 L = 0.2642 gal; heat of combustion of gasoline = 46.7 kJ g^{-1} ; acceleration due to gravity = 9.8 ms^{-2})

1. (a) Name (do not define) the four basic thermodynamic processes.

(b)



State the efficiency of the above system in terms of the temperature of the heat reservoirs.

(c) One gram of water at 100°C is converted to steam at the same temperature. The volume of water becomes 1671 cm^3 on boiling. Calculate the change in internal energy per mole of the system if the heat of vapourisation is 40.8 kJ mol^{-1}

2. (a). Outline in 6 lines, how you will attempt to attain a temperature of 10^{-6} K in the laboratory. Give one reason why it may be necessary to attain this temperature range in the laboratory. [5 marks]

(b). When a liquid is compressed its Gibbs energy is increased. To a first approximation the increase in molar Gibbs energy can be calculated using $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$, assuming a constant molar volume. What is the change in the molar Gibbs energy for liquid water when it is compressed to 10^8 Nm^{-2} ? [5 marks]

(c). Calculate $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ for the formation of a quantity of air containing 1 mole of gas by mixing nitrogen and oxygen at 298 K . $\bar{V}_T$ may be taken to be 80% nitrogen and 20% oxygen.

Answer ALL questions

Write your Name and Registration Number. Also append your signature on your answer scripts.

- (a) A thermoflask contains milk as a system. The milk is vigorously shaken. Answer Yes or No
- (i) Has the internal energy changed?
 - (ii) Will there be a rise in temperature?
 - (iii) Has work been done on the system?
 - (iv) Has there been a change in heat quantity?
 - (v) Write an equation that is consistent with the behaviour of the system.
 - (b) Which of the following is /are inexact differential(s); dE , dH , dT , dP , dQ , dA , and dG .
- (c) $w = nR \theta_2 \ln v_2/v_1 + nR \theta_1 \ln v_1/v_2$
Which of the process of the Carnot cycle contribute to the work function as shown by the equation above? In two lines why is it so?
- (d) (i) Write the combined equation for the first and second laws of thermodynamics.
- (ii) Five moles of an ideal gas expand from 5 dm^3 to 20 dm^3 . If the gas is heated from 200 K to 800 K . Calculate the entropy change that attends both processes noting that reversible and irreversible entropy changes are the same $C_v = 3R/2$.
- (a) What is the implication of a system for which $dS = 0$?
- (b) Show, in a maximum of 5 lines, that $(\partial H / \partial P)_T = -u_{P,T} C_p$
- (c) Calculate the enthalpy change for heating two moles of an ideal diatomic gas from 0°C to 100°C ($C_v = 3R/2$).
- (d) The spontaneous net reaction in the Galvanic cell symbolically represented as $\text{Ag}/\text{HCl}/\text{Cl}_2(\text{g})/\text{Pt}/\text{Ir}$ is $\text{Ag}(\text{s}) + \frac{1}{2}\text{Cl}_2 \rightarrow \text{AgCl}(\text{s})$
For the cell, $E^\circ = 1.1362$ and $(\partial E^\circ / \partial T)_P = -5.95 \times 10^{-4} \text{ V K}^{-1}$. Calculate the value of the entropy change for the cell reaction at 25°C .

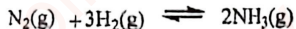
SECTION A

QUESTION ONE

- a. Define the following thermodynamic terms
- (i) Closed system (ii) Isolated system (iii) Adiabatic process
(iv) Isothermal process (v) Isobaric process [5 marks]
- b. Consider an ideal gas that occupies 2.25 L at 1.33 bar. Calculate the work required to compress the gas isothermally to a volume of 1.5 L at a constant pressure of 2.0 bar followed by another isothermal compression to 0.8 L at a constant pressure of 2.5 bar. [7 marks]
- c. Starting with $dU = dq - pdV$, Show that $dq = C_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV$ [3 marks]
- d. State the second law of thermodynamics. [2 marks]

QUESTION TWO

- a. One mole of an ideal gas at 300.0 K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. Calculate the entropy changes in the system and the surroundings. Also, calculate the total entropy change for the process. [12 marks]
- b. Consider the following reaction:



At 1000 K, $\Delta H_{\text{rxn}}^\circ = -123.77 \text{ kJ mol}^{-1}$. What is the enthalpy of formation for NH_3 (gas) at 300 K? The molar heat capacities are: $C_p \ominus 3.502R$, $3.466R$, and $4.217R$ for N_2 (g), H_2 (g) and NH_3 (g) respectively. State any approximation(s) used. [8 marks]

3(a). The isobaric coefficient of thermal expansion is defined by $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and the isothermal compressibility by $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$. Show that (a) $\alpha = 1/T$ (b) $\kappa = 1/P$ for an ideal gas. (5 marks)

(b). For reversible adiabatic expansion show that

$$P_1 V_1^\gamma = \text{constant}$$

Where P is pressure, V is volume and $\gamma = C_p / C_v$. C_p and C_v is heat capacity at constant pressure

and volume respectively.

(8 marks)

(c) A sample of hydrogen at one atmosphere expands adiabatically and reversibly from 1.0 dm^3 to 2.0 dm^3 . Calculate the final temperature if the initial temperature was 298K. What were the work output and the change in internal energy? ($C_v = 12.6 \text{ J mol}^{-1} \text{ K}^{-1}$) (7 marks)

SECTION B

Answer question 4 and any one other question in this section

4. (a) (i) In not more than two lines, define Osmotic pressure (2 marks)

b. Outline the steps you will take to achieve a temperature as low as 10^{-6} K in the laboratory (4 marks)

(b) One mole of an ideal gas at 0°C is allowed to expand isothermally from a pressure of 100 atm to 10 atm. Calculate w , q , ΔE and ΔH for the following cases.

(i) Expansion is reversible

(ii) The gas is allowed to expand freely into vacuum.

• (a) Define the term system

(b) Name the following systems below

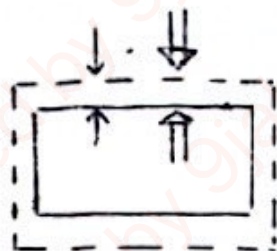


Fig. 1

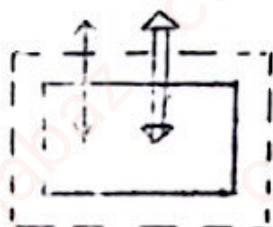


Fig. 2

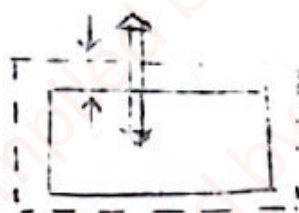


Fig. 3

 = System

 = Boundary

 Matter Flow

 Heat Flow

2. Write the missing terms

(a) $dE = dq -$

(b) $G = H - S$

(c) $= E + pV$

(d) $A = - TS$

.../2.

3. Considering E as function of any two of the variables P , V , and T , prove that

$$\left(\frac{\partial E}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V = - \left(\frac{\partial E}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T$$

1. A closed thermoflask as a system. The milk is vigorously shaken. Answer yes or No in front of each question

- (i) Has the energy changed? ~~YES~~ **NO** ✓
 (ii) Will there be rise in temperature? ~~NO~~ **YES** ✓
 (iii) Has work been done on the system? ~~YES~~ **NO** ✓
 (iv) Has there been change in heat quantity? ~~NO~~ **YES** ✓
 (v) Write an equation that is consistent with the behavior of the system
 $du = dv + dw$ ✓ $\therefore v = 0$ $u = 0 + w$
 $du = 0 + dw$, $v = 0 + w$ $u = w$
 (vi) Which of the following is/are inexact differential(s); dE , dH , dT , dP , dQ , dA and dG

~~dE, dH, dT, dP, dA are exact differential~~
 ~~dQ is an inexact differential~~ [11 marks]

2. One gram of water at 100 °C is converted to steam at the same temperature and 1 atmosphere. The volume of water becomes 1671 cm³ on boiling. Calculate the change in internal energy per mole of the system if the heat of vaporization is 40.8 kJ mol⁻¹. [H = 1; O = 16] Take density of water = 1 g/cm³ [5 marks]

$m = 1g$
 $\rho = \frac{m}{V}$ $\therefore V = \frac{m}{\rho} = \frac{1}{1} = 1 \text{ cm}^3$ $n = \frac{\text{mass}}{\text{molar mass}}$ of H_2O
 $n = \frac{1}{18} \text{ mol}^{-1}$ $n = 0.056$
 $\Delta u = q + w$ $q = 40.8 \text{ kJ} \rightarrow 1 \text{ mol}$
 $w = -P \Delta V$ $\Rightarrow 0.056 \text{ mol}$
 $w = -1 \times (1671 - 1)$ $\Rightarrow 40.8 \text{ kJ} \times 0.056 \text{ mol} = 2.28 \text{ kJ}$
 $w = -1670 \text{ J}$ $\Rightarrow 2.28 + 8 \text{ kJ}$

3. The partial derivative of, $\left(\frac{\partial U}{\partial V}\right)_S = -P$ give the intensive and extensive properties equivalent to the following partial derivatives: [4 marks]

$\left(\frac{\partial U}{\partial S}\right)_V$ T ✓ $\left(\frac{\partial H}{\partial P}\right)_S$ V ✓ (iii) $\left(\frac{\partial G}{\partial P}\right)_T$ V ✓ (iv) (iii) $\left(\frac{\partial A}{\partial V}\right)_T$ P ✓
 $= 38.330 \text{ J}$
 $= 38.33 \text{ kJ}$



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc., Degree (Chemistry) Examination
Part III Rein Semester 2021/2022

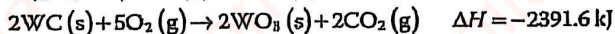
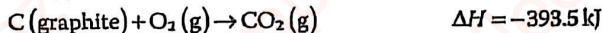
CHM 304: Thermodynamics

Time Allowed: 2 1/2 hrs

ANSWER ANY TWO QUESTIONS FROM EACH SECTION

SECTION A (ANSWER ANY TWO QUESTIONS)

1. (a) Define heat of formation under standard conditions
(b) The heat of formation of tungsten carbide, a network covalent solid, is difficult to measure directly since it only forms at 1400°C with the reaction: $W(s) + C(s)$, graphite $\rightarrow WC(s)$
Estimate the ΔH for the formation of 1 mol of $WC(s)$ at 25°C from the listed reactions below:



- (c) Calculate the ΔH_f° for the formation of $WC(s)$ at 1400°C, assuming that all the C_p values are constant and knowing the states for the reactants and products do not change.

$C_p = 20.84 \text{ kJ/mol}$
heat capacity of tungsten carbide
product = 20.84 kJ/mol

2. (a) Explain the term "adiabatic process".
(b) An ideal gas is expanded adiabatically against a constant pressure of 1 atm until it doubles in volume. If the initial temperature is 25 °C, and the initial pressure is 5 atm, calculate T_2 ; then calculate Q , W , ΔU , and ΔH per mole of gas for the transformation.

then
then
then

3. (a) Toluene, $C_6H_5CH_3$, has a melting point of -95.0°C while that for benzene, C_6H_6 , is 5.6°C. If the ΔH_{fus} values are 6.64 kJ/mol and 9.90 kJ/mol, respectively, which substance has the higher ΔS_{fus} ? (Prove your choice.)
(b) Compare the ΔS when 1.0 mol of an ideal monatomic gas is heated from 300 to 500 K when:
i. The volume is held constant
ii. The pressure is held constant

$W = 20.84$
 $Q = 14.2$
 $\Delta H = 20.84$
1.71

iii. Why would there be a difference between the answers for i and ii above?

- (c.) For each of the following processes, state which (if any) of the variables, ΔU , ΔH , ΔS , or ΔG , is equal to zero:

- i. Isothermal reversible expansion of an ideal gas. $\Delta U = 0$ $\Delta T = 0$ $\Delta H = 0$ $\Delta S = +$
- ii. Vaporization of liquid water at 80°C and 1 bar pressure ΔH $q = -w$
- iii. Vaporization of liquid water at 100°C and 1 bar pressure. ΔH
- iv. Reaction between H_2 and O_2 in a thermally insulated bomb calorimeter. $w = 0$
everything equals 0.
 $u = q + w$

SECTION B (ANSWER ANY TWO QUESTIONS)

4. (a) Calculate ΔG , ΔS , ΔH and ΔV , per mole of mixing N_2 , O_2 and H_2 in equal proportion at 300K and 1 atm. You can assume that the thermodynamic quantity for each gas corresponds to its expansion from its partial pressure in mixture of an ideal gases. [Any answer more than 3 significant figures should be quoted in kilojoules to 2 decimal places] [8 marks]

(b) Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under 2.53×10^5 Pa at the same temperature. [H = 1; O = 16; take density of water = $1g/cm^3$] [9 marks]

5. (a) State the phase rule in mathematical form for a single phase, two-component condensed system [2 marks]

(b) Define the following (i) colligative properties (ii) boiling point (iii) osmotic pressure [6 marks]

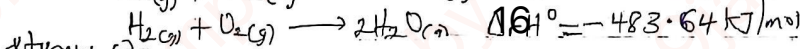
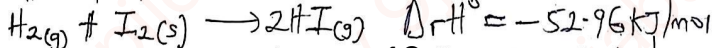
(c) A solution of 0.5126 g of naphthalene (Molar Mass = 128.7) in 50.00 g of CCl_4 yields a boiling point elevation of 0.402 °C, while a solution of 0.6216 g of an unknown solute in the same weight of solvent gives a boiling point elevation of 0.647 °C. Find the molar mass of the unknown solute. [7 marks]

- (a) Define ideal solution [2 marks].

(b) The phase diagram below shows the dependence of temperature on the mole fraction of N in a mixture of M and N. A compound is also formed between M and N. The numbers 1 – 12 represent the phase and the thermophysical states of M, N and compound formed between M and N. List what 1 – 12 represent and write the formula of the compound formed between M and N [6 marks]

For the reaction $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta_r H^\circ = -1373 kJ/mol$
298K. calculate $\Delta_r H^\circ$
 $p = p_2 + (p_1 - p_2) x_1$

Que - Given that





Department of Chemistry
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
 Part III B.Sc. Chemistry Degree Examination
RAIN SEMESTER EXAMINATION, 2022/2023 SESSION

CHM 304: CHEMICAL THERMODYNAMICS

DATE: Tuesday, 23RD July 2024

TIME ALLOWED: 2 HOURS

Instructions:

- There are two sections in the Paper; A and B
- Answer Two questions from each Section
- Separate sections A from B with a blank page
- Use separate page for each question.
- Write your Name and Registration Number on the cover page of your answer booklet

CONSTANTS: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

SECTION A

1. (a) (i) What do you understand by the term "system" [2 marks]

(ii) List any five types of thermodynamic processes you know [5 marks]

(b) Write the form of Kirchhoff equation for which the heat capacities of the reactants and products are largely independent of temperature. [1 mark]

(c) (i) Find the heat of reaction at 500 K for the formation of carbon(IV) oxide given that the standard heat of formation of carbon(IV) oxide is -393 kJ mol^{-1} and that the mean heat capacities are

$$C_p(\text{carbon}) = -1.265 \text{ J mol}^{-1} \text{ K}^{-1}.$$

$$C_p(\text{oxygen}) = -6.148 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p(\text{CO}_2) = -6.214 \text{ J mol}^{-1} \text{ K}^{-1}.$$

[5 marks]

(ii) State the cyclic rule with respect to the fundamental thermodynamic variables

[2 marks]

2. (a) Tabulate the following into extensive and intensive properties: enthalpy, refractive index, density, viscosity, volume, heat capacity, specific heat, kinetic energy, vapour pressure, elevation of boiling point, molecular mass, universal gas constant (R), molar volume, free energy (G).

[5 marks]

(b) A Carnot cycle has one mole of an ideal gas as the working substance and operates from condition of compressed 10 atm and 327°C . It expands isothermally to a pressure of 1 atmosphere, and then adiabatically compresses at a temperature of 27°C .

(i) Calculate U, q, and w for each step

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} C_p dT$$

C_p

CO_2 CO O_2

(ii) Calculate the net-work and the efficiency of the cycle [10 marks]

3. (a) (i) Write down a mathematical expression for the combined first law of thermodynamics.

(ii) Use the expression and the fundamental relation: $H = U + PV$ to show that

$$\Delta U = (q)_V \text{ and } \Delta H = (q)_P \quad [6 \text{ marks}]$$

(b) (i) What is the implication for a system for which $dS = 0$? [1 marks]

(ii) Calculate the enthalpy change of heating two moles of an ideal diatomic gas from 0°C to 100°C ($C_V = 5R/2$) [4 marks]

(c) For a particular reaction $\Delta H = -85.2 \text{ kJ mol}^{-1}$ and $\Delta S = -170.2 \text{ JK}^{-1} \text{ mol}^{-1}$. If these values are independent of temperature, calculate ΔG for the reaction at 5000 K and state the direction in which the reaction will proceed at each temperature.

[2 marks]

SECTION B

4. The density of various liquid mixtures of isopropanol, $(\text{CH}_3)_2\text{CHOH}$ [MW 60.096], and methanol CH_3OH [MW 32.042], have been measured at 25°C . If a mixture of 64.084 g CH_3OH



DEPARTMENT OF CHEMISTRY

CHEMICAL THERMODYNAMICS (CHM 304) TEST 2023/2024 Session (40 minutes)

NAME OF CANDIDATE: _____

REG. NO. _____

DEPARTMENT: _____

SIGNATURE _____

$1 \text{ atm.} = 101325 \text{ Nm}^{-2}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

1. (a) The expansion of a gas from 150 kPa to 100 kPa led to its cooling by 0.625 K. Calculate the experimental Joule-Thompson coefficient of this gas. [4 marks]

(b) Consider the following list and underline the state function(s): Pressure, Enthalpy, Volume, Work, Heat, Free energy [4 marks]

2. Calculate the work done when 0.8 mole of ideal monatomic gas initially at pressure of $15.2 \times 10^5 \text{ Nm}^{-2}$ and 300 K expands adiabatically and reversibly until its pressure is $10.1 \times 10^5 \text{ Nm}^{-2}$ [$C_v = 12.47 \text{ J mol}^{-1} \text{ K}^{-1}$] [8 marks]

3. Write the expression for the combined first and second law of thermodynamics. From the expression and the natural variable of the internal energy, obtain the expression for (i) Temperature (ii) Pressure in terms of the change in internal energy.

CHM 304 MID-SEMESTER TEST (2023-2024 SESSION)

Time allowed: 30 min.

1. Which of the following has a higher chemical potential? If neither, answer "same". (a) $\text{H}_2\text{O}(\text{s})$ or $\text{H}_2\text{O}(\text{l})$ at water's normal melting point, (b) $\text{H}_2\text{O}(\text{s})$ at -5°C and 1 bar or $\text{H}_2\text{O}(\text{l})$ at -5°C and 1 bar, (c) benzene at 25°C and 1 bar or benzene in a 0.1-M toluene solution in benzene at 25°C and 1 bar.
2. At 45°C , the vapour pressure of water is 65.76 mmHg for a glucose solution in which the mole fraction of glucose is 0.080. calculate the activity and activity coefficient of the water in the solution. The vapour pressure of pure water at 45°C is 71.88 mmHg.
3. Calculate the molal boiling-point elevation constant (K_b) for water. The molar enthalpy of vaporization ($\Delta_{\text{vap}}\bar{H}$) of water is $40.79 \text{ kJ mol}^{-1}$ at 100°C . $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, molar mass of water is 18.02 g mol^{-1} .



RAIN SEMESTER EXAMINATION 2023/2024 SESSION
CHM 304: CHEMICAL THERMODYNAMICS

22nd July 2025

TIME ALLOWED: 2 HOURS, 15 MINUTES

Instructions:

- There are two sections in the Paper; A and B
- Answer All questions
- Separate sections A from B with a blank page
- Use separate page for each question.
- Write your Name and Registration Number on the cover page of your answer booklet

CONSTANTS: R = 8.314 J mol⁻¹ K⁻¹ or 0.08206 L atm K⁻¹ mol⁻¹

SECTION A

$dq = T ds$

1. (a) State the second law of thermodynamics.

[2 marks]

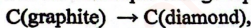
- (b) Consider U as a function of any two of the variables P, V, and T. Show that

$\left(\frac{\partial U}{\partial T}\right)_P$

$\left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = - \left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$

[7 marks]

- (c) For the allotropic change represented by the equation:



$\Delta H = C_p dT$

$\Delta H = +1.9$ kJ mol⁻¹. If 6.0 g of diamond and 6.0 g of graphite are burnt completely in separate experiment, in which of the reaction will the heat liberated be higher and by how much? Show how you arrived at your answer. [C = 12 g/mol]

[7 marks]

2. (a) The pressure dependence of Joule Thompson Coefficient for air can be expressed as:

$\mu^{J,T} = 0.266 \text{ atm}^{-1} - 8.95 \times 10^{-4} \text{ atm}^{-2} P$ What is the change in temperature if air, under normal conditions expand from 20 atm to 1 atm. Comment on your answer

[4 marks]

- (b) A Carnot engine absorbed 1.0 kJ of heat at 300 K, and exhausted 400 J of heat at the end of the cycle. What is the temperature at the end of the cycle?

[6 marks]

- (c) The vapour pressure of water is 101325 Nm⁻² at 373K and the enthalpy of vaporization is 40.7 kJ mol⁻¹. Estimate the vapour pressure at (i) 90°C and (ii) 110°C. Compare the results c(i) and c(ii) above and make a one sentence comment on your observation.

[6 marks]

SECTION B

3. (a) What is the difference between the molarity and molality of a solution?

[2 marks]

- (b) Define colligative properties.

[2 marks]

$\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = - \left(\frac{\partial H}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$

$U = H - PV$

$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial T}{\partial P}\right)_V - P$

$\left(\frac{\partial H}{\partial T}\right)_P = C_p$

$dH = C_p dT$

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$U = U(T, V)$

$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P$

$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_P + \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P$

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$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{\partial u}{\partial T}\right)_v + \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial u}{\partial T}\right)_v \quad (2)$$

(c) Sketch a **well labelled** plot to illustrate how the change in the chemical potential, μ of a pure solvent, compared to that of the solvent in solution with a nonvolatile solute, affect the freezing point and the boiling point of the solvent. [3 marks]

(d) Respond to the following questions. If neither, answer "same".

- Which of benzene C_6H_6 in a 0.01 M toluene solution in benzene at 1 bar **or** benzene in a 0.1 M toluene solution in benzene at 1 bar has a higher boiling point?
- Which of $H_2O(l)$ **or** $H_2O(g)$ at 100 °C has a higher chemical potential?
- Which of $H_2O(l)$ at 100 °C and 1 bar **or** $H_2O(l)$ in a 39.1 g NaCl solution at 100 °C and 1 bar has a higher chemical potential?
- Which of H_2O at 1 bar **or** H_2O in a 45.20 g sucrose solution at 1 bar has a higher freezing point? [6 marks]

(e) An ideal solution is made from 5.00 mol of benzene and 3.25 mol of toluene. If the temperature is 298K and pressure is 1 bar, determine

- the ΔG_{mixing}
- the ΔS_{mixing}
- if the mixing is spontaneous

$$dH = u + w$$

[7 marks]

4. (a) State **any three (3)** properties of ideal solution. [3 marks]

(b) With the aid of at least two different sketches (stating a specific example in each case), briefly explain **positive** and **negative** deviations from the Raoult's law. [4 marks]

(c) At 298 K and 1 atm, the molar volume of water is 0.018 L, while that of ethanol is 0.058 L. Mixing half a mole of each liquid should result in a combined volume of 0.038 L. However, 0.036 L was obtained.

- Account for the shrinkage of volume. [2 marks]
- What does that infer about **volume** in **Real** solutions? [1 mark]

(d) The average human of 70 kg weight has a blood volume of 5.00 L. The Henry's law constant for the solubility of N_2 in H_2O is 9.04×10^4 bar at 298 K. Assume that this is also the value of the Henry's law constant for N_2 in blood and that the density of blood is 1.00 kg L^{-1} . Calculate the number of moles of nitrogen absorbed in this amount of blood in air of composition 78.08% N_2 at sea level, where the pressure is 1 bar. [5 marks]

$$\left(\frac{\partial u}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = - \left(\frac{\partial u}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T$$

$$\left(\frac{\partial u}{\partial T}\right)_p \frac{\partial p}{\partial u}$$

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial u}{\partial T}\right)_p + \left(\frac{\partial u}{\partial p}\right)_T$$

$$b = K \cdot x$$