

CY11001, DEPARTMENT OF CHEMISTRY

MIDSEM EXAMINATION

Q.1(a) What is the correct expression for f in the thermodynamic equation

$$\left(\frac{\partial U}{\partial p}\right)_T = V - f?$$

[2]

(i) $T \left(\frac{\partial V}{\partial T}\right)_p$	(ii) $T \left(\frac{\partial T}{\partial p}\right)_V$	(iii) $T \left(\frac{\partial p}{\partial V}\right)_T$	(iv) $\left(\frac{\partial U}{\partial V}\right)_T$
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Q.1(b) A Carnot engine whose low temperature reservoir is at 7 °C has an efficiency of 40%. By how many degrees should the temperature of the source be increased if one wants to increase the efficiency to 50 %?

[2]

(i) 560 K	(ii) 466 K	(iii) 250 K	(iv) 93.5 K
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Q.1(c) Show that $\mu_{JT} = - \frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T$. [4]

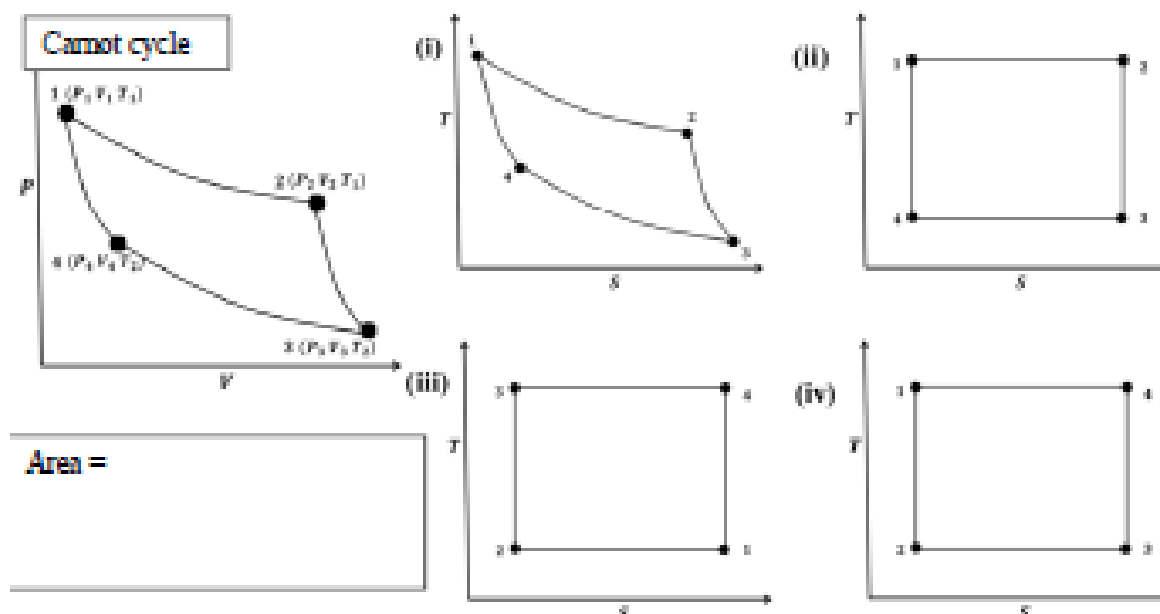
Q.1(d) One mole of argon gas ($\gamma=1.66$) is expanded reversibly and adiabatically from 2.5 m³ at 300 K to 5 m³. The molar heat capacity, $C_{v,m}$ of argon is 12.55 JK⁻¹ mol⁻¹. Assuming ideal behavior, calculate

- final temperature (in K) and pressure (in N m⁻²) of the gas.
- w , q and ΔU of the process (in kJ).

[4]

Q.2(a) Mark (with ✓) the correct T - S diagram corresponding to the P - V diagram shown below for Carnot cycle. What is the area of the part enclosed by the cyclic path in T - S diagram?

[2+1]



Q.2(b) In the indirect conversion, $A \rightarrow C \rightarrow D \rightarrow B$ of $A \rightarrow B$, the values of $\Delta S_{(A \rightarrow C)}$, $\Delta S_{(C \rightarrow D)}$, and $\Delta S_{(D \rightarrow B)}$ are respectively, 100, 80 and 50 J K^{-1} . Mark (with ✓) the correct value of $\Delta S_{(A \rightarrow B)}$ in J K^{-1} .

[2]

(i) - 230	(ii) - 130	(iii) + 130	(iv) + 230
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Q.2(c) One mole of an ideal gas is first heated at constant pressure from temperature T to $3T$ and then cooled back to T at constant volume. Show that ΔS_{net} of the overall process is equal to that when the gas is isothermally expanded at temperature T from V to $3V$, where V is the original volume.

[3]

Q.2(d) One mole of an ideal gas at 300 K expands isothermally from 1.0 L to 2.0 L against a constant pressure of 10 atm. Calculate ΔS_{net} in J K^{-1} .

[4]

Q.3(a) Mark (with ✓) the correct expression for the slope of pressure, p vs temperature, T plot at a constant volume, V .

[α : isobaric expansion coefficient, κ_T : isothermal compressibility, C_V : heat capacity at constant volume and C_p : heat capacity at constant pressure]

[2]

(i) α/κ_T	(ii) α/C_V	(iii) κ_T/α	(iv) κ_T/C_p
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Q.3(b) Complete the table given below for one mole of a real gas (with van der Waals constants a and b) that obeys the following equation of state,

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Given, $x = \frac{RT}{(V-b)^2}$; $y = \frac{a}{V^2}$; $z = \frac{R}{V-b}$.

[2×5=10]

(A)	For the isobaric expansion coefficient (α), the value of $V\alpha$ in terms of x, y and z is				(Write the correct option)
	(i) $\frac{x}{x-2y}$	(ii) $\frac{x}{x-y}$	(iii) $\frac{x}{x+2y}$	(iv) $\frac{x}{x+y}$	
(B)	For the isothermal compressibility, (κ_T), the value of $V\kappa_T$ in terms of x, y and z is				(Write the correct option)
	(i) $\frac{x}{x-2y}$	(ii) $\frac{1}{x-2y}$	(iii) $\frac{1}{x-y}$	(iv) $\frac{1}{x-z}$	
(C)	The ratio $\frac{\alpha}{\kappa_T} = \frac{z}{\ell}$				$\ell =$
(D)	For Gibbs free energy (G), $\left[\frac{\partial}{\partial T} \left(\frac{G}{T}\right)\right]_p = \frac{m}{T^2}$				$m =$
(E)	For Gibbs free energy (G), $\left[\frac{\partial}{\partial T} \left(\frac{G}{T}\right)\right]_V - \left[\frac{\partial}{\partial T} \left(\frac{G}{T}\right)\right]_p = \frac{x^n}{T}$				$n =$

Show the derivation of each part (A-D) of Q. 3(b) in the next page(s).

Q.4(a) Which of the following relations correctly represents a system, consisting of the components *A* and *B*, at equilibrium at a given temperature and pressure?

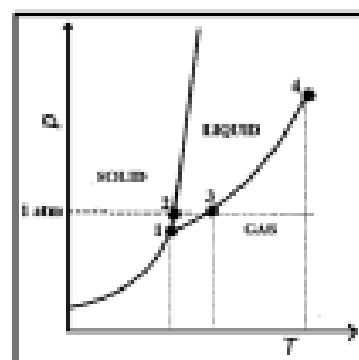
[2]

(i) $dn_A = - \left(\frac{n_B}{n_A} \right) dn_B$	(ii) $d\mu_A = - \left(\frac{n_B}{n_A} \right) d\mu_B$
(iii) $d\mu_A = \left(\frac{n_B}{n_A} \right) d\mu_B$	(iv) $dn_A = \left(\frac{\mu_B}{\mu_A} \right) dn_B$

Q.4(b) Label the points in a typical phase diagram shown in the figure.

[2]

Point 1:
Point 2:
Point 3:
Point 4:



Q.4(c) Calculate the change in chemical potential to predict the effect of an increase in pressure of 1.00 bar on the liquid and solid phases of carbon dioxide (molar mass 44.0 g mol^{-1}) in equilibrium. The densities of liquid and solid CO_2 are $2.35 \times 10^3 \text{ kg m}^{-3}$ and $2.50 \times 10^3 \text{ kg m}^{-3}$, respectively.

[3]

$\Delta\mu$ (liquid):
$\Delta\mu$ (solid):
Prediction:

Q.4(d) Estimate the triple point temperature (in K) and pressure (in Torr) of sulfur dioxide when the temperature dependence of the vapour pressure of solid sulfur dioxide is given by:

$$\log_{10} p = 10.5916 - \frac{1871.2}{T}$$

And the vapour pressure of that of liquid sulfur dioxide by:

$$\log_{10} p = 8.3186 - \frac{1425.7}{T}$$

[3]

Temperature at the Triple point (in K):
Pressure at the Triple point (in Torr):

Q.5(a) A mixture of ideal gases react according to the following equation:



Mark (with ✓) the TRUE statement(s). [2]

- (i) K_p (pressure equilibrium constant) is dimensionless.
- (ii) K°_p (standard-state pressure equilibrium constant) is a function of temperature but is independent of pressure.
- (iii) ΔH° must be independent of T .
- (iv) When the mixture is held at constant T and at a constant (total) pressure of 1 bar and one mole of A reacts, the observed ΔS per mole of the reaction equals ΔS° .

Q.5(b) At 400 K, $K^\circ_p = 36$ for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Mark (with ✓) the correct value of K°_p at 400 K for the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$. [2]

(i) 6	(ii) 18	(iii) 0.028	(iv) 0.167
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Q.5(c) For the gas-phase reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, a closed system initially contains 4.0 mol of N_2 , 4.0 mol of H_2 , and 1.0 mol of NH_3 . Give the maximum and minimum possible values at equilibrium of each of the following quantities: (i) ξ (extent of reaction), (ii) number of moles of N_2 , and (iii) number of moles of NH_3 . [2+2]

Q.5(d) The reaction $N_2(g) \rightleftharpoons 2N(g)$ has $K^\circ_p = 2.5 \times 10^{-6}$ at 4000 K. In a certain gas mixture containing N_2 , N , and He at 4000 K, the partial pressures $P_{N_2} = 700$ torr, $P_N = 0.10$ torr, and $P_{He} = 300$ torr. Is the mixture in reaction equilibrium? Justify your answer. Given 1 bar = 750 torr. [4]