

Bachelor of Metallurgical Engineering 2nd Year 2nd Semester Examination, 2023

Thermodynamics of Materials

Time: Three Hours

Full Marks-100

Answer Question No. 1 and any Four from the rest.

1. i) Apply the 1st law of thermodynamics, $\delta q = dU + \delta w$, to an isolated system and show that the latter is a system of constant U and constant V, doing no non-mechanical work. 2
- ii) Is the reversible heat interaction between the system (1 mole of an ideal gas) and surrounding greater than, equal to, or less than the irreversible one in a) an isothermal expansion and b) a constant pressure heating? 3
- iii) Is the relation $dS = \delta q/T$ valid for a fixed mass, fixed composition system undergoing a) constant temperature, reversible process, b) constant temperature, irreversible process c) constant pressure, reversible process, and d) constant pressure, irreversible process? Explain. 3
- iv) For a given mass/mole of an ideal gas as system, find if the following statements are True or False:
- $G = f(P, T)$
 - $G = f(V, T)$
 - $G = f(U, T)$
 - $G = f(U, V)$
- 3
- v) Derive the following expression for $C_p - C_v$:
- $$C_p - C_v = [V - (\partial H / \partial P)_T](\partial P / \partial T)_V.$$
- 4
- vi) Given: $dM = Z_1 dn_1 + Z_2 dn_2 + VdP - SdT$
Prove: $(\partial Z_2 / \partial P)_{n_2, n_1, T} = (\partial V / \partial n_2)_{P, n_1, T}$ 2
- vii) Show that
 $-(\partial S / \partial P)_V (\partial T / \partial P)_S = (C_v / C_p) (\partial V / \partial P)_T$ 4
- viii) To show that the cyclic integration $\oint (\delta q_{rev} / T)$ is equal to zero for any reversible cycle, consider a reversible cycle comprised of four alternate isothermal and constant pressure steps and prove. Consider n moles of ideal gas as the system. 4
- ix) Check if the expression $2x(\log y)dx + (x^2/y)dy$ is a perfect differential. 2

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- x) Write the criteria of spontaneity and equilibrium in terms of the entropy (S) of the system involving non-mechanical work $\delta w'$. 3
- xi) Can we apply the condition $dG_{P,T} < 0$ for the verification of irreversibility of any process with 1 mole of ideal gas as system? Explain. 2
- xii) Give the expression for the vibrational (internal) energy for the diatomic gas molecule and derive the corresponding expression for the vibrational heat capacity at constant volume. 3
- xiii) Starting from $dH = TdS + VdP$, show that for a reversible adiabatic process with n moles of an ideal gas
- $$\Delta H = nc_p (T_2 - T_1). \quad \text{3}$$
- xiv) Explain if glass has zero entropy at 0 K in accordance with the 3rd law of thermodynamics. 2

2. When coal is gasified with air or oxygen, the process is strongly exothermic; when gasified with steam, the process is strongly endothermic. Thus the process can be thermally balanced by using oxygen and steam together.

Assume that pure C at 298 K, O₂ at 298 K, and H₂O (g) at 500 K are fed to a reactor which yields a gas at 1200 K composed entirely of CO and H₂. The reactor, which is a constant pressure system, is well insulated so that $q = 0$ for the process.

Find the consumption rates of O₂ and H₂O *each* in moles per mole of C fed to the reactor.

Given: Standard enthalpies of formation at 298 K:

CO	-110.54 kJ/mol
H ₂ O (g)	-241.83 kJ/mol

Enthalpy changes, $H_T - H_{298}$:

	<u>T = 500 K</u>	<u>T = 1200 K</u>	
O ₂	6.09 kJ/mol	29.77 kJ/mol	
H ₂ O (g)	6.92 kJ/mol	13.56 kJ/mol	
H ₂	5.88 kJ/mol	26.80 kJ/mol	
CO	5.92 kJ/mol	28.43 kJ/mol	
C (s)	2.38 kJ/mol	16.23 kJ/mol	15

3. i. We are interested to find the effect of pressure on the internal energy of a system with fixed mass and fixed composition.
- a) For this purpose; show that $(\partial U / \partial P)_T$ can be written as $V(-\alpha T + \beta P)$.
- b) Find the value of the above derivative in the case of an ideal gas.

(Note, α is the isobaric expansivity and β is the isothermal compressibility of the system.)

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- ii. Find the change in Gibbs free energy, ΔG , for the constant pressure process 1 \rightarrow 2 (see Figure 1), carried out with 1 mole of an ideal gas for which the molar heat capacities C_p and C_v are $5/2(R)$ and $3/2(R)$, respectively, and the molar entropy $S_{298K, 1 atm} = 120 J/K$.

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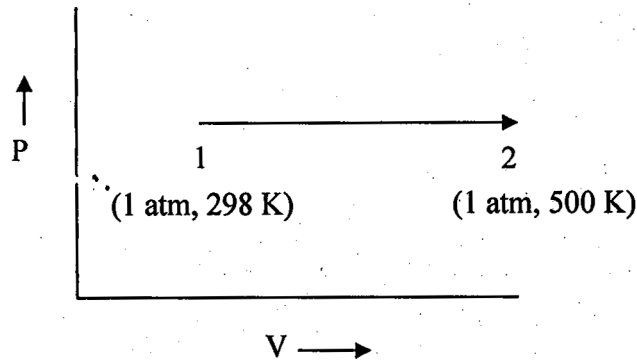


Fig. 1

4. i. Two moles of a monatomic ideal gas, with the molar heat capacity $C_p = (5/2)R$, are initially taken in a closed system at 600 K and 3 atm pressure. The gas is then irreversibly and adiabatically expanded against 2 atm (external) pressure to the final volume V_2 . Find the change in entropy $S_2 - S_1$.
- ii. Find the work interaction $w_{3\rightarrow 1}$ in the step 3 \rightarrow 1 of the reversible cycle 1-2-3-1, given in Figure 2. The system is 1 mole of a monatomic ideal gas.

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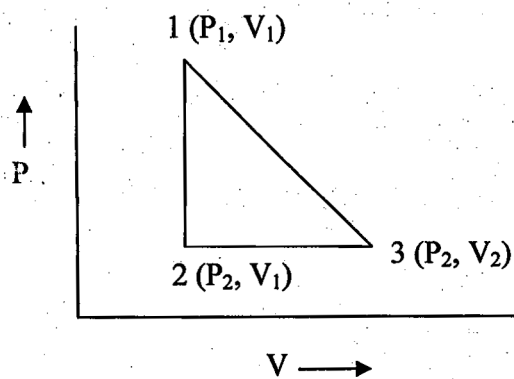


Fig. 2

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5. i. Four moles of metal M(s), 10 moles of oxygen (O₂), and 1 mole of metal oxide MO(s) are initially taken in an isolated system at 298 K and 1 atm pressure. After 2 moles of M have reacted to form MO, the temperature of the system increases to 1200 K. Find the standard enthalpy of formation of MO at 298 K. Given,

M(s):	$C_V = 25 \text{ J/mol.K}$	$C_P = 30 \text{ J/mol.K}$
MO(s):	$C_V = 57 \text{ J/mol.K}$	$C_P = 65 \text{ J/mol.K}$
O ₂ (g):	$C_V = 22 \text{ J/mol.K}$	$C_P = 30 \text{ J/mol.K}$

(Note all data may not be required.)

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- ii. Explain why the electronic heat capacity of metals are best detected at either high temperatures or very low temperatures.

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6. In the Thermit welding process, molten iron is made by reacting a mixture of Fe₂O₃, Al, and Fe to give Fe and Al₂O₃. The reactants are at room temperature (298 K) before ignition, and consist of a stoichiometric mixture of Fe₂O₃ and Al, plus some metallic iron. After completion of the reaction, the products are to be at 2000 K.

Calculate the mass of iron to be added to 214 gm of the Al + Fe₂O₃ mixture to attain the desired result. Assume no heat loss (adiabatic, constant pressure process).

Data: i. $\Delta H_{\text{Al}_2\text{O}_3, 298\text{K}} = -1,676,000 \text{ J/mol}$	viii. $T_{\text{m,Fe}} = 1812 \text{ K}$
ii. $\Delta H_{\text{Fe}_2\text{O}_3, 298\text{K}} = -810,520 \text{ J/mol}$	ix. $\Delta H_{\text{m,Fe}, 1812\text{K}} = 13,800 \text{ J/mol}$
iii. $C_{\text{P, Fe (s)}} = 28.2 \text{ J/mol.K}$	x. At wts of Fe: 56, Al: 27, O:16.
iv. $C_{\text{P, Fe (l)}} = 46 \text{ J/mol.K}$	(Note, all data may not be needed)
v. $C_{\text{P, Al}_2\text{O}_3 \text{ (s)}} = 106.6 \text{ J/mol.K}$	
vi. $C_{\text{P, Fe}_2\text{O}_3 \text{ (s)}} = 98.3 \text{ J/mol.K}$	
vii. $C_{\text{P, Al (s)}} = 20.7 \text{ J/mol.K}$	

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