National Exams - May 2019

12-Mtl-A1, Materials Thermodynamics

3 hours duration

NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.

2. This is a CLOSED BOOK EXAM but one aid sheet written on both sides is allowed. **An approved Casio or Sharp calculator is allowed.**

3. All FIVE (5) questions need to be answered.

4. The value of each question is listed at the end of the question.

5. Clarity and organization of the answer are important.

6. Values of the Universal Gas Constant (R) in various units are listed below:

Table A.2: Values of the Universal Gas Constant

$$R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}} = 8.314\ \mathrm{m^3\ Pa\ mol^{-1}\ K^{-1}}$$
$$= 83.14\ \mathrm{cm^3\ bar\ mol^{-1}\ K^{-1}} = 8{,}314\ \mathrm{cm^3\ kPa\ mol^{-1}\ K^{-1}}$$
$$= 82.06\ \mathrm{cm^3 (atm)\ mol^{-1}\ K^{-1}} = 62{,}356\ \mathrm{cm^3 (torr)\ mol^{-1}\ K^{-1}}$$
$$= 1.987\mathrm{(cal)\ mol^{-1}\ K^{-1}} = 1.986\mathrm{(Btu)(lb\ mole)^{-1}(R)^{-1}}$$
$$= 0.7302\mathrm{(ft)^3(atm)(lb\ mol)^{-1}(R)^{-1}} = 10.73\mathrm{(ft)^3(psia)(lb\ mol)^{-1}(R)^{-1}}$$
$$= 1{,}545\mathrm{(ft)(lb_f)(lb\ mol)^{-1}(R)^{-1}}$$

1. The partial molar excess Gibbs free energies for chromium in binary solutions with nickel for various liquid-phase compositions at a temperature of 1600 °C are listed below:

X_{Cr}	ΔG^E_{Cr} , in Joules
0.1	- 12714
0.3	- 5442
0.5	- 339
0.7	- 921
0.9	- 1227

Determine the following:

(a) Activity coefficient of Cr in the dilute region
(b) Activity coefficient of Ni in the Cr-Ni binary solution at $X_{Ni} = 0.7$
(c) Partial molar excess Gibbs free energy of Ni at $X_{Ni} = 0.7$
(d) Integral molar excess Gibbs free energy of mixing of the solution at $X_{Ni} = 0.7$
(e) Integral molar Gibbs free energy of mixing of the solution at $X_{Ni} = 0.7$

(25%)

2. The equilibrium constants for the reversible reactions

$FeO\ (s) + CO\ (g) \leftrightarrow Fe\ (s) + CO_2\ (g)$ equilibrium constant = K_1
$FeO\ (s) + H_2\ (g) \leftrightarrow Fe\ (s) + H_2O\ (g)$ equilibrium constant = K_2

at various temperatures are given below:

T (°C) →	600	800	1000
K_1 →	0.900	0.535	0.396
K_2 →	0.332	0.499	0.668

Calculate the equilibrium constant and standard Gibbs free energy change for the following reversible reaction at temperatures of 600, 800, and 1000 °C:

$CO\ (g) + H_2O\ (g) \leftrightarrow$ at 727 °C $CO_2\ (g) + H_2\ (g)$

(15%)

3. Equimolar quantities of zinc oxide and carbon are placed in a closed reactor with idealistically no air left, and then heated to a temperature of 897 °C. The following equilibrium chemical reactions take place:

$$ZnO\ (s) + C\ (s) \leftrightarrow Zn\ (g) + CO\ (g)$$

$$CO_2\ (g) + C\ (s) \leftrightarrow 2CO\ (g)$$

Assuming the activities of the pure solids to be 1, determine the partial pressures of Zn vapor, CO, and CO_2 after equilibrium has been established.

Standard Gibbs Free Energy Change (ΔG^o) in J/K

For $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$	$\Delta G^o = -\ 111{,}700 - 87.65\ T$
For $C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$	$\Delta G^o = -\ 394{,}100 - 0.84\ T$
For $Zn\ (g) + \frac{1}{2}\ O_2\ (g) \rightarrow ZnO\ (s)$	$\Delta G^o = -\ 460{,}200 + 198\ T$

(20%)

4. Consider the following reaction

$$7\ Cr_3C_2\ (s) + 2.5\ O_2\ (g) \rightarrow 3\ Cr_7C_3\ (s) + 5\ CO\ (g)$$

(a) Obtain an expression for the standard Gibbs free energy (ΔG^o) as a function of temperature (T).

(b) Calculate ΔG^o for the reaction at T = 1500 K and 298 K.

(c) Calculate ΔG^o for the reaction at T = 1500 K and 298 K using the equation $\Delta G^o = \Delta H^o_{298} - T\ \Delta S^o_{298}$.

(d) Compute the percentage difference in ΔG^o for the reaction at T = 1500 K and 298 K from the results obtained in part (b) and part (c).

Molar Specific Heat (C_p) in cal/mol K

For $Cr_7C_3 \rightarrow$	$C_p = 56.96 + (14.54 \times 10^{-3}\ T) - (10.12 \times 10^5\ T^{-2})$
For $CO \rightarrow$	$C_p = 6.79 + (0.98 \times 10^{-3}\ T) - (0.11 \times 10^5\ T^{-2})$
For $Cr_3C_2 \rightarrow$	$C_p = 30.03 + (5.58 \times 10^{-3}\ T) - (7.46 \times 10^5\ T^{-2})$
For $O_2 \rightarrow$	$C_p = 7.16 + (1.00 \times 10^{-3}\ T) - (0.40 \times 10^5\ T^{-2})$

Standard Molar Heat of Formation (ΔH^o_{298}) in cal/mol

For Cr_7C_3 → $\Delta H^o_{298} = -54{,}500$
For CO → $\Delta H^o_{298} = -26{,}420$
For Cr_3C_2 → $\Delta H^o_{298} = -26{,}200$
For O_2 → $\Delta H^o_{298} = 0$

Standard Entropy of Formation (ΔS^o_{298}) in cal/mol K

For Cr_7C_3 → $\Delta S^o_{298} = 48.00$
For CO → $\Delta S^o_{298} = 47.22$
For Cr_3C_2 → $\Delta S^o_{298} = 20.40$
For O_2 → $\Delta S^o_{298} = 49.00$

(25%)

5. For the equilibrium reaction

$$ZrO_2\ (s) \leftrightarrow Zr\ (s) + O_2\ (g)$$

the standard Gibbs free energy change is given by the equation

$$\Delta G^o = 1{,}089{,}329 + 26.96\ T \log T - 276.27\ T \text{ in J/mole}$$

Calculate the following at a temperature of 2073 K:

(a) Equilibrium constant
(b) Equilibrium partial pressure of oxygen
(c) Predict the possibility of decomposing a pure ZrO_2 crucible under a vacuum of 10^{-8} atm. Assume the initial composition of the gas in the evacuated chamber to be that of air.

OR

Calculate the equilibrium constant for the following reaction at 727 °C:

$$FeO\ (s) + CO\ (g) \leftrightarrow Fe\ (s) + CO_2\ (g)$$

Will pure FeO form if a pure iron sheet is annealed at 727 °C in an atmosphere containing 12% by volume CO, 1.5% by volume CO_2 and 86.5% by volume N_2?

Standard Gibbs Free Energy Change (ΔG^o) in J/K

For $C (s) + ½ O_2 (g) \rightarrow CO (g)$	$\Delta G^o = - 111{,}700 - 87.65 T$
For $C (s) + O_2 (g) \rightarrow CO_2 (g)$	$\Delta G^o = - 394{,}100 - 0.84 T$
For $Fe (s) + ½ O_2 (g) \rightarrow FeO (s)$	$\Delta G^o = - 263{,}700 + 64.35 T$

(15%)