QUIZ II

Q.1

a) (5 pts)   Attached is the Gibbs energy- temperature (Ellingham) diagram for oxides. Give three most important observations one can make from the diagram.

b) (10 pts)   For a chemical reaction,
$$aA + bB + \ldots\ldots = cC + dD + \ldots\ldots,$$
show that $\Delta G = \Delta G^\circ + RT \ln J$

c) (20 pts)   For the following reaction;
$$C_3H_7OH \ (g) = (CH_3)_2CO \ (g) + H_2 \ (g),$$
by using $K_p = 0.151$ at 422.0 K and $K_p = 1.58$ at 491.6 K
a) Calculate $\Delta_r H^\circ$, and $\Delta_r S^\circ$; b) Calculate $\Delta_r G^\circ$ at 450 K.

Q.2

a) (5 pts)   Explain phase equilibria

b) (10 pts)   Show that for a two phase equilibrium,

$$\frac{dT}{dP} = \frac{(V^{II} - V^I) \, T}{\Delta H}$$

This relationship is called Clapeyron equation.

c) (20 pts)   Find the Gibbs energy change for the following phase transformation:
$$\text{Graphite} \rightarrow \text{Diamond}$$

The equilibrium pressure P as a function of temperature is given by linear

equation: $P(\text{bar}) = 7,100 + 27.00 \, T$

The change of volume $(\Delta V) = V(\text{diamond}) - V(\text{graphite}) = -1.77 \ cm^3/mol$.
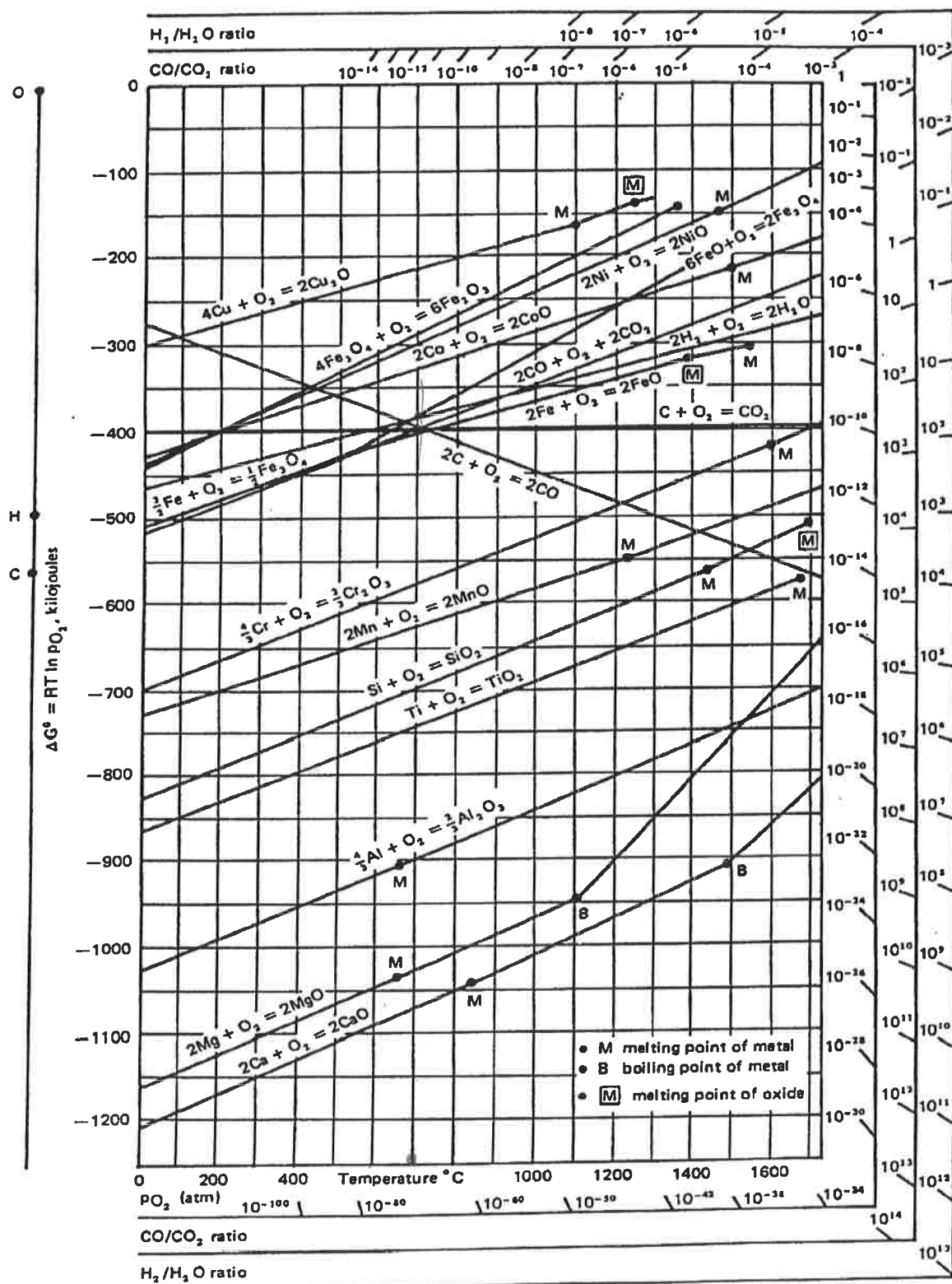
1 atm = 1 bar = 101325 Pa or (N/m^2).

Q.3

a) (10 pts)   Explain the following.
(1) Henry's law;   (2) Sievert's law

b) (20 pts)   Determine the fugacity of CO_2 at 40.5 bar pressure from the following equation for compressibility factor (Z) as a function of pressure (P) at 350K and at a reference state $P^\circ = f^\circ$
$$Z = 1 - 3.908 \times 10^{-3} \, P - 1.988 \times 10^{-5} \, P^2$$

Figure: The Ellingham diagram for metallurgically important oxides

H_2/H_2O ratio

CO/CO$_2$ ratio

$\Delta G^\theta = RT \ln pO_2$, kilojoules

$4Cu + O_2 = 2Cu_2O$

$4Fe_3O_4 + O_2 = 6Fe_2O_3$

$2Co + O_2 = 2CoO$

$2Ni + O_2 = 2NiO$

$6FeO + O_2 = 2Fe_3O_4$

$2CO + O_2 + 2CO_2$

$2H_2 + O_2 = 2H_2O$

$2Fe + O_2 = 2FeO$

$C + O_2 = CO_2$

$\frac{3}{2}Fe + O_2 = \frac{1}{2}Fe_3O_4$

$2C + O_2 = 2CO$

$\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$

$2Mn + O_2 = 2MnO$

$Si + O_2 = SiO_2$

$Ti + O_2 = TiO_2$

$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$

$2Mg + O_2 = 2MgO$

$2Ca + O_2 = 2CaO$

M melting point of metal
B boiling point of metal
M melting point of oxide

Temperature °C

PO$_2$ (atm)

CO/CO$_2$ ratio

H_2/H_2O ratio

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$\Delta U = Q + W + W' + \ldots$ (1st Law)

$H = U + PV$

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$C_P = \left.\dfrac{\partial Q}{\partial T}\right|_P = \left.\dfrac{\partial H}{\partial T}\right|_P$

$C_V = \left.\dfrac{\partial Q}{\partial T}\right|_V = \left.\dfrac{\partial U}{\partial T}\right|_V$

$C_V = \dfrac{3}{2} R$ (1 mol ideal monatomic gas)

$C_V = \dfrac{5}{2} R$ (1 mol ideal diatomic gas)

$C_P = C_V + R$

$C_P^o = \alpha + 2\beta T - 2\varepsilon / T^2$

$dQ = 0$ (adiabatically closed system)

$dU = 0$ (isothermal process)

$\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{R/C_V}$

$\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{R/C_P}$ (adiabatic process)

$\dfrac{P_2}{P_1} = \left(\dfrac{V_1}{V_2}\right)^{C_P/C_V}$ (adiabatic process)

$Z = \dfrac{PV}{RT}$ (compressibility factor)

$\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$ (1 mole, Van der Waals equation)

$dW = -PdV$

$\Delta H_P = (H_2 - H_1)_P = Q_P$

$H_T^o - H_{298}^o = \displaystyle\int_{298}^{T} C_P \, dT$

$\eta = \dfrac{Q_2 + Q_1}{Q_2} = -\dfrac{W}{Q_2}$

1

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$dS = \frac{dQ_{rev}}{T}$$

$$dU = TdS - PdV \qquad \text{(1}^{\text{st}}\ \&\text{2}^{\text{nd}}\ \text{Laws)}$$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

$$\Delta S_V = C_V \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_T = R\ln\left(\frac{V_2}{V_1}\right) = -R\ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta S_P = C_P \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = -R\sum_{i=1}^{i} x_i \ln x_i$$

$$S_\beta - S_\alpha) = \Delta S_P = \left(\frac{Q_{rev}}{T_{\alpha\beta}}\right)_P = \left[\frac{\left(H_\beta - H_\alpha\right)}{T_{\alpha\beta}}\right]_P$$

$$C_P - C_V = \frac{\alpha^2\ TV}{\beta}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_V$$

$$A = U - TS$$

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\left(A_2 - A_1\right)_T = -\int_{V_1}^{V_2} PdV = RT\ln\frac{V_1}{V_2}$$

$$\left(G_2 - G_1\right)_T = -\int_{P_1}^{P_2} VdP = RT\ln\frac{P_2}{P_1}$$

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$$dS_{system} = \frac{dQ_{rev}}{T}$$ (reversible, under equilibrium)

$$dS_{system} > \frac{dQ_{rev}}{T}$$ (irreversible, spontaneous)

$$[\partial(\Delta G/T)/\partial T]_P = -\Delta H/T^2$$

$$[\partial(\Delta G/T)/\partial(1/T)]_P = \Delta H$$

$$\frac{dP}{dT} = \frac{S^{II} - S^{I}}{V^{II} - V^{I}} = \frac{\Delta S}{\Delta V} \Rightarrow \text{Clapeyron Equation}$$

$$\Delta G(P,T) = \Delta G^{o}(T) + RT \ln J$$

$$\Delta G^{o} = -RT \ln K$$

$$\Delta G = 0$$ (equilibrium)

$$\Delta G < 0$$ (Possible- Spontaneous)

$$\Delta G > 0$$ (Impossible – Non-spontaneous)

$$S_T = S_0 + \int_0^T \frac{dU + PdV}{T}$$

$$\ln P = -\frac{A}{T + B} + C$$

$$\gamma = C - \varphi + 2$$ (Gibbs Phase Rule)

$$G - G^{o} = RT \ln P$$

$$dG = RTd \ln P$$

$$G(P,T) = G^{o}(P = 1, T) + RT \ln P$$

$$\Phi = \frac{f}{P}$$ (fugacity coefficient)

$$RTd \ln f = VdP$$ (pure gas)

$$f_i = f_{i(P)} \cdot x_i$$

$$\ln\left(\frac{f}{P}\right) = Z - 1$$

$$\ln f = \frac{\left(H - H^{o}\right)}{RT} - \frac{\left(S - S^{o}\right)}{R}$$

$$\ln\left(\frac{f_2}{f_1}\right) = \left(\frac{H - H^{o}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$a_i \cong \frac{P_i}{P_i^{o}}$$

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$$a_i = \gamma_i x_i \qquad\qquad (\gamma_i = \textit{activity coefficient})$$

$$\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_2}$$

$$\overline{G}_i = \overline{H}_i - T\overline{S}_i$$

$$\overline{G}_i^{ex} = \overline{G}_i^{M} - \overline{G}_i^{id}$$

$$\overline{G}_i^{ex} = RT\ln\gamma_i$$

$$\overline{G}_i^{ex} = \overline{H}_i^{ex} - T\overline{S}_i^{ex}$$

$$\alpha_i = \frac{\ln\gamma_i}{(1-x_i)^2}$$

$$\ln\gamma_1 = \ln\gamma_1^0 + x_1\varepsilon_1^1 + x_2\varepsilon_1^2 + x_3\varepsilon_1^3 + \ldots\ldots\ldots + x_j\varepsilon_i^j$$

$$\ln f_1 = x_1\varepsilon_1^1 + x_2\varepsilon_1^2 + x_3\varepsilon_1^3 + \ldots\ldots\ldots + x_j\varepsilon_i^j$$

$$\log f_i = e_i^1(\%1) + e_i^2(\%2) + \ldots\ldots\ldots + e_i^j(\%j) \quad \text{where } f_i = \frac{h_i}{(\%i)}$$

$$x_A d\overline{G}_A + x_B d\overline{G}_B = 0 \quad (P, T \text{ constant})$$

$$x_A d\ln a_A + x_B d\ln a_B = 0$$

$$\sum_{i=1}^{i} Z_{i^+} m_{i^+} + \sum_{j=1}^{j} Z_{j^-} m_{j^-} = 0 (Z_{i^+} > 0; Z_{j^-} < 0) \quad \text{Principle of Electrical Neutrality}$$

$$\ln\gamma_\pm = \frac{Z_+ Z_- 132.853(\rho_1 I)^{0.5}}{(DT)^{1.5}(1+ka^\circ)} \qquad \text{Debye-Hückel equation}$$

$I = 0.5\,\Sigma m_i Z_i^2$ $\qquad\qquad$ Ionic Strength

$\ln\gamma_\pm = Z_+Z_- 1.171(I)^{0.5}/(1+I^{0.5})$ $\quad$ (25°C, solvent H2O)

$\ln\gamma_\pm = Z_+Z_- 1.171(I)^{0.5};$ $\qquad$ D – H limiting equation

$\ln\gamma_\pm = Z_+Z_- \alpha(I)^{0.5}/(1+I^{0.5})$ $\qquad$ where $\alpha = 132853\rho 10.5/(DT)1.5 = 1.171$

$a_{(A2B)} = [A^+]^2[B^-]$ $\qquad$ Temkin Rule

$\Delta G(P,T) = -ZFE$

$\Delta S_p = ZF(\partial E/\partial T)_p$

$\Delta H_p = -ZF[E - T(\partial E/\partial T)_p]$ $\qquad$ Gibbs-Helmholtz equations

$pt|H_2(g)|HCl\,(aq., m)|Hg_2Cl_2(s)|Hg(l)$ $\quad$ Hydrogen-Calomel Cell

Table 1.1 Fundamental constants, derived constants, and conversion factors.[*]

Name	Symbol	Value and Units
Fundamental constants:		
(Ice + water + vapor) point		273.1600 Kelvin
Molar volume of perfect gas (0°C, 1 bar)	V^0	0.02271108 m^3 mol^{-1} 22.71044 L mol^{-1}
Avogadro Number	N_A	6.022137×10^{23} mol^{-1}
Gas constant	R	8.31451 J mol^{-1} K^{-1} 1.987216 cal mol^{-1} K^{-1} 0.083143 L bar K^{-1} mol^{-1} 82.058 cm^3 atm mol^{-1} K^{-1}
Boltzmann constant	$k = R/N_A$	1.380658×10^{-23} J K^{-1}
Faraday constant	$\mathbf{F}$	96485.31 C mol^{-1} 23,060.54 cal mol^{-1} Volt^{-1}
Velocity of light in vacuum	$\rlap{/}c$	299,792,458 m s^{-1}
Planck constant	h	6.626076×10^{-34} J s
Proton charge (-electronic charge)	e^+	$1.60217733 \times 10^{-19}$ C
Permittivity of vacuum	$e_0 = 10^7/(4\pi c^2)$	8.854188×10^{-12} F m^{-1}
Defined constants and conversion factors:		
Thermochemical calorie	cal	4.1840 Joules (J)
Standard gravity	g^0	9.80665 m s^{-2}
Standard pressure	bar	10^5 Pa
Atmosphere of pressure	atm	101325 Pa (Newton m^{-2})
Newton	N	10^5 dynes
Joule	J	10^7 ergs
Liter	L	1000.028 cm^3
Electron volt	eV	96485.31 J mol^{-1} 23060.54 cal mol^{-1}
Kelvin	K	273.1500 + °C

Fixed points (1990 scale), freezing points of pure elements in K: (In, 429.7485), (Sn, 505.078), (Zn, 692.677), (Al, 933.473), (Ag, 1234.93), (Au, 1337.33), (Cu, 1357.77).[**]

[*] I. Mills, T. Cvitas, K. Homann, N. Kallay, and K. Kuchitsu, "Quantities, Units and Symbols in Physical Chemistry", Int. Union of Pure & Appl. Chem. (IUPAC), Blackwell Scientific Publ. (1993). E. T. Cohen and P. Giacomo, Physica *146A*, 1 (1987). B. N. Taylor and E. R. Cohen, J. Res., NIST, *95*, 497 (1990).

[**] Bull. Alloy Phase Diag. (BAPD), *11* (2), 107 (1990). See Gen. Ref. (18) and (25) for other units and conversion factors.