Name:

Physical Chemistry   GEO2-1202   Student no:
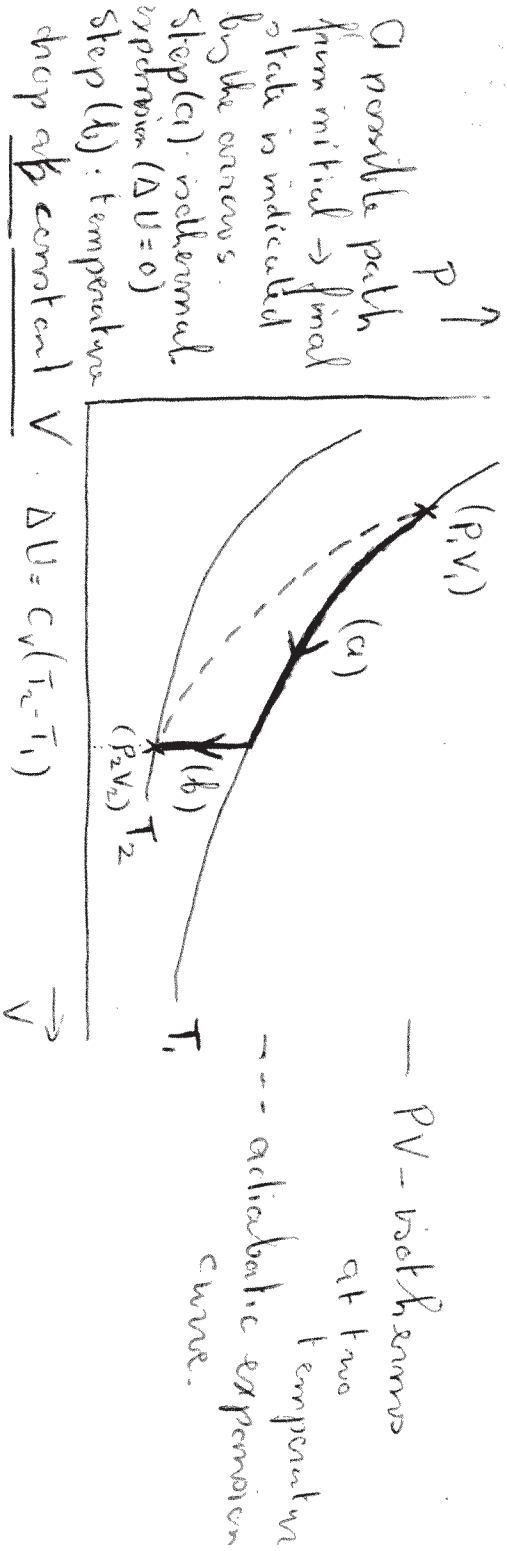
Deeltentamen

Question 1

a) The change in internal energy during the reversible, adiabatic expansion of an ideal gas is

$$\Delta U = C_V (T_2 - T_1)$$

where T_1 and T_2 are the temperatures of the initial and final states. Explain by means of a P-V-diagram why the heat capacity at constant volume is used in this equation, whereas the volume is not kept constant.

b) Calculate the work done by the reaction

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

When 1 mole of hydrogen gas is collected at 273 K and 1 atm. (Neglect volume changes other than the change in gas volume.)

A possible path from initial → final state is indicated by the arrows.

Step (a): isothermal expansion (ΔU = 0)

Step (b): temperature drop at constant V : ΔU = C_v(T_2 - T_1)

— PV - isotherms at two temperatures

-- - adiabatic expansion curve.

$(P_1 V_1)$ (a) (b) $(P_2 V_2)$ T_2 T_1

Volume of 1 mole $H_2(g)$ at 273K and 1 atm ;

$$PV = 1RT$$

$$1 \times V = 0.0806 \times 273$$

$$= 22.4$$

$$V = 22.4 \, L$$

Against a constant pressure of 1 atm ; when irreversible expansion

$$w = - P\Delta V$$

$$= - 22.4 \, Latm$$

$$= - 22.4 \times 101.34 = -2.270 \, kJ$$

Question 2

Calculate the values ΔU, ΔH and ΔS for the following process:

1 mole of liquid water at +5 °C and 1 atm → 1 mole of ice at 0 °C and 1 atm.

The molar heat of fusion (melting) of water at 273 K is 6.01 kJ mol^{-1}
The molar heat capacity of water is 75.5 J K^{-1} mol^{-1}.

Assume:
- the molar heat capacity is independent of temperature
- the molar volumes of water and ice are equal

2 steps: 1) cooling of H_2O (l) from $5°C \to 0°C$
          2) phase transformation $H_2O(l) \to H_2O(s)$ at $0°C$

Step 1

$\Delta H = C_p \Delta T = 75.5 \times (-5) = -377.5$ J mol^{-1}

$\Delta U = \Delta H - \Delta(PV) = \Delta H = -377.5$ J mol^{-1}

$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) = 75.5 \ln\left(\frac{273}{278}\right) = 75.5 \times (-0.018)$

$= -1.37$ J K^{-1} mol

Step 2

$\Delta H = -6.01$ kJ mol^{-1}

$\Delta U = \Delta H = -6.01$ kJ mol^{-1}

$\Delta S = \frac{q}{T} = \frac{\Delta H_f}{273} = \frac{-6.01 \times 1000}{273} = -22.0$ J K^{-1} mol

Step 1 + Step 2

$\Delta H_{TOT} = \frac{-377.5 - 6010}{1000} = \boxed{-6.39 \text{ kJ mol}^{-1}}$

$\boxed{\Delta U_{TOT} = -6.39 \text{ kJ mol}^{-1}}$

$\Delta S_{TOT} = -1.37 - 22.0 = \boxed{-23.37 \text{ J K}^{-1} \text{mol}^{-1}}$

<u>Question 3</u>
Oxalic acid ($H_2C_2O_4 \equiv Ox$) is a poisonous compound in many plants and vegetables.
Calciumoxalate ($CaC_2O_4 \equiv CaOx$) is only slightly soluble in water.
Given:

The Ca^{2+} and Ox^{2-} ions are in a 0.01 M $Ca(NO_3)_2$ solution. This concentration fixes the calcium concentration.
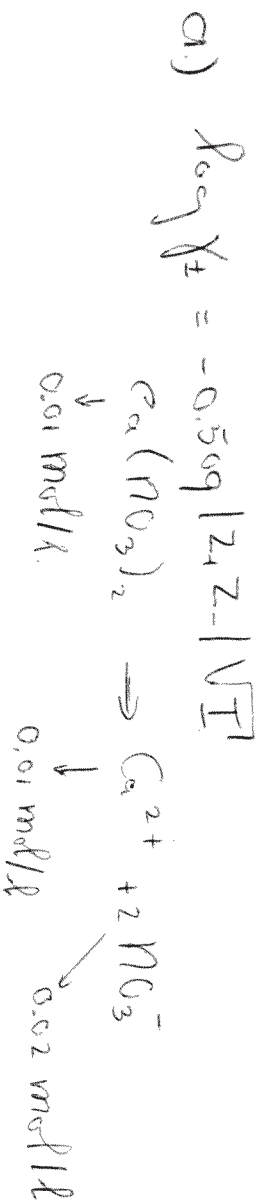In this solution the *apparent* solubility product of CaOx
$K_{sp} = 3.0\times10^{-9}$ at 25°C.
$\log \gamma_\pm = -0.509|Z_+Z_-|\sqrt{I}$

a) Calculate the mean ionic activity coefficient and the *thermodynamic* solubility product $(K_{sp}°)$ of CaOx.
b) Calculate the concentrations of the calcium and oxalate ions in this solution.

a) $\log \gamma_\pm = -0.509 |Z_+Z_-| \sqrt{I}$

$\underset{\underset{0.01\,mol/L}{\downarrow}}{Ca(NO_3)_2} \longrightarrow \underset{\underset{0.01\,mol/L}{\downarrow}}{Ca^{2+}} + \underset{\underset{0.02\,mol/L}{\downarrow}}{2NO_3^-}$

$I = \frac{1}{2} \sum m_i z_i^2$

$= \frac{1}{2}(0.01 \times 4 + 0.02 \times 1) = \frac{1}{2} \times 0.06 = 0.03$

$Z_+ = 2+ \quad (Ca^{2+})$
$Z_- = 2- \quad (Ox^{2-})$

$\log \gamma_\pm = -0.509 \times 4 \sqrt{0.03}$

$= -0.35$

$\gamma_\pm = 10^{-0.35} = \underline{0.44}$

$K_{sp}° = \gamma_\pm^2 K_{sp} = (0.44)^2 \times 3.0 \times 10^{-9} = \underline{0.59 \times 10^{-9}}$

b)

$m_{Ca^{2+}} \; m_{Ox^{2-}} = 3.0 \times 10^{-9}$

$\boxed{\begin{array}{l} C_{Ca^{2+}} \approx 0.01\,M \approx 0.01\,m. \\[2pt] C_{Ox^{2-}} = 3.0 \times 10^{-7}\,m. \end{array}}$

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Question 5
Given:

	N_2	O_2	NO
$\Delta_f G°$ (in kJ mol^{-1})	0	0	86.7
$\Delta_f H°$ (in kJ mol^{-1})	0	0	90.4

Nitric oxide from car exhaust is a primary air pollutant.

a) Calculate the equilibrium constant at 25 °C for the reaction:

$$N_2 (g) + O_2 (g) \Leftrightarrow 2 NO (g)$$

b) Calculate the equilibrium constant at 1500 °C, which is the typical temperature inside the cylinders of a running car.

Van 't Hoff equation:

$$\ln (K_2/K_1) = (\Delta_r H°/R)(1/T_1 - 1/T_2)$$

a) $\Delta_r G° = -RT \ln K_p$

$$\Delta_r G° = 2\,\Delta_f G°(no) - \Delta_f G°(N_2) - \Delta_f G°(O_2)$$

$$= 2 \times 86.7$$

$$= 173.4 \text{ kJ} \cdot mol^{-1}$$

$$\ln K_p = \frac{-173.4 \times 10^3}{8.314 \times 298}$$

$$= -70 \longrightarrow K_p = e^{-70} \approx \underline{4 \times 10^{-31}}$$

$$(\text{negligible})$$

b) $$\ln\left(\frac{K_2}{4 \times 10^{-31}}\right) = \frac{\Delta_r H°}{R}\left(\frac{1}{298} - \frac{1}{1773}\right)$$

$$\Delta_r H° = 2 \times 90.4 - 0 - 0 = 180.8 \text{ kJ} \cdot mol^{-1} \equiv 1.81 \times 10^{5} \text{ J} \cdot mol^{-1}$$

$$\ln(K_2/4 \times 10^{-31}) = 60.77$$

$$\longrightarrow K_2 = 4 \times 10^{-31} e^{60.77}$$

$$= 9.86 \times 10^{-5}$$

Question 4

Consider the following dissolution reaction of the mineral calcite at 25 °C, 1 bar:

$$CaCO_{3 \, (calcite)} + H^+ (aq) \leftrightarrow Ca^{2+}(aq) + HCO_3^- (aq)$$

with $\Delta_r G° = -27.43$ kJ mol^{-1}

a) Calculate the thermodynamic equilibrium constant of the reaction.

b) The apparent solubility constant of the reaction is defined as

$$K_m = (m_{Ca2+} \cdot m_{HCO3}) / a_{H+}$$

where m and a stand for molality and activity, respectively.
What is the value of K_m in a solution of ionic strength $I = 0.001$ m (at 25 °C,
1 bar) ? The following formulation of the Debye-Hückel law is appropriate:

$$\log \gamma_i = -0.509 z_i^2 \sqrt{I}$$

a)
$$\Delta_r G° = -RT \ln K_{eq}$$

$$-27.43 \times 10^3 = -8.314 \times 298 \ln K_{eq}$$

$$\ln K_{eq} = 11.07$$

$$K_{eq} = 64216$$

$$\underline{K_{eq} = 64216}$$

b.)
$$K_{eq} = \gamma_{Ca^{2+}} \times \gamma_{HCO_3^-} \times K_m$$

$$K_m = \frac{K_{eq}}{\gamma_{Ca^{2+}} \gamma_{HCO_3^-}}$$

$$\log \gamma_{Ca^{2+}} = -0.509 \times 4 \times \sqrt{0.001}$$
$$= -0.064$$
$$\gamma_{Ca^{2+}} = 10^{-0.064} = 0.862$$

$$\log \gamma_{HCO_3^-} = -0.509 \times 1 \times \sqrt{0.001}$$
$$\gamma_{HCO_3^-} = 10^{-0.016} = 0.964$$
$$= -0.016$$

$$K_m = \frac{64216}{0.862 \times 0.964} = \underline{77189}$$