Problem 1 (max. 15 points)

(a) For each of the following reactions give (1) the balanced reaction equation with the products of the reaction, (2) the type of reaction (redox, acid-base, precipitation, gas-evolution) and (3) the expression for the equilibrium constant of the reaction.

(i) 1M NaF (aq) with 1M $Mg(NO_3)_2$ (aq)

$2Na^+(aq) + 2F^-(aq) + Mg^{2+}_{aq} + 2NO_3^- \rightleftharpoons MgF_2(s) + 2Na^+ + 2NO_3^-$

precipitation reaction

$K = \frac{1}{[Mg^{2+}][F^-]^2}$

(ii) 0.1M $Fe_2(SO_4)_3$ (aq) with 0.1M Cu_2SO_4 (aq)

$\cancel{2}Fe^{3+} + 3SO_4^{2-} + \cancel{2}Cu^+ + SO_4^{2-} \rightleftharpoons \cancel{2}Fe^{2+} + \cancel{2}Cu^{2+} + 3SO_4^{2-}$

redox reaction

$K = \frac{[Fe^{2+}][Cu^{2+}]}{[Fe^{3+}][Cu^+]}$

(iii) $KHCO_3$ (aq) with 1M $NaHSO_4$ (aq)

(1) $\cancel{K^+} + HCO_3^- + \cancel{Na^+} + HSO_4^- \rightleftharpoons H_2CO_3 + SO_4^{2-} + \cancel{K^+} + Na^+$ acid-base, $K = \frac{[H_2CO_3][SO_4^{2-}]}{[HCO_3^-][HSO_4^-]}$

(2) $H_2CO_3 \rightleftharpoons H_2O + CO_2(g)\uparrow$ gas evolution $K = \frac{[CO_2(g)]}{[H_2CO_3]}$

(b) A volume of 50 mL of a 2 mM solution of $CaCl_2$ is added to 50 mL of a 2 mM solution of Ag_2SO_4. Describe what will happen, and explain your answer by giving the relevant reaction equations and calculations.

$Ca^{2+} + 2Cl^- + 2Ag^+ + SO_4^{2-} \longrightarrow 2AgCl + Ca^{2+} + SO_4^{2-}$

conc 1 mM 2 mM 2 mM 1 mM

→ Combining these 2 solutions may lead to precipitation of $CaSO_4$ and/or AgCl

→ Will $CaSO_4$ precipitate from reaction mixture?

~~Ca + Cl~~ $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(s)$

$K_c = \frac{1}{[Ca^{2+}][SO_4^{2-}]} = 1/K_{sp} = 1/1.7\,10^{-5} = 58\,10^3$

$Q = \frac{1}{[Ca^{2+}][SO_4^{2-}]} = \frac{1}{10^{-3} \times 10^{-3}} = 10^6 > 58.10^3$

→ reaction runs to left, no precipitate

→ Will AgCl precipitate from reaction mixture

$Ag^+ + Cl^- \rightleftharpoons AgCl$ $K = 1/K_{sp} = 1/1.77\,10^{-10} = 56\,10^8$

$Q = \frac{1}{[Ag^+][Cl^-]} = \frac{1}{2\,10^{-3} . 2\,10^{-3}} = 25\,10^4 << 56\,10^8$

reaction runs to right → precipitate

Problem 2 (max 25 points)

(a) Without carrying out calculations, give for the reactions (i-iii) the sign of ΔS_{sys} and ΔS_{sur}, and indicate the temperature range (low, high or all temperatures) at which the reaction will proceed spontaneously (6p). Explain your answer briefly.

(i) $Pb^{2+}(aq) + 2\,I^{-}(aq) \rightarrow PbI_2(s)$ ΔH^0_{rxn} = -62.9 kJ/mol

$\Delta S_{sys} < 0$
$\Delta S_{sur} > 0$

$\Delta G = \underset{<0}{\Delta H} - \underset{<0}{T\Delta S} \rightarrow \Delta G < 0$ only for low T !

(ii) $CH_3COOH\ (l) \rightarrow CH_4\ (g) + CO_2\ (g)$ ΔH^0_{rxn} = +16.2 kJ/mol

$\Delta S_{sys} > 0$
$\Delta S_{sur} < 0$

$\Delta G = \underset{>0}{\Delta H} - \underset{>0}{T\Delta S} \rightarrow \Delta G < 0$ only for high T !

(iii) $2\,O_3\ (g) \rightarrow 3\,O_2\ (g)$ ΔH^0_{rxn} = -285 kJ/mol

$\Delta S_{sys} > 0$
$\Delta S_{sur} > 0$

$\Delta G = \underset{<0}{\Delta H} - \underset{>0}{T\Delta S} \rightarrow \Delta G < 0$ for all T !

(b) By doing a calculation, determine if the reaction given below proceeds spontaneously at standard conditions (6p)

$HCO_3^-(aq) + S^{2-}(aq) \rightarrow HS^-(aq) + CO_3^{2-}(aq)$ ΔH^0_{rxn} = -12.4 kJ/mol
ΔS^0_{rxn} = -108 J/mol.K

answer 1 based on ΔH^0_{RXN}, ΔS^0_{RXN} given above:

$\Delta G^0_{RXN} = \Delta H^0_{RXN} - T\Delta S^0_{RXN}$, T = 298 K

$= -12.4\ 10^3 - 298 \cdot (-108)$ J

$= +19.8$ kJ/mol > 0

non-spontaneous

continued on next page

(c) Calculate the equilibrium constant for the reaction given at problem 2b (6p)

(based on numbers ~~for~~ given at 2b)

$$K = e^{-\Delta G^{\circ}_{RXN}/RT} = e^{\left(-19.8\,10^{3}/8.31 \times 298\right)}$$

$$= 3.37\,10^{-4}$$

(for alternative anwer see other page)

(d) By doing a calculation, determine if the reaction given at problem 2b proceeds spontaneously for the following conditions [HCO_3^{2-}] = 0.1 M, [S^{2-}] = 0.1 M, [HS^-] = 0.1 M, [CO_3^{2-}] = 0.1 M, and T=298K (7p)

(based on numbers give at 2b)

$$\Delta G_{RXN} = \Delta G^{\circ}_{RXN} + RT \ln Q$$

$$= \Delta G^{\circ}_{RXN} + RT \ln \frac{[HS^-][CO_3^{2-}]}{[HCO_3^-][S^{2-}]}$$

$$= 19.8 \text{ kJ/mol} + 8.31 \times 298 \times \ln \frac{0.1 \times 0.1}{0.1 \times 0.1}$$

$$= 19.8 \text{ kJ/mol} + 8.31 \times 298 \times \underbrace{\ln(1)}_{= 0}$$

$$= 19.8 \text{ kJ/mol}$$

$\Rightarrow$ still < 0, non spontaneous

(for alternative answer see other page)

problem 2 b, c, d

answers based on data from tables appendix.

2b $\Delta G^\circ_{RXN} = G^\circ_f(HS^-_{aq}) + G^\circ_f(CO_3^{2-}) - G^\circ_f(HCO_3^-) - G^\circ_f(S^{2-})$

$= 12.4 \text{ kJ/mol} + (-527.8 \text{ kJ/mol}) - (-586.8 \text{ kJ/mol}) - (+83.7 \text{ kJ/mol})$

$= -12.3 \text{ kJ/mol}$

$\Delta G^\circ_{RXN} < 0 \rightarrow$ spontaneous reaction.

2c $\Delta G^\circ_{RXN} = -RT \ln K \Leftrightarrow K = e^{-\Delta G^\circ_{RXN}/RT}$

$= e^{(12.3 \cdot 10^3 / 8.31 \times 298)}$

$= \underline{\underline{1.4 \cdot 10^2}}$

2d $\Delta G_{RXN} = \Delta G^\circ_{RXN} + RT \ln Q$ (see also other answer to 2d)

$\ln Q = \ln \dfrac{[HS^-][CO_3^{2-}]}{[HCO_3^-][S^{2-}]}$

$= \ln \dfrac{0.1 \times 0.1}{0.1 \times 0.1} = \ln(1) = 0$

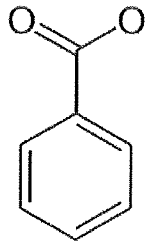
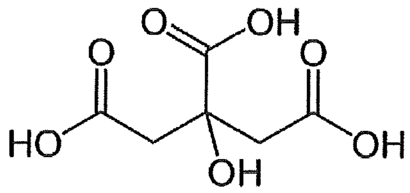
$\Rightarrow \Delta G_{RXN} = \Delta G^\circ_{RXN}$

$= -12.3 \text{ kJ/mol}$

$\rightarrow$ spontaneous reaction

Problem 3 (max 25 points) acid-base

Benzoic acid (E210) and citric acid (E330) are common food preservatives, but suffer from the drawback that they cause the food to taste slightly acidic. The acid ionisation constants are K_a= 6.5 10^{-5} for benzoic acid, and K_{a1} = 7.4 10^{-4}, K_{a2} = 1.7 10^{-5}, and K_{a3} = 4.0 10^{-7} for citric acid.

H-BA =   = H_3C.

E210 E330

(a) Give the balanced acid ionisation reactions belonging to these acid ionisation constants.

E210: (a) $HBA + H_2O \rightleftharpoons BA^- + H_3O^+$ K_a

E330: (a1) $H_3C + H_2O \rightleftharpoons H_2C^- + H_3O^+$ K_{a1}

(a2) $H_2C + H_2O \rightleftharpoons HC^{2-} + H_3O^+$ K_{a2}

(a3) $HC^{2-} + H_2O \rightleftharpoons C^{3-} + H_3O^+$ K_{a3}

(b) Which of a 0.1 M aqueous solution of each compound E210 or E330 is most acidic? What happens to the pH of the solutions upon dilution with an equal volume of water? Explain your answer by using the relevant equilibrium equations.

~~E330 is~~ ~~A~~ 0.1 M solution of E330 is more acidic than a 0.1 M solution of E210 because $K_{a1}(E330) > K_a(E210)$. Therefore, equilibrium (a1) of probl. 3a is shifted ~~more~~, to the right than equilibrium (a) of prob. 3a and thus has a higher $[H_3O^+]$.

Upon dilution with an equal amount of water all equilibria are distorted to the ~~r~~ left, and will restore by a shift to the right. However they will not reach the same ~~levels of~~ concentrations of products at the right as before addition of water, and hence the final pH will be higher

(c) Calculate the pH of a solution of 5 g benzoic acid (E210) in 100 mL of water. Give the complete calculation and clearly indicate the assumptions you've made.

5 g benzoic acid (= HBA) $\hat{=} \frac{5\ g}{122\ g/mol}$ mol HBA in 100 ml

$$\hat{=} \frac{5}{122 \times 0.1} \frac{dm^3}{mol} = \frac{5}{122 \times 0.1} \left(\frac{mol}{dm^3}\right)$$

equilibrium

$$HBA + H_2O \rightleftharpoons BA^- + H_3O^+$$

conc: $\frac{5}{122 \times 0.1}$ $\quad 0 \quad 0$

$-x \quad x \quad x$

$\left(\frac{5}{122 \times 0.1} - x\right) \quad x \quad x$

$$K = \frac{x^2}{\left(\frac{5}{122 \times 0.1} - x\right)} = 6.5\,10^{-5}$$

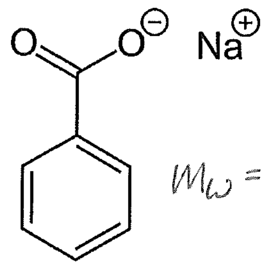
assume $x << \frac{5}{122 \times 0.1}$

$$x = \sqrt{\frac{5 \times 6.5\,10^{-5}}{122 \times 0.1}}$$

$x = 0.005$

$\Rightarrow$ pH = 2.28

(d) Also sodium benzoate (E211) is often used as a food preservative in addition to benzoic acid. Calculate the pH of the resulting solution if 5 g of sodium benzoate (E211) has been added to a solution of 5g of benzoic acid (E210) in 100 mL of water.



$M_w = 144$

$$[HBA]_0 = \frac{5}{122 \times 0.1} \qquad [BA^-]_0 = \frac{5}{144 \times 0.1}$$

$$HBA + H_2O \rightleftharpoons H_3O^+ + BA^-$$

conc: $\frac{5}{122 \times 0.1} \quad 0 \quad \frac{5}{144 \times 0.1}$

$-x \quad +x \quad +x$

$\left(\frac{5}{122 \times 0.1} - x\right) \quad x \quad \left(\frac{5}{144 \times 0.1} + x\right)$

$$K = \frac{x\left(\frac{5}{144 \times 0.1} + x\right)}{\left(\frac{5}{122 \times 0.1} - x\right)}$$

assume $x << \frac{5}{144 \cdot 0.1}$

$$\Rightarrow K = \frac{x\left(\frac{5}{144 \cdot 0.1}\right)}{\left(\frac{5}{122 \cdot 0.1}\right)} = 6.5\,10^{-5}$$

$$x = \frac{\cancel{5}}{122 \times \cancel{0.1}} \times \frac{144 \times \cancel{0.1}}{\cancel{5}} \times 6.5\,10^{-5} = 7\cancel{7}\,10^{-5}$$

$$pH = -\log[H_3O^+] = -\log(7 \cdot 10^{-5}) = 4.12$$

Problem 4 (max. 25 points) (kinetics)

Given the following exothermic chemical reaction :

$$A_2 + 2B \rightarrow 2AB$$

Compound A_2 reacts via intermediate A with compound B to product AB. Analysis of the initial rates of formation of AB ($v_{i,AB}$) for different initial concentrations of A_2 en B ($[A_2]_i$ and $[B]_i$, respectively) gives the following results:

experiment	$v_{i,AB}$ (M/s)	$[A_2]_i$ (M)	$[B]_i$ (M)
1	20	0.1	0.1
2	40	0.2	0.1
3	20	0.1	0.2
4	40	0.2	0.2

a) By using the data in the Table, give the rate equation for the formation of product AB expressed in concentrations of A_2 en B. Explain your answer.

compare exp 1 and 2 : (or exp 2 and 4) $[A_2]_i$ doubles, $[B]_i$ constant, $v_{i\,AB}$ doubles

$\rightarrow$ 1st order in $[A_2]$

compare exp 1 and 3 : (or exp 3 and 4) $[A_2]_i$ constant, $[B]_i$ doubles, $v_{i\,AB}$ constant

$\rightarrow$ zero order in $[B]$

rate equation $\frac{1}{2}\frac{d[AB]}{dt} = -\frac{d[A_2]}{dt} = k[A_2]$

or $\boxed{\frac{d[AB]}{dt} = 2k[A_2]}$

b) By using the data in the Table, calculate the reaction rate constant k for the formation of product AB. Give the complete calculation and clearly indicate the units of k.

$$\frac{d[AB]}{dt} = v_{0,AB} = 2k[A_2]_i$$

for initial rates and initial concentrations from the table, e.g. exp 1 :

$$20\left(\frac{M}{s}\right) = 2k\ 0.1\ (M)$$

$$\Leftrightarrow \quad k = \frac{20\left(\frac{M}{s}\right)}{2 \times 0.1\ (M)} = \underline{\underline{100\ (s^{-1})}}$$

c) Propose a plausible reaction scheme for the formation of AB that is consistent with the data in the Table and the rate equation for the formation of AB.

In first rate determining step dissociation of A_2 in first order reaction

$$A_2 \rightarrow 2A$$

then

$$A + B \rightarrow AB$$

d) Draw the reaction coordinate-energy diagram for the reaction of A_2 to product AB. In this reaction coordinate-energy diagram clearly indicate the following:

-reactants, intermediates, and products

-the energy of activation and the reaction enthalpy

-the rate limiting step