Name A.N. 't Woorden Student number

Test 1 for AESB1120ST

19 September 2014, from 10.45 - 12.30

On chapter 1-6, 12-17 from "Principles of Chemistry", Nivaldo Tro

- **FIRST, PLEASE READ THIS PAGE CAREFULLY**
- Please mark each page of this exam with your name and student number.
- This exam consists of 4 problems and counts 8 pages, including this cover page. Each problem consists of a number of questions.
- You will have 1 hour and 45 minutes (105 minutes) to complete this test.
- During the first 30 minutes of the test you are not allowed to leave the room.
- You will be able to score 90 points for this exam, and 10 points for marking each page of your answers to this exam with your name and student number.
- Mark Test 1 = (total number of earned points) / 10
- First, study the problem carefully and prepare your answer on scratch paper. Then, write your answer in the open space on the problems sheets.
- The problems should be answered in either dutch or english, in clear hand-written text.
- The completed exam consisting of the problem sheets with answers should be handed in. You are not allowed to keep this exam.
- The exam with the correct answers will be published on the Blackboard pages for this course the next working day following the exam.
- The results of this exam will be published on the Blackboard pages for this course on September 26.
- This exam was composed by J. van Esch and R. Eelkema.
- Mobile telephones and other communication devices should be switched off and stored out of reach.
- **Before continuing, mark each page of this exam with your name and student number.**

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Problem 1 (15 points)

The bubbling of $CO_2(g)$ through 1 L of a solution of 0.1 mM $Ca(OH)_2$ in water turns the originally clear solution into a milky white suspension. The temperature is 298K.

(a) For each of the reaction steps that occur during the above described events, give (i) the balanced reaction equation, (ii) the type of reaction (acid-base, gas evolution, redox, or precipitation reaction), and (iii) the expression for the equilibrium constant in terms of the concentrations of reactants and products. (9pt).

1. (1) $CO_{2(g)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(aq)}$ REVERSE GAS EVOLUTION (1)

2. (1) $H_2CO_{3(aq)} + 2\,OH^-_{(aq)} \rightleftarrows CO_3^{2-}{}_{(aq)} + 2\,H_2O_{(l)}$ ACID-BASE (1)

3. (1) $CO_3^{2-}{}_{(aq)} + Ca^{2+}{}_{(aq)} \rightleftarrows CaCO_{3(s)}$ PRECIPITATION (1)

$K = \dfrac{[H_2CO_3]}{[CO_2]}$ (1) $\quad K = \dfrac{[CO_3^{2-}]}{[H_2CO_3]\cdot[OH^-]^2}$ (1) $\quad K = \dfrac{1}{[CO_3^{2-}][Ca^{2+}]}$ (1)

(b) Calculate how much (in Liters) of $CO_2(g)$ at least, one has to bubble through the solution before a precipitate starts to form and the solution becomes milky (6 pts).

$K_s = 4{,}96\cdot10^{-9}$ $\quad CaCO_{3(s)} \rightleftarrows Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

(1) $[Ca^{2+}][CO_3^{2-}] = 4{,}96\cdot10^{-9}$

(1) $0{,}1\cdot10^{-3}\ A = 4{,}96\cdot10^{-9}$

(1) $A = 4{,}96\cdot10^{-5}\ M$

Assumption: Equilibrium of reaction 1 and 2 above are completely to the right

(1) $V = \dfrac{nRT}{P} = \dfrac{4{,}96\cdot10^{-5}\,\text{mol}\cdot0{,}08206\,\frac{L\cdot atm}{mol\cdot K}\cdot 298\,K}{1\ atm} = 1{,}21\cdot10^{-3}\ L$ (1)

$CO_{2(g)}$

Assumption: Standard temperature and pressure (STP)

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Problem 2 (max 25 points)

A significant amount of pure hydrogen fluoride has been spilled in a pool because of an accident in a nearby production plant.

a) Give the reaction equation and the equilibrium equation that describe the change of the pH caused by the addition of hydrogen fluoride to the water of the pool. Is the equilibrium constant for this equilibrium an acid or a base ionization constant? (6p)

(2) $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$ (2) $K_a = \frac{[H_3O^+] \cdot [F^-]}{[HF]}$

(2) Acid ionization constant

b) A total of 200 kg of pure hydrogen fluoride has been spilled into the pool, containing 1000 m³ of water. Calculate the resulting pH of the pool. (nb. the value for the molecular weight of hydrogen fluoride can be rounded of to a whole number). (10p)

$200\ kg = 2{,}00 \cdot 10^5\ g$ HF, $M_w = 20\ g/mol$ (1) $1000\ m^3 = 1{,}000 \cdot 10^6\ L$

$\frac{2{,}00 \cdot 10^5\ g}{20\ g/mol} = 1{,}0 \cdot 10^4\ mol$ HF $\quad \frac{1{,}0 \cdot 10^4\ mol}{1{,}000 \cdot 10^6\ L} = 0{,}01\ mol/L$ (1)

$K_a = 3{,}5 \cdot 10^{-4}$

(2)	$[HF]$	$\rightleftharpoons$	$[H_3O^+]$	+	$[F^-]$
I	$0{,}01$		0		0
C	$-x$		$+x$		$+x$
E	$0{,}01-x$		$+x$		$+x$

(2) $K_a = \frac{x^2}{0{,}01-x} = 3{,}5 \cdot 10^{-4}$

$x^2 - 3{,}5 \cdot 10^{-6} + 3{,}5 \cdot 10^{-4} x = 0$

a c b (2)

abc-formula $x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-3{,}5 \cdot 10^{-4} \pm \sqrt{(-3{,}5 \cdot 10^{-4})^2 - 4 \cdot 1 \cdot -3{,}5 \cdot 10^{-6}}}{2 \cdot 1}$

(1) $x = 1{,}7 \cdot 10^{-3}\ mol/L$ Only one solution is positive

(1) $pH = -\log(1{,}7 \cdot 10^{-3}) = 2{,}77$

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c) The fire brigade proposes to neutralize the water in the pool by adding more chemicals. Rank the chemicals i-iii in order of increasing suitability to neutralize the pool content. Explain your answer clearly for each chemical. (9p)

(i) $NaHSO_4$ (ii) $NaHCO_3$ (iii) $Ca(OH)_2$

(2) (i) $NaHSO_4$ $K_a = 1{,}2 \cdot 10^{-2}$ Weak acid, even weaker base

(2) (ii) $NaHCO_3$ $K_b = 1{,}7 \cdot 10^{-9}$ Weak base

(2) (iii) $Ca(OH)_2$ ~~$K_b = 1{,}7 \cdot 10^{-3}$~~ Strong base (3) Bonus: CaF_2 Precipitation

Suitability

(3) $NaHSO_4 < NaHCO_3 < Ca(OH)_2$

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Problem 3 (max 25 points) TD

Titanium dioxide is a white pigment which is used in many products ranging from tooth paste to wall paint. Titanium dioxide is usually produced by a gas-phase reaction of water with titanium tetrachloride, according to the following reaction equation:

$$TiCl_4(g) + 2H_2O(g) \leftrightarrows TiO_2(s) + 4\,HCl(g)$$

(a) Usually the reaction is carried out at 410K, which is above the boiling point of the two reactants. Verify this statement, by calculating the boiling point of titanium tetrachloride at atmospheric pressure. (8p)

(2) Boiling Point: $\Delta G_{gas} = \Delta G_{liquid}$ (2) $\Delta G = \Delta H - T\Delta S$

$H_{gas} - S_{gas} \cdot T = H_{liquid} - S_{liquid} \cdot T$ $\quad T = \dfrac{H_{gas} - H_{liquid}}{S_{gas} - S_{liquid}}$

$H_{gas} - H_{liquid} - (S_{gas} - S_{liquid}) \cdot T = 0$

(2) Correct values (2) $\dfrac{(-763{,}2 + 804{,}2) \cdot 10^3\ J/mol}{353{,}2 - 252{,}3\ J/mol \cdot K} = 406{,}3\,K$

(b) Is the above reaction exothermic or endothermic? Also for this reaction, what are the entropy changes for the system and for the surroundings? Give the appropriate calculations and explain your answer clearly. (9p)

$\Delta G = \Delta H - T\Delta S$ $\quad \Delta H < 0$ (1) Exothermic

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ (1) $\quad \Delta S_{surr} > 0$

$\Delta S_{sys} > 0$

(1) $= \Delta S_{sys} + \dfrac{-\Delta H}{T} = 162\ J/mol\,K$

$= \Delta S_{tot}$

(3) $\Delta S_{Sys} = (S_{TiO_2(g)} + 4 \cdot S_{HCl(g)}) - (S_{TiCl_4(g)} + 2 \cdot S_{H_2O(g)})$

$= (50{,}6 + 4 \cdot 186{,}9) - (363{,}2 + 2 \cdot 188{,}8) = 67{,}4\ J/mol\,K$

(3) $\Delta H = (H_{TiO_2(g)} + 4 \cdot H_{HCl(g)}) - (H_{TiCl_4(g)} + 2 \cdot H_{H_2O(g)})$

$= (-944{,}0 + 4 \cdot -92{,}3) - (-763{,}2 + 2 \cdot -241{,}8) =$

$-66{,}4$ kJ/mol

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(c) Obviously, at 410K the formation of titanium dioxide from titanium tetrachloride and water in the gas-phase is a spontaneous reaction. Is this gas-phase reaction spontaneous only at high temperatures, at low temperatures, or at all temperatures? Give the appropriate calculations and explain your answer clearly. (8p)

(2) $\Delta G = \Delta H - T\Delta S$

(2) $\Delta H < 0$ (See 3.b)

$\Delta S > 0$

(2) $\Delta G < 0$ (2) Reaction occurs spontaneous at all temperatures

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Problem 4 (max. 25 points)

Consider the following exothermic reaction:

$2A + B \rightarrow A_2 + B$

Compound A reacts in the presence of B to product A_2. An analysis of the initial rates of the formation of A_2 ($v_{A2,i}$) for different initial concentrations of A and B ($[A]_i$ and $[B]_i$, respectively) gave the following results:

Experiment	($v_{A2,i}$) (M/s)	$[A]_i$ (M)	$[B]_i$ (M)
1	20	0.1	0.1
2	80	0.2	0.1
3	40	0.1	0.2
4	160	0.2	0.2

(a) By using the data in the Table, give the rate equation for the formation of product A_2 expressed in concentrations of A en B. Explain your answer. (5p)

(1) A: Compare experiment 1 and 2 — When [A] is doubled then V_{A_2} is quadrupled. A is 2nd order

(1) B: Compare experiment 1 and 3 — When [B] is doubled then V_{A_2} is doubled. B is 1st order

$$-\frac{dA}{dt} \overset{(1)}{=} 2\frac{dA_2}{dt} = k \cdot [A]^{\overset{(2)}{2}} \cdot [B]$$

(b) Calculate the reaction rate constant k for the formation of A_2, and clearly indicate the units of k. (5p)

(1) $\text{Rate} = \frac{1}{2} \cdot k \cdot [A]^2 \cdot [B]$

$$k = \frac{2 \cdot \text{Rate}}{[A]^2 \cdot [B]} = \frac{\overset{(1)}{2} \cdot 20\ M/s}{(0.1\ M)^2 \cdot 0.1\ M} = 4{,}0 \cdot 10^{\overset{(1)}{4}}\ s^{-1} \cdot M^{\overset{(2)}{-2}}$$

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(c) What will be the rate of formation of A_2 if (explain your answers):
(i) the concentrations of all reactants are twice the concentrations in experiment 4. (3p)

(2) $Rate = \frac{1}{2} k [A]^2 [B]$

$= \frac{1}{2} k [2A_0]^2 [2B_0] = \frac{1}{2} k \cdot [A_0]^2 \cdot [B_0] \cdot 8$

(1) $8 \cdot 160 = 1280\ M/s$

(ii) when compound B is not present? (3p)

(2) $[B] = 0 \qquad Rate = \frac{1}{2} k [A]^2 [0] = 0$

(1) Reaction does not occur

(d) In the same graph, draw the Reaction Coordinate / Energy diagrams for the reaction of A to product A_2 in (i) the presence of B and (ii) in the absence of B.
In these diagrams clearly indicate the following elements: reactants, products, transition state, activation energies, reaction enthalpy. (9p)