Name:________________________________ Student Number:________________

CARLETON UNIVERSITY

Final Examination

April 2013

Marks	
Total	
A	
B1	
B2	
B3	
C1	
C2	
C3	
C4	
C5	

DURATION: 3 **HOURS** No. of Students: ________________

Department Name & Course Number: **CHEM 1002 A and V**

Instructor Bob Burk

AUTHORIZED MEMORANDA:

CALCULATOR ONLY

Students MUST count the number of pages in this examination question paper before beginning to write, and report any discrepancy immediately to a proctor. This question paper has 11 pages. This examination paper MAY NOT be taken from this examination room.

A periodic table and list of constants appears on page 12. You may tear off that page if you wish.

Part A. Answer all twelve questions with a few sentences or equations (5 marks each).

1. [5] Consider the equilibrium reaction $BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$, which is endothermic. Which direction will the reaction shift (left, right or no change) if we:

(a) Add some $BaSO_{4(s)}$ **No change** (since $BaSO_{4(s)}$ is a solid)

(b) Add some $H_2O_{(l)}$ **Right** (since $[Ba^{2+}_{(aq)}][SO_4^{2-}{}_{(aq)}]$ is a constant)

(c) Heat the mixture **Right** (heating causes a reaction to move in the endothermic direction)

(d) Add some $Na_2SO_{4(s)}$ **Left** (to reduce $[SO_4^{2-}{}_{(aq)}]$)

(e) Add some $Pb^{2+}_{(aq)}$ ($PbSO_{4(s)}$) is insoluble)

Right (to replace the $SO_4^{2-}{}_{(aq)}$ lost by precipitation of $PbSO_{4(s)}$)

2. [5] Why does adding a catalyst increase the rate of a reaction?

The presence of a catalyst allows the reaction to proceed by a different mechanism that has a lower activation energy.

3. [5] Are the entropy changes for the following processes positive, negative, or approximately zero?

(a) $2\,Na_{(s)} + F_{2(g)} \rightarrow 2\,NaF_{(s)}$	**Negative** ($\Delta n = -1$)
(b) $2\,CH_3OH_{(l)} + 3\,O_{2(g)} \rightarrow 2\,CO_{2(g)} + 4\,H_2O_{(g)}$	**Positive** ($\Delta n = +3$)
(c) $CO_{2(g)}$ at 100°C is heated to 200°C	**Positive** (ΔS is positive for heating a substance)
(d) $CO_{2(l)} \rightarrow CO_{2(s)}$	**Negative** (solids have lower entropies than liquids)
(e) $C_2H_{4(g)} + 3\,O_{2(g)} \rightarrow 2\,CO_{2(g)} + 2\,H_2O_{(g)}$	**Approximately zero** ($\Delta n = 0$)

4. Does adding 100 mL of 0.1 M $NaOH_{(aq)}$ to 100 mL of 0.1 M $HF_{(aq)}$ make a buffer? Show the relevant reactions and explain.

NaOH is a strong base and so it reacts with the weak acid HF according to:

$HF_{(aq)} + NaOH_{(aq)} \rightarrow F^{-}_{(aq)} + Na^{+}_{(aq)} + H_2O_{(l)}$. Because there is an equal number of moles of NaOH as HF, all of the HF will be destroyed, creating an equivalent amount of the $F^{-}_{(aq)}$. Since there is no weak acid remaining [3], this cannot act as a buffer [2]

5. [5] Why is $HF_{(aq)}$ a weaker acid than $HCl_{(aq)}$?

F is a more electronegative atom than Cl. This makes the H–F bond more ionic than the H–Cl bond. Ionic bonds are stronger, which makes HF a weaker acid.

6. [5] Write the reaction occurring at the anode of the electrochemical cell that has the shorthand notation:

$$Pt_{(s)}\,|\,C_2O_4^{2-}{}_{(aq)}\,|\,CO_{2(g)}\,\|\,Ag^{+}_{(aq)}\,|\,Ag_{(s)}$$

$C_2O_4^{2-} \rightarrow 2\,CO_{2(g)} + 2\,e^{-}$

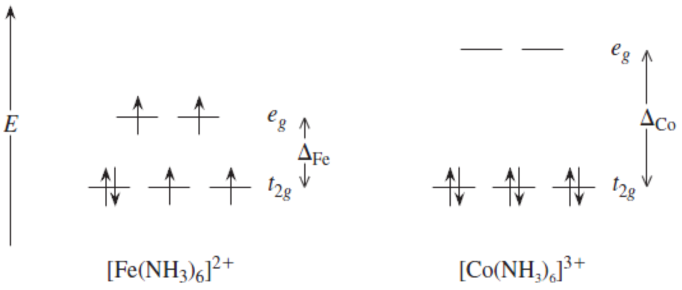
7. What functional groups must be on the monomers to make a polyester?

[5] Esters are formed by reacting alcohols with carboxylic acids, so the monomers must contain these functional groups.

8. [5] How many d–electrons are there in the following ions?

(a) Sc^{3+}	**0**
(b) V^{5+}	**0**
(c) Mn^{+}	**6**
(d) Co^{2+}	**7**
(e) Zn^{2+}	**10**

9. The crystal field splitting diagrams for $[Fe(NH_3)_6]Cl_2$ and $[Co(NH_3)_6]Cl_3$ are shown below. Which compound is yellow in water and which is green? How do you know?



Green photons are higher in energy than yellow. This means that photons of a lower energy must have been absorbed by the green compound, and this compound must have the smaller value of Δ [3]. Thus $[Fe(NH_3)_6]Cl_2$ is green and $[Co(NH_3)_6]Cl_3$ is yellow [2].

10. [5] Name five allotropes of carbon.

Any five of: Graphite, diamond, carbon nanotubes, fullerenes, nanobuds, grapheme, amorphous carbon

11. [5] Why do most stable nuclei have N/Z > 1?

Neutrons stabilize the nucleus because they experience the attractive strong nuclear force, but do not repel one another. Having fewer neutrons there makes the nucleus less stable.

12. [5] Chemical reactions are often accompanied by the release of energy. Why do we not observe a change in mass according to $\Delta E = \Delta mc^2$, in a chemical reaction?

The energies are small in chemical reactions. Although there is in fact a change in mass, it is too small to observe easily.

Part B. Answer all three questions B1, B2 and B3 (20 marks each).

B1. (a) [4] Name the four steps in radical polymerization.

- generate a radical initiator
- generate a carbon radical (“initiation”)
- propagate the carbon radical chain (“propagation”)
- terminate the chain (“termination”)

(b) [3]What is cross–linking in a polymer and why is it done?

Cross–linking is making bonds between polymer molecules. This makes the polymer stronger.

(c) [3] Name three natural polysaccharides.

Starch, cellulose, chitin, any disaccharide (e.g. fructose),…

(d) [2] How many different proteins could be made from a random sequence of 10 amino acids?

20^{10} ($= 1.024 \times 10^{13}$)

(e) [2] Fluorine gas is manufactured from molten HF•2KF. Why do we not just electrolyze $NaF_{(aq)}$?

Oxidation of $F^{-}_{(aq)}$ requires a very high and negative potential. Water is easily oxidized at a more positive potential, so this will preferentially happen in an aqueous solution.

(f) [3]Rank the following ions in increasing order of hardness and explain your answer: Al^{3+}, Tl^{+} and Tl^{3+}.

The Tl ions are the softest because they are in row 6 of the periodic table and so are much larger than the Al^{3+} ion. The softest is Tl^{+}, followed by Tl^{3+} (higher charge).

Thus Tl^{+}, Tl^{3+}, Al^{3+} from softest to hardest.

(g) [3]Will the following reaction occur? Why or why not? $5\ SF_4 + 4\ AsCl_5 \rightarrow 5\ SCl_4 + 4\ AsF_5$

S is harder than As (smaller atom)
F is harder than Cl (smaller atom)

Thus, the hardest acid and hardest base are paired up already, so no reaction occurs.

B2. (a) Name the following coordination complexes:

(i) [4] $K_2[Pb(OH)_4]$ **potassium tetrahydroxoplumbate(II)**

(ii) [4] $[Au(H_2O)_2(en)_2]Br_3$ **diaquo*bis*ethylenediaminegold(III) bromide**

(b) Write the formulas of the following coordination complexes:

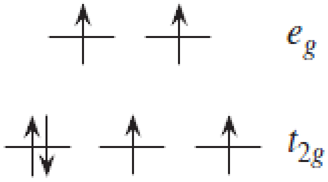
(i) [4] Tricarbonylchlorochromium(III)chloride **$[Cr(CO)_3Cl]Cl_2$**

(ii) [4] Potassium chlorooxalatoiodoargentate(I) **$K_3[AgCl(C_2O_4)I]$**

(c) [4] The spectrochemical series is: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< NO_2^- < CN^- < CO$. Draw the crystal field diagram for the $[Co(Cl)_6]^{3-}$ ion and explain why this ion is paramagnetic.

The Co in this complex is Co^{3+}. Co has the electronic configuration …s^2d^7. Co^{3+} is therefore a d^6 ion.

Chloride is near the lower end of the spectrochemical series. This suggests that the value of Δ, the crystal field splitting energy, is small. Electrons can therefore be placed into the e_g level using less energy than what is required to pair them up in the t_{2g} level. This results in unpaired electrons as shown below, which leads to paramagnetism.



B3. (a) Balance the following nuclear reactions by filling in the blanks:

[2] $^{235}_{92}\mathrm{U} + \mathrm{n} \rightarrow {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} +$ ________________ $^{141}_{56}\mathrm{Ba}$

[2] $^{15}_{8}\mathrm{O} \rightarrow \beta^{+} +$ ________________ $^{15}_{7}\mathrm{N}$

[2] $^{246}_{98}\mathrm{Cf}$ ______________ $\rightarrow \alpha + {}^{242}_{96}\mathrm{Cm}$

(b) [8]Calculate the energy released (kJ mol^{-1}) by the reaction $^{250}_{98}\mathrm{Cf} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{246}_{96}\mathrm{Cm}$. The masses of the nuclei (in amu) are ^{250}Cf 250.0766; ^{4}He 4.0026; ^{246}Cm 246.0674

$$\begin{aligned}\Delta m &= m({}^{4}_{2}\mathrm{He}) + m({}^{246}_{96}\mathrm{Cm}) - m({}^{250}_{98}\mathrm{Cm})\\ &= 4.0026 + 246.0674 - 250.0766\\ &= -0.0066\ \mathrm{amu}\\ &= -0.0066\ \mathrm{g\ mol^{-1}}\\ &= -6.6\times10^{-6}\ \mathrm{kg\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta E &= \Delta mc^{2}\\ &= (-6.6\times10^{-6}\ \mathrm{kg\ mol^{-1}})(3.00\times10^{8}\ \mathrm{m\ s^{-1}})^{2}\\ &= -5.94\times10^{11}\ \mathrm{J\ mol^{-1}}\\ &= -5.94\times10^{8}\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

(or 5.94 × 10^{8} kJ mol^{-1} released)

(c) [6] The ratio of $\dfrac{^{40}\mathrm{K}}{\mathrm{Total\ K}}$ in a rock sample is found to be 0.15 times that of potassium in the environment. The half–life of ^{40}K is 1.26 × 10^{9} y. How old is the rock?

$$\ln\frac{[^{40}\mathrm{K}]}{[\mathrm{Total\ K}]} = -kt$$

$$\begin{aligned}t &= \frac{1}{k}\ln\frac{[\mathrm{Total\ K}]}{[^{40}\mathrm{K}]}\\ &= \frac{t_{1/2}}{0.693}\ln\frac{[\mathrm{Total\ K}]}{[^{40}\mathrm{K}]}\\ &= \frac{1.26\times10^{9}\ \mathrm{y}}{0.693}\ln\frac{1}{0.15}\\ &= 3.4\times10^{9}\ \mathrm{y}\end{aligned}$$

Part C. Answer any three of the five questions C1 – C5. If you answer more than three, the best three will be used to calculate your mark (20 marks each).

C1. (a) [12] A certain reaction has an activation energy of 44.00 kJ/mol. At what temperature (in °C) will the reaction proceed 3.00 times faster than it did at 88°C?

88.0°C = 88.0 + 273.1 = 361.1 K. Let the higher temperature be T_2.

$$k_{361.1} = Ae^{\frac{-E_a}{R(361.1K)}}$$

$$k_{T_2} = Ae^{\frac{-E_a}{RT_2}}$$

$$\frac{k_{T_2}}{k_{361.1}} = 3.00 = \frac{Ae^{\frac{-E_a}{RT_2}}}{Ae^{\frac{-E_a}{R(361.1K)}}} = \frac{e^{\frac{-E_a}{RT_2}}}{e^{\frac{-E_a}{R(361.1K)}}} = e^{\frac{E_a}{R(361.1K)} - \frac{E_a}{RT_2}}$$

$$\text{thus, } \ln(3.00) = \frac{E_a}{R(361.1K)} - \frac{E_a}{RT_2}$$

$$\frac{R}{E_a}\ln(3.00) = \left(\frac{1}{361.1\,K} - \frac{1}{T_2}\right)$$

$$\frac{1}{T_2} = \frac{1}{361.1\,K} - \frac{R}{E_a}\ln(3.00)$$

$$T_2 = \left(\frac{1}{361.1\,K} - \frac{R}{E_a}\ln(3.00)\right)^{-1} = \left(\frac{1}{361.1\,K} - \frac{8.314\,J\,K^{-1}mol^{-1}}{44,000\,J\,mol^{-1}}\ln(3.00)\right)^{-1}$$

$$= 390.4\,K$$

$$= 117.2^{\circ}C$$

(b) [8] The rate constant for the reaction A → products is 0.360 $M^{-1}s^{-1}$ at 300 °C. How long (in seconds) would it take for the concentration of A to decrease from 0.690 M to 0.200 M?

Looking at the units of the rate constant, we see that this is a second order reaction. Thus,

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

$$t = \frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right)$$

$$= \frac{1}{0.360\,M^{-1}s^{-1}}\left(\frac{1}{0.200\,M} - \frac{1}{0.690\,M}\right)$$

$$= 9.86\,s$$

C2. (a) [10] A liquid has a vapour pressure of 1.23×10^4 Pa at 23.0°C and 3.01×10^4 Pa at 45.0°C.

Calculate the enthalpy of vapourization of the liquid (kJ/mol).

$$\ln(p_2) = \ln(p_1) + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{thus } \Delta H_{vap} = \frac{R\ln\left(\frac{p_2}{p_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$= \frac{8.314\ \text{J K}^{-1}\text{mol}^{-1}\ln\left(\frac{3.01\times10^4\ \text{Pa}}{1.23\times10^4\ \text{Pa}}\right)}{\left(\frac{1}{296.1\ \text{K}} - \frac{1}{318.1\ \text{K}}\right)}$$

$$= 3.19\times10^4\ \text{J mol}^{-1}$$

$$= 31.9\ \text{kJ mol}^{-1}$$

(b) [10] Calculate the boiling point of the liquid (°C).

The liquid boils when the vapour pressure becomes 1 atm (= 1.01325×10^5 Pa).

Thus, $p_2 = 1.01325 \times 10^5$ Pa at T_b. We can use either of the other two points, say $T_1 = 296.1$ K and $p_1 = 1.23\times 10^4$ Pa:

$$\ln(p_2) = \ln(p_1) + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{1.01\times10^5\ \text{Pa}}{1.23\times10^4\ \text{Pa}}\right) = \frac{31900\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{296.1\ \text{K}} - \frac{1}{T_b}\right)$$

$$\frac{\ln\left(\frac{1.01\times10^5\ \text{Pa}}{1.23\times10^4\ \text{Pa}}\right)}{\frac{31900\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}} = \left(\frac{1}{296.1\ \text{K}} - \frac{1}{T_b}\right)$$

$$T_b = \left(\frac{1}{296.1\ \text{K}} - \frac{\ln\left(\frac{1.01\times10^5\ \text{Pa}}{1.23\times10^4\ \text{Pa}}\right)}{\frac{31900\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}}\right)^{-1}$$

$$= 353.5\ \text{K}$$

$$= 80.4^{\circ}\text{C}$$

C3. (a) [12] Benzoic acid (C_6H_5COOH) has $K_a = 6.3 \times 10^{-5}$. Calculate the concentration of this acid in water that will give a pH of 4.55.

$$C_6H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5COO^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

If pH = 4.55, then $[H_3O^+{}_{(aq)}] = 10^{-4.55} = 2.82 \times 10^{-5}$ M. Thus $[C_6H_5COO^-{}_{(aq)}] = 2.82 \times 10^{-5}$ M also.

$$\frac{[C_6H_5COO^-_{(aq)}][H_3O^+_{(aq)}]}{[C_6H_5COOH]} = 6.3\times10^{-5}$$

"Concentration of this acid" means how much of it we dissolve in water, not how much of it remains at equilibrium. First we find its equilibrium concentration:

$$\frac{(2.82\times10^{-5})^2}{[C_6H_5COOH]-2.82\times10^{-5}} = 6.3\times10^{-5}$$

$$6.3\times10^{-5}([C_6H_5COOH]-2.82\times10^{-5}) = (2.82\times10^{-5})^2$$

$$6.3\times10^{-5}[C_6H_5COOH]-1.78\times10^{-9} = 7.95\times10^{-10}$$

$$[C_6H_5COOH] = \frac{7.95\times10^{-10}+1.78\times10^{-9}}{6.3\times10^{-5}}$$

$$= 4.09\times10^{-5}\,\mathrm{M}$$

How much was originally dissolved in water must therefore be $4.09 \times 10^{-5} + 2.82 \times 10^{-5} = 6.91 \times 10^{-5}$ M

(b) [8] A solution is made by adding 100 g of sodium benzoate ($C_6H_5COONa_{(s)}$) to 500 mL of 1 M benzoic acid. Calculate the pH of this solution. Assume the total volume is 500 mL.

$[C_6H_5COOH] = 1.00$ M

$$n_{C_6H_5COO^-_{(aq)}} = n_{C_6H_5COOH_{(aq)}} = \frac{100\ \mathrm{g}}{144\ \mathrm{g\ mol^{-1}}} = 0.694\ \mathrm{mol}$$

$$[C_6H_5COO^-_{(aq)}] = \frac{0.694\ \mathrm{mol}}{0.500\ \mathrm{L}} = 1.38\ \mathrm{M}$$

$pK_a = -\log_{10}(K_a) = -\log_{10}(6.3 \times 10^{-5}) = 4.20$

$$\mathrm{pH} = \mathrm{p}K_a - \log_{10}\left(\frac{[C_6H_5COOH_{(aq)}]}{[C_6H_5COO^-_{(aq)}]}\right)$$

$$= 4.20 - \log_{10}\left(\frac{1.00\ \mathrm{M}}{1.38\ \mathrm{M}}\right)$$

$$= 4.34$$

C4. An electrochemical cell having the following shorthand notation is constructed:

$$Cu_{(s)} \mid CuI_{(s)} \mid I^{-}_{(aq)} \parallel Cl^{-}_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)}$$

Standard reduction potentials are:

$CuI_{(s)} + e^{-} \rightarrow Cu_{(s)} + I^{-}_{(aq)}$ $E^{o} = –0.185$ V
$AgCl_{(s)} + e^{-} \rightarrow Ag_{(s)} + Cl^{-}_{(aq)}$ $E^{o} = 0.222$ V

(a) [6] Determine the overall cell reaction and the standard cell potential.

From the shorthand notation, we know that the $Cu_{(s)}$ must be getting oxidized to $CuI_{(s)}$. The reactions must therefore be:

Oxidation: $Cu_{(s)} + I^{-}_{(aq)} \rightarrow CuI_{(s)} + e^{-}$ $E^{o} = 0.185$ V
Reduction: $AgCl_{(s)} + e^{-} \rightarrow Ag_{(s)} + Cl^{-}_{(aq)}$ $E^{o} = 0.222$ V

Overall: $Cu_{(s)} + I^{-}_{(aq)} + AgCl_{(s)} \rightarrow CuI_{(s)} + Ag_{(s)} + Cl^{-}_{(aq)}$ $E^{o}_{cell} = 0.407$ V

(b) [8] Calculate the cell potential at 50°C if $[Cl^{-}_{(aq)}] = 0.220$ M and $[I^{-}_{(aq)}] = 0.440$ M.

$$Q = \frac{[Cl^{-}_{(aq)}]}{[I^{-}_{(aq)}]} = \frac{0.220\text{ M}}{0.440\text{ M}} = 0.500$$

$$E = E^{o} - \frac{RT}{nF}\ln(Q)$$

$$= 0.407\text{ V} - \frac{8.314\text{ J K}^{-1}\text{mol}^{-1}(50+273.1)\text{K}}{1(96487\text{ C mol}^{-1})}\ln(0.500)$$

$$= 0.426\text{ V}$$

(c) [6] If this cell was used as a battery, for how long (in hours) could it produce a current of 1.00 A if we begin with 1.00 mol of $Cu_{(s)}$ and limitless $I^{-}_{(aq)}$ and $AgCl_{(s)}$?

n = 1, since this is a one electron process.

$$it = nF$$

$$t = \frac{nF}{i} = \frac{1\text{ mol}(96487\text{ C mol}^{-1})}{1.00\text{ A}} = 96487\text{ s} = 26.8\text{ h}$$

C5. [20] For the reaction $H_{2(g)} + Se_{(s)} \rightleftharpoons H_2Se_{(g)}$, the following data are given:

	$H_{2(g)}$	$Se_{(s)}$	$H_2Se_{(g)}$
ΔH^o_f (kJ mol^{-1})			29.7
S^o (J K^{-1} mol^{-1})	130.7	42.4	219.0

Calculate the equilibrium partial pressures of $H_{2(g)}$ and $H_2Se_{(g)}$ (in bar) at 100°C if vessel is filled with 100 bar $H_{2(g)}$ (measured at 100°C) and excess $Se_{(s)}$. Assume the $Se_{(s)}$ occupies a negligible volume.

To solve this we need an equilibrium constant for the reaction:

$$\Delta H^o = \Delta H^o_f(H_2Se_{(s)}) - \Delta H^o_f(H_{2(g)}) - \Delta H^o_f(Se_{(s)}) = 29.7 - 0 - 0 = 29.7 \text{ kJ mol}^{-1}$$

$$\Delta S^o = S^o(H_2Se_{(s)}) - S^o(H_{2(g)}) - S^o(Se_{(s)}) = 219.0 - 130.7 - 42.4 = 45.9 \text{ J K}^{-1}\text{mol}^{-1}$$

Assuming that ΔH^o and ΔS^o do not vary with temperature, we can calculate the free energy change at 100°C:

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

$$= 29700 \text{ J mol}^{-1} - (100 + 273.1)\text{K}(45.9 \text{ J K}^{-1}\text{mol}^{-1}) \quad [6]$$

$$= 12910 \text{ J mol}^{-1}$$

From which we get the equilibrium constant:

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

$$= e^{\frac{-(12910 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(100+273.1)K}} \quad [6]$$

$$= 0.0156$$

	$H_{2(g)}$	$H_2Se_{(g)}$
Initial, bar	100	0
Change, bar	–x	+x
Equilibrium, bar	100 – x	x

$$K = \frac{p_{H_2Se}}{p_{H_2}} = \frac{x}{100 - x} = 0.0156$$

$$0.0156(100 - x) = x$$

$$1.56 - 0.0156x = x$$

$$1.56 = 1.0156x$$

$$x = \frac{1.56}{1.0156} = 1.54 \text{ bar}$$

Thus at equilibrium, p_{H2Se} = 1.54 bar and p_{H2} = 100–x = 98.5 bar [8]