

## General Equilibrium Problems

1983

a) two points

$$n = 3.509 \text{ g} \div 135.0 \text{ g/mol}$$

$$P = (nRT) / V$$

$$= [(0.02600 \text{ mol}) (0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1}) (375 \text{ K})] / 1.00 \text{ L}$$

$$P = 0.800 \text{ atm}$$

b) three points

$$P_{\text{SO}_2\text{Cl}_2} = 0.800 \text{ atm} - y \text{ atm}$$

$$P_{\text{SO}_2} = P_{\text{Cl}_2} = y \text{ atm}$$

$$P_{\text{tot}} = P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2}$$

$$1.43 \text{ atm} = 0.800 \text{ atm} - y + y + y \text{ (by substitution)}$$

$$P_{\text{SO}_2} = P_{\text{Cl}_2} = y = 0.63 \text{ atm}$$

$$P_{\text{SO}_2\text{Cl}_2} = 0.800 - 0.63 = 0.17 \text{ atm}$$

c) three points

$$K_p = (P_{\text{SO}_2} \times P_{\text{Cl}_2}) / P_{\text{SO}_2\text{Cl}_2}$$

$$K_p = (0.63 \text{ atm})^2 / 0.17 \text{ atm}$$

$$K_p = 2.3 \text{ atm}$$

Alternative approach in (b) and (c) is to determine the number of moles of each species, then molarity, and finally  $K_c$ .

$$n_{\text{SO}_2\text{Cl}_2} = 0.0260 - z$$

$$n_{\text{SO}_2} = n_{\text{Cl}_2} = z \text{ mol}$$

$$n_{\text{tot}} = n_{\text{SO}_2\text{Cl}_2} + n_{\text{SO}_2} + n_{\text{Cl}_2}$$

$$n_{\text{tot}} = PV / RT = (1.43 \text{ atm} \times 1.00 \text{ L}) / (0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 375 \text{ K})$$

$$n_{\text{tot}} = 0.0465 \text{ mol} = 0.0260 - z + z + z$$

$$n_{\text{Cl}_2} = n_{\text{SO}_2} = z = 0.0205 \text{ mol}$$

$$n_{\text{SO}_2\text{Cl}_2} = 0.0260 - 0.0205 = 0.00550 \text{ mol}$$

$$K_c = ([\text{SO}_2] [\text{Cl}_2]) / [\text{SO}_2\text{Cl}_2]$$

$$K_c = [0.0205]^2 / [0.0055]$$

$$K_c = 0.076 \text{ M}$$

d) one point

An endothermic process absorbs heat during dissociation so  $K_{500} > K_{375}$  or a stress is placed upon the system and  $K$  increases in order to remove the stress.

A maximum of 1 point was deducted for math for unit errors or for reporting an unreasonable number of significant figures. This same procedure was also used for Problems 2 and 3.

1988

Average score = 4.95

a) four points

$$(1) 89.7 \text{ g SbCl}_5 / 299.0 \text{ g mole} = 0.300 \text{ mole SbCl}_5$$

$$[\text{SbCl}_5] \text{ initial} = 0.300 \text{ mole} / 15.0 \text{ liter} = 0.0200 \text{ M}$$

$$(2) T = 182 \text{ }^\circ\text{C} + 273 = 455 \text{ K}$$

$$P = nRT / V = [(0.300 \text{ mole}) (0.0821 \text{ L atm}) (455 \text{ K})] / [(15.0 \text{ L}) (\text{mole K})] = 0.747 \text{ atm}$$

OR

$$(15.0 \text{ L} / 0.300 \text{ mol}) \times (273 \text{ K} / 455 \text{ K}) = 30.0 \text{ L} / \text{mol} \text{ (at std. temperature)}$$

$$1 \text{ atm} \times [(22.4 \text{ L} / \text{mol}) \div (30.0 \text{ L} / \text{mol})] = 0.747 \text{ atm}$$

b) three points

Equilibrium concentrations:

$$[\text{SbCl}_3] = [\text{Cl}_2] = (0.0200 \text{ mol} / \text{L}) \times 0.292 = 5.84 \times 10^{-3} \text{ M}$$

$$[\text{SbCl}_5] = (0.0200 \text{ mol L}) \times 0.708 \text{ L} = 1.42 \times 10^{-2} \text{ M}$$

$$K_c = ([\text{SbCl}_3][\text{Cl}_2]) \div [\text{SbCl}_5] = (5.84 \times 10^{-3})^2 \div (1.42 \times 10^{-2}) = 2.41 \times 10^{-3}$$

OR

Equilibrium pressures:

$$P_{\text{SbCl}_3} = P_{\text{Cl}_2}$$

$$= 0.747 \text{ atm} \times 0.292 = 0.218 \text{ atm}$$

$$P_{\text{SbCl}_5} = 0.747 \text{ atm} \times 0.708 = 0.529 \text{ atm}$$

$$K_p = (P_{\text{SbCl}_3} \times P_{\text{Cl}_2}) \div P_{\text{SbCl}_5} = (0.218)^2 \div 0.529 = 8.98 \times 10^{-2}$$

c) two points

$$K = ([\text{SbCl}_3][\text{Cl}_2]) / [\text{SbCl}_5] = 0.117$$

Equilibrium concentrations:

$$[\text{SbCl}_5] = (1.00 - 0.70) \text{ mol} / 2.00 \text{ L} = 0.15 \text{ M}$$

$$[\text{SbCl}_3] = 0.700 \text{ mole} / 2.00 \text{ L} = 0.350 \text{ M}$$

$$[\text{Cl}_2] = x$$

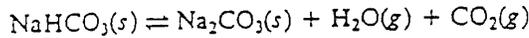
$$K_c = [(0.350)(x)] \div (0.15) = 0.117$$

$$x = [\text{Cl}_2] = 0.50 \text{ M}$$

$$\text{Moles Cl}_2 \text{ at equilibrium} = 0.050 \text{ mol L} \times 2.00 \text{ L} = 0.10 \text{ mol}$$

$$\text{Moles Cl}_2 \text{ needed to make } 0.300 \text{ mol SbCl}_3 \text{ into SbCl}_5 = 0.30 \text{ mol}$$

$$\text{Moles Cl}_2 \text{ that must be added} = 0.40 \text{ mol}$$



1.

Solid sodium hydrogen carbonate,  $\text{NaHCO}_3$ , decomposes on heating according to the equation above.

- (a) A sample of 100. grams of solid  $\text{NaHCO}_3$  was placed in a previously evacuated rigid 5.00-liter container and heated to  $160.^\circ\text{C}$ . Some of the original solid remained and the total pressure in the container was 7.76 atmospheres when equilibrium was reached. Calculate the number of moles of  $\text{H}_2\text{O}(g)$  present at equilibrium.
- (b) How many grams of the original solid remain in the container under the conditions described in (a)?
- (c) Write the equilibrium expression for the equilibrium constant,  $K_p$ , and calculate its value for the reaction under the conditions in (a).
- (d) If 110. grams of solid  $\text{NaHCO}_3$  had been placed in the 5.00-liter container and heated to  $160.^\circ\text{C}$ , what would the total pressure have been at equilibrium? Explain.

1 (ca)  $PV = nRT$  [1] Substitution of T  
[1] Substitution of P, V, R and n  
 (3 pts)  $n_{\text{gas}} = \frac{(7.76 \text{ atm})(5.00 \text{ L})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(433 \text{ K})}$

$n_{\text{gas}} = 1.09 \text{ mol}$   
 $\text{mol H}_2\text{O} = \frac{1}{2}(1.09 \text{ mol}) = 0.545 \text{ mol H}_2\text{O}(g)$  [1]  $\frac{1}{2}$  of moles gas

(b)  $\text{mol NaHCO}_3 \text{ decomposed} = 0.545 \text{ mol H}_2\text{O}(g) \times \frac{2 \text{ mol NaHCO}_3}{1 \text{ mol H}_2\text{O}(g)}$  [1] Processing of answer in (a)  
 $= 1.09 \text{ mol NaHCO}_3$  mass  
 (2 pts)  $\text{mass NaHCO}_3 \text{ decomposed} = 1.09 \text{ mol NaHCO}_3 \times \frac{84.01 \text{ g NaHCO}_3}{\text{mol NaHCO}_3}$   
 $= 91.6 \text{ g NaHCO}_3$

$\text{mass NaHCO}_3 \text{ remain} = 100. \text{ g} - 91.6 \text{ g} = 8.4 \text{ g}$  [1] By Difference

OR  $\text{mass solid remains} = 100. \text{ g} - (0.545 \text{ mol H}_2\text{O} \times \frac{18.0 \text{ g}}{\text{mol}} + 0.545 \text{ mol CO}_2 \times \frac{44.0 \text{ g}}{\text{mol}})$   
 $= 100. \text{ g} - 33.8 \text{ g} = 66.2 \text{ g}$

(c)  $K_p = P_{\text{H}_2\text{O}} P_{\text{CO}_2}$  [or  $K_p = (\text{H}_2\text{O})(\text{CO}_2)$  or  $K_p = [\text{H}_2\text{O}][\text{CO}_2]$ ] [1]  
 (2 pts)  $= (3.88 \text{ atm})(3.88 \text{ atm})$  [1] Equal pressures or 7.76 atm -  $P_{\text{H}_2\text{O}}$  from a calc. to equal  $P_{\text{CO}_2}$   
 $= 15.1 \text{ atm}^2$

(d) Pressure would remain at 7.76 atm. [1] Since some solid remained when 100. g was used (and there has been no temperature change), then using 110 g will not affect the equilibrium. [1]

Note: math error } -1  
 s.f. ( $\pm 3$  sf) }

## QUESTION 1

(9 pts.)

$$\begin{aligned} \text{a) } x_{\text{CO}} &= \frac{\text{moles CO}}{\text{moles (CO + CO}_2\text{ + H}_2\text{O + H}_2\text{)}} \\ &= \frac{0.55}{0.55+0.55+0.20+0.30} = \frac{0.55}{1.60} = 0.34 \text{ (or, 34\%)} \end{aligned}$$

Either  $x_{\text{CO}}$  definition as above or numerator or denominator correct (1 pt.)

Numerator, denominator, and calculation correct or fraction 11/32 (1 pt.)

Note: 1 point deducted if units included with answer

$$\text{b) } K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{(0.55)(0.55)}{(0.20)(0.30)} = 5.0$$

Correct setup and/or correct substitution (1 pt.)

Calculated answer (1 pt.)

Notes: 1 point deducted if expression(s) inverted but otherwise correct  
1 point deducted if H<sub>2</sub>O missing

$$\text{c) } K_p = K_c(RT)^{\Delta n} ; \Delta n = 0, \text{ therefore } K_p = K_c \text{ (or, } K_p = 5.0) \text{ (1 pt.)}$$

Notes: consistent  $\Delta n$  calculation is allowed  
numerical value same as part b) is allowed

$$\text{d) moles CO reacting = moles H}_2\text{O reacting = moles CO}_2\text{ formed = 0.16 mole (1 pt.)}$$

$$\begin{aligned} \text{equilibrium [ ]'s at lower } T: \quad &[\text{H}_2] = 0.36 \text{ mol/L} \\ &[\text{CO}_2] = 0.46 \text{ mol/L} \\ &[\text{H}_2\text{O}] = [\text{CO}] = 0.39 \text{ mol/L} \end{aligned}$$

$$K_c = \frac{(0.39)^2}{(0.46)(0.36)} = 0.92 \text{ (1 pt.)}$$

$$\text{e) } x = \text{number of moles that react}$$

	[H <sub>2</sub> ]	[CO <sub>2</sub> ]	[H <sub>2</sub> O]	[CO]	
Initial	0.50/3.0	0.50/3.0	0	0	
Change	-x/3.0	-x/3.0	x/3.0	x/3.0	(1 pt.)
Equilibrium	(0.50-x)/3.0	(0.50-x)/3.0	x/3.0	x/3.0	

$$\frac{x^2/9}{[(0.50-x)/3.0]^2} = 5.0 ; \quad \frac{x}{0.50-x} = 2.2 ; \quad x = 0.34 \text{ mol (1 pt.)}$$

$$[\text{CO}] = \frac{0.34 \text{ mol}}{3.0 \text{ L}} = 0.11 \text{ mol/L}$$

Notes: without final correct [CO], one point awarded if:  
all 3.0's in denominators missing, or  
all four [ ]'s substituted correctly, or  
any two [ ]'s and proper K substituted correctly

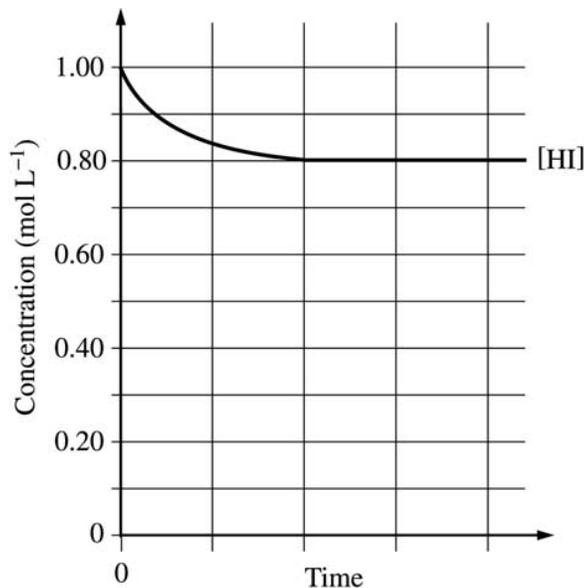
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**2003 SCORING GUIDELINES (Form B)**

**Question 1**

**Total Score 10 points**



1. After a 1.0 mole sample of  $\text{HI}(g)$  is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of  $\text{HI}(g)$  as a function of time is shown below.



- (a) Write the expression for the equilibrium constant,  $K_c$ , for the reaction.

$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$	1 point for correct expression
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- (b) What is  $[\text{HI}]$  at equilibrium?

From the graph, $[\text{HI}]_{eq}$ is 0.80 M	1 point for equilibrium $[\text{HI}]$
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**Question 1 (cont'd.)**

(c) Determine the equilibrium concentrations of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ .

$2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px 10px 2px 10px;">I</td> <td style="padding: 2px 10px 2px 10px;">1.0 M</td> <td style="padding: 2px 10px 2px 10px;">0</td> <td style="padding: 2px 10px 2px 10px;">0</td> </tr> <tr> <td style="padding: 2px 10px 2px 10px;">C</td> <td style="padding: 2px 10px 2px 10px;">-0.20 M</td> <td style="padding: 2px 10px 2px 10px;">+0.10 M</td> <td style="padding: 2px 10px 2px 10px;">+0.10 M</td> </tr> <tr> <td style="padding: 2px 10px 2px 10px;">E</td> <td style="padding: 2px 10px 2px 10px;">0.80 M</td> <td style="padding: 2px 10px 2px 10px;">0.10 M</td> <td style="padding: 2px 10px 2px 10px;">0.10 M</td> </tr> </table> <p style="text-align: center; margin-top: 5px;"><math>[\text{I}_2] = [\text{H}_2] = 0.10 \text{ M}</math></p>	I	1.0 M	0	0	C	-0.20 M	+0.10 M	+0.10 M	E	0.80 M	0.10 M	0.10 M	<p>1 point for stoichiometric relationship between HI reacting and <math>\text{H}_2(\text{g})</math> or <math>\text{I}_2(\text{g})</math> forming</p> <p>1 point for <math>[\text{H}_2]_{eq}</math> and <math>[\text{I}_2]_{eq}</math></p>
I	1.0 M	0	0										
C	-0.20 M	+0.10 M	+0.10 M										
E	0.80 M	0.10 M	0.10 M										

(d) On the graph above, make a sketch that shows how the concentration of  $\text{H}_2(\text{g})$  changes as a function of time.

<p>From the graph, <math>[\text{H}_2]_{eq}</math> is 0.10 M</p> <p>The curve should have the following characteristics:</p> <ul style="list-style-type: none"> <li>- start at 0 M;</li> <li>- increase to 0.1 M;</li> <li>- reach equilibrium at the same time [HI] reaches equilibrium</li> </ul>	<p>1 point for any two characteristics</p> <p>2 points for all three characteristics</p>
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(e) Calculate the value of the following equilibrium constants for the reaction at 700. K.

(i)  $K_c$

$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{[0.10][0.10]}{[0.80]^2} = 0.016$	<p>1 point for correct substitution (must agree with parts (b) and (c))</p>
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(ii)  $K_p$

<p><math>K_p = K_c = 0.016</math></p> <p>The number of moles on the product side is equal to the number of moles on the reactant side</p> $K_p = K_c(RT)^{\Delta n}$ $\Delta n = 2 - 2 = 0$ $K_p = K_c(RT)^0$ $K_p = K_c$	<p>1 point for <math>K_p = K_c</math> (with verification)</p>
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**Question 1 (cont'd.)**

- (f) At 1,000 K, the value of  $K_c$  for the reaction is  $2.6 \times 10^{-2}$ . In an experiment, 0.75 mole of HI(g), 0.10 mole of  $H_2(g)$ , and 0.50 mol of  $I_2(g)$  are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of HI(g) will be greater than, equal to, or less than the initial concentration of HI(g). Justify your answer.

$Q = \frac{[H_2][I_2]}{[HI]^2} = \frac{[0.10][0.50]}{[0.75]^2} = 8.9 \times 10^{-2}$ $K_c = 2.6 \times 10^{-2}$ $Q > K_c$ <p>To establish equilibrium, the numerator must decrease and the denominator must increase. Therefore, [HI] will increase.</p>	<p>1 point for calculating <math>Q</math> and comparing to <math>K_c</math></p> <p>1 point for predicting correct change in [HI]</p>
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## General Equilibrium Essay Questions

1988

Average score = 4.31

a) two points

The equilibrium pressure of  $\text{NH}_3$  gas would be unaffected  $K_p = (P_{\text{NH}_3}) (P_{\text{H}_2\text{S}})$ . Thus the amount of solid  $\text{NH}_4\text{HS}$  present does not affect the equilibrium.

b) two points

The equilibrium pressure of  $\text{NH}_3$  gas would decrease. In order for the pressure equilibrium constant,  $K_p$ , to remain constant, the equilibrium pressure of  $\text{NH}_3$  must decrease when the pressure of  $\text{H}_2\text{S}$  is increased.

$$K_p = (P_{\text{NH}_3}) (P_{\text{H}_2\text{S}})$$

(A complete explanation based on Le Chatelier's principle is also acceptable.)

c) two points

The mass of  $\text{NH}_4\text{HS}$  increases. A decrease in volume causes the pressure of each gas to increase. To maintain the value of the pressure equilibrium constant,  $K_p$ , the pressure of each of the gases must decrease. That decrease realized by the formation of more solid  $\text{NH}_4\text{HS}$ .

$$K_p = (P_{\text{NH}_3}) (P_{\text{H}_2\text{S}})$$

(A complete explanation based on Le Chatelier's principle is also acceptable.)

d) two points

The mass of  $\text{NH}_4\text{HS}$  decreases because the endothermic reaction absorbs heat and goes nearer to completion (to the right) as the temperature increases. (One point was assigned for each correct prediction and one point for each correct explanation.)

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### Question 7

(8 points)

1997

- (a)  $\Delta S^\circ$  is positive (or “+”, or “> 0”) 1 point  
 Moles products > moles reactants 1 point

Note: all species are gaseous, so (g) need not be indicated. To earn credit, number of particles (moles) must be discussed. No explanation point earned for just noting that disorder increases, or that  $\text{PCl}_5$  is decomposing or dissociating.

- (b)  $\Delta G^\circ$  will decrease (or become more negative, or become smaller). 1 point  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , and since  $\Delta S^\circ$  is positive,  $T\Delta S^\circ$  is positive (> 0).  
 Thus increasing  $T$  will result in a larger term being subtracted from  $\Delta H^\circ$ , or,  
 $\Delta G^\circ = -RT \ln K$  and  $K \uparrow$  (since  $T \uparrow$ ). } 1 point

Note: Full credit earned for part (b) if:

$\Delta S^\circ < 0$  in part (a)  $\Rightarrow \Delta G^\circ$  is increasing because  $T\Delta S^\circ$  is added to  $\Delta H^\circ$ , or,  
 $\Delta S^\circ = 0$  in part (a)  $\Rightarrow$  no change in  $\Delta G^\circ$

- (c) No change 1 point

$p_{\text{He}}$  is not part of the:  $\left. \begin{array}{l} \text{reaction (He is not involved)} \\ \text{law of mass action} \\ \text{reaction quotient} \\ \text{equilibrium constant expression} \end{array} \right\}$ , hence 1 point

altering  $p_{\text{He}}$  has no effect on the position at equilibrium.

- (d) Moles of  $\text{Cl}_2$  will decrease 1 point

The decrease in volume leads to an increase in pressure (concentration), therefore the reaction shifts to the left because:

$Q > K_p$  ( $Q > K_c$ ), or,  
 the rate of the reverse reaction increases more than the rate of the forward reaction, or,  
 the reaction shifts toward the lesser moles of gas. } 1 point

Note: “Le Châtelier’s principle” alone is not sufficient to earn explanation point. If response suggests that the number of moles of  $\text{Cl}_2$  is halved because the system is “cut” in half, only 1 point is earned.

**Question 7**  
(8 points)

1998

- (a) The number of moles of CO will decrease *1 pt*  
*because*  
adding H<sub>2</sub> will make the reaction shift to the left,  
OR, *1 pt*  
adding H<sub>2</sub> will make the reaction quotient larger than *K*, thus the  
reaction shifts to the left.
- (b) The number of moles of CO will increase *1 pt*  
*because*  
since the reaction is endothermic, addition of heat (as a reactant) will *1 pt*  
drive the reaction to the right.
- (c) The number of moles of CO will decrease *1 pt*  
*because*  
there are more moles of gas (2) on the right than on the left (1), thus *1 pt*  
decreasing the volume which increases the pressure causes the reaction  
to shift to the left.
- (d) The number of moles of CO will stay the same *1 pt*  
*because*  
Solids are not involved in the equilibrium expression  
OR *1 pt*  
solids have no effect on the equilibrium.