

ALL work must be shown to receive full credit. **Due at the beginning of lecture on Wednesday, October 31, 2001.**

- PS8.1. A 1.00 liter container initially holds 0.257 moles of NOBr at a given temperature. The reaction which occurs is:



- At equilibrium analysis shows 0.240 moles of NO and 0.120 moles of Br₂.
a) Which direction did the reaction proceed to establish (reach) equilibrium?

Reaction proceeds from left to right (L → R)

- b) How many moles of NOBr reacted in order to form 0.240 moles of NO and 0.120 moles of Br₂?

If 0.240 mol of NO are formed in the reaction, then;

$$0.240 \text{ mol NO} \left(\frac{2 \text{ mol NOBr}}{2 \text{ mol NO}} \right) = 0.240 \text{ mol NOBr reacted}$$

If 0.120 mol of Br₂ are formed in the reaction, then;

$$0.120 \text{ mol Br}_2 \left(\frac{2 \text{ mol NOBr}}{1 \text{ mol Br}_2} \right) = 0.240 \text{ mol NOBr reacted}$$

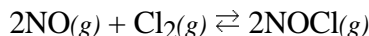
- c) How many moles of NOBr remain after equilibrium was established?

$$\begin{aligned} [\text{NOBr}]_{\text{eq}} &= [\text{NOBr}]_0 + [\text{NOBr}]_{\text{reacted}} = 0.257 \text{ M} - 0.240 \text{ M} \\ [\text{NOBr}]_{\text{eq}} &= 0.017 \text{ M} \end{aligned}$$

- d) What is the magnitude of K_c?

$$K_c = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} = \frac{[0.240]^2[0.120]}{[0.017]^2} = 23.9$$

PS8.2. In a container, the partial pressure of NOCl is initially 0.340 atm at a given temperature. The chemical equation which describes the reaction is:



At equilibrium analysis shows the partial pressure of NO is 0.0916 atm.

- a) Which direction did the reaction proceed to establish (reach) equilibrium?

Reaction proceeds from right to left (R → L)

- b) What is the partial pressure of NOCl which reacted in order for the partial pressure of NO to be 0.0916 atm?

For the partial pressure of NO to be 0.0916 atm, the amount of NOCl which must react is,

$$0.0916 \text{ atm NO} \left(\frac{2 \text{ atm NOCl}}{2 \text{ atm NO}} \right) = 0.0916 \text{ atm NOCl}$$

- c) What is the partial pressure of Cl₂ at equilibrium?

Since the initial partial pressure of Cl₂ is zero, the amount of Cl₂ formed is equal to the amount at equilibrium.

$$0.0916 \text{ atm NO} \left(\frac{1 \text{ atm Cl}_2}{2 \text{ atm NO}} \right) = 0.0458 \text{ atm Cl}_2$$

$$(P_{\text{Cl}_2})_{\text{eq}} = (P_{\text{Cl}_2})_0 + (P_{\text{Cl}_2})_{\text{forming}}$$

$$(P_{\text{Cl}_2})_{\text{eq}} = 0 + 0.0458 \text{ atm} = 0.0458 \text{ atm}$$

- d) What is the partial pressure of NOCl at equilibrium?

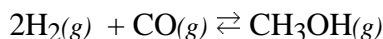
$$(P_{\text{NOCl}})_{\text{eq}} = (P_{\text{NOCl}})_0 - (P_{\text{NOCl}})_{\text{reacted}}$$

$$(P_{\text{NOCl}})_{\text{eq}} = 0.340 \text{ atm} - 0.0916 \text{ atm} = 0.248 \text{ atm}$$

- e) What is the magnitude of K_p?

$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}} \cdot P_{\text{Cl}_2}} = \frac{(0.248)^2}{(0.0916)^2(0.0458)} = 160$$

PS8.3. A 1.00 liter container holds 1.06 moles of H₂ and 1.57 moles of CO at a temperature of 162 °C. At this temperature, the following reaction occurs,



After equilibrium is established, analysis shows 0.200 moles of CH₃OH in the container. Calculate the [CO]_{eq}, [H₂]_{eq} and K_c.

	2H₂(g)	+	CO(g)	⇌	CH₃OH(g)	
Initial	1.06 M		1.57 M		0	let x = [CO] _{reacting}
Change	-2x		-x		+x	
Equilibrium	1.06 - 2x		1.57 - x		0 + x	

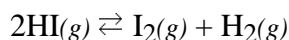
$$[\text{CH}_3\text{OH}]_{\text{eq}} = 0.200 \text{ M} = x$$

$$[\text{H}_2]_{\text{eq}} = 1.06 - 2x = 1.06 - 2(0.2 \text{ M}) = 0.660 \text{ M}$$

$$[\text{CO}]_{\text{eq}} = 1.57 - x = 1.57 - (0.2 \text{ M}) = 1.37 \text{ M}$$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2[\text{CO}]} = \frac{(0.200)}{(0.660)^2 \cdot (1.37)} = 0.335$$

PS8.4. The following reaction,



occurs at 298K. If 2.00 mol of HI are placed into a 1.00 liter container and permitted to react, at equilibrium it is found that 20.0 % of the HI has decomposed. Calculate K_c and K_p.

	2HI	⇌	H₂	+	I₂
initial	2.00		0		0
change	-2x		+x		+x
equilibrium	1.60		+.2		+.2

At equilibrium, 20% of the HI has decomposed; therefore, 0.20(2.0 M) = 0.4 M is the amount of HI that reacts.

$$0.4 \text{ M} = 2x$$

$$0.2 \text{ M} = x$$

Substituting

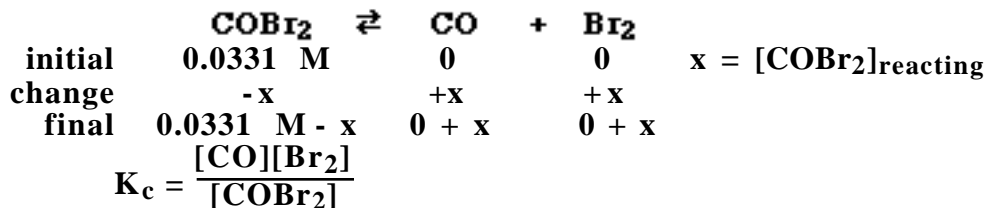
$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(.2)(.2)}{(1.6)^2} = 0.0156$$

$$K_p = K_c = .0156$$

PS8.5. A 0.622 gram quantity of COBr_2 is sealed in a glass bulb of 0.100 L volume and heated to a temperature of 73°C . At 73°C the COBr_2 partially decomposes according to the equation



for which $K_c = 0.190$. Calculate the concentration of each species at 73°C .



$$0.190 = \frac{(x)^2}{0.0331 - x}$$

rearranging

$$x^2 + 0.190x - 6.29 \times 10^{-3} = 0$$

solving the quadratic equation $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x = \frac{-0.190 \pm \sqrt{(0.190)^2 - 4(1)(-6.29 \times 10^{-3})}}{2(1)}$$

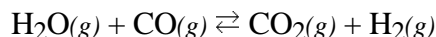
$$x = \frac{-0.190 \pm 0.248}{2}$$

Use only the positive root

$$x = 0.0288 \text{ M} \quad [\text{CO}] = [\text{Br}_2] = x = 0.0288 \text{ M}$$

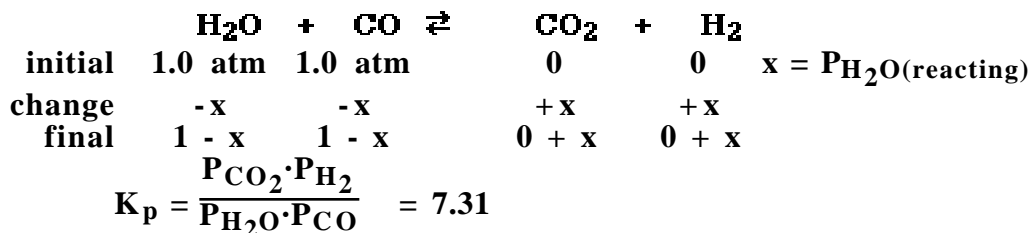
$$[\text{COBr}_2] = 0.0330 \text{ M} - x = 0.0330 \text{ M} - 0.0288 \text{ M} = 0.0042 \text{ M}$$

PS8.6. The equilibrium constant, K_p , for the reaction



is 7.31. Calculate the partial pressure of all species at equilibrium for each of the following original mixtures:

a) 1.0 atm of CO and 1.0 atm of H_2O .



$$7.31 = \frac{x^2}{(1-x)^2}$$

taking the square root of both sides

$$2.70 = \frac{x}{1.0 - x}$$

solving for x

$$x = 0.730 \text{ atm}$$

$$P_{\text{CO}_2} = P_{\text{H}_2} = x = 1.00 \text{ atm} - 0.730 \text{ atm} = 0.270 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = P_{\text{CO}} = 1 - x = 0.730 \text{ atm}$$

PS8.6. (CONTINUED)

b) 1.0 atm of CO, 1.0 atm of H₂O and 1.00 atm of H₂.

	H₂O	+	CO	⇌	CO₂	+	H₂	
initial	1.0 atm		1.0 atm		0		1.0 atm	
change	-x		-x		+x		+x	x = P _{H₂O} (reacting)
final	1 - x		1 - x		0 + x		1.0 + x	

$$K_p = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}} = 7.31$$

$$7.31 = \frac{x(1+x)}{(1-x)^2}$$

rearranging

$$6.31x^2 - 15.62x + 7.31 = 0$$

solving the quadratic equation

$$x_1 = +1.85 \text{ atm} \quad x_2 = 0.627 \text{ atm}$$

root x_1 is too large

$$P_{\text{CO}_2} = 0.627 \text{ M: } P_{\text{H}_2} = 1.0 + x = 1.627 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = P_{\text{CO}} = 1.0 - x = 0.373 \text{ atm}$$

c) 1.0 atm of H₂ and 1.0 atm of CO₂.

	H₂O	+	CO	⇌	CO₂	+	H₂	
initial	0		0		1.0 atm		1.0 atm	
change	+x		+x		-x		-x	x = P _{CO₂} (reacting)
final	+x		+x		1.0 - x		1.0 - x	

$$K_p = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}} = 7.31$$

$$7.31 = \frac{(1-x)^2}{x^2}$$

taking the square root of both sides

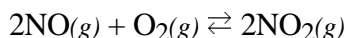
$$2.7 = \frac{(1-x)}{x}$$

$$x = 0.270 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = P_{\text{CO}} = x = 0.270 \text{ atm}$$

$$P_{\text{CO}_2} = P_{\text{H}_2} = 1 - x = 1.00 \text{ atm} - 0.270 \text{ atm} = 0.730 \text{ atm}$$

PS8.7. At 1000 K the equilibrium constant, K_c , for the reaction



is 0.833. Calculate the concentrations of all species at equilibrium when 0.200 moles of NO_2 are placed in a 2.00 L container at 1000 K.

	2NO	+	O₂	\rightleftharpoons	2NO₂	
initial	0		0		.10 M	$2x = [\text{NO}_2]_{\text{reacting}}$
change	+2x		+x		-2x	
final	0+2x		0+x		.10-2x	

$$K_c = 0.833 = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$.833 = \frac{(.10-2x)^2}{(2x)^2(x)}$$

$$.833 = \frac{(.10-2x)^2}{4x^3}$$

Oh, no! A cubic equation: it can be solved by iteration
 x must be greater than 0, but less than .050. First guess .02

Guess x	$(.10-2x)^2$	$4x^3$	Q	K	
.02	3.6×10^{-3}	3.2×10^{-5}	112	.833	1st guess too large
.040	4.0×10^{-4}	2.56×10^{-4}	1.56	.833	2nd guess too large
.045	1×10^{-4}	3.64×10^{-4}	.274	.833	2nd guess too small
.042	2.56×10^{-4}	2.96×10^{-4}	.864	.833	close enough

$$[\text{NO}_2] = .1 - 2x = .1 - 2(.042) = 0.016 \text{ M}$$

$$[\text{NO}] = 2x = 2(.042) = 0.084 \text{ M} \quad [\text{O}_2] = x = 0.042 \text{ M}$$

or

you can find the roots using your calculator (assuming it solve polynomials of order of two or greater). You will get the same answer as above, although you must choose the root.

PS8.8. The equilibrium constant, K_p , for the reaction



is 6.25 at 25 °C and $\Delta H^\circ = 34.4 \text{ kJ}$. Calculate the magnitude of the equilibrium constant at 50 °C.

$$\ln \frac{K_1}{K_2} = \frac{\Delta H_{\text{rxn}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{K_1}{6.25} = \frac{34400 \text{ J}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(\frac{1}{298 \text{ K}} - \frac{1}{323 \text{ K}} \right)$$

$$\ln \frac{K_1}{6.25} = 1.07$$

$$e^{\left(\ln \frac{K_1}{6.25} \right)} = e^{1.07}$$

$$\frac{K_1}{6.25} = 2.93 \quad K_1 = 18.3$$

PS8.9. Given the reaction



A 10.0 liter vessel at 298 K initially contains a sample of XeF₄ at 0.750 atm. After the reaction achieves equilibrium, the total pressure in the vessel is 1.95 atm. Calculate K_p from this data.

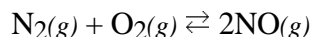
	XeF₄	⇌	Xe	+	2F₂	
initial	.750	0	0		x =	
change	-x	+x	+2x		P _{XeF₄(reacted)}	
equilibrium	.750-x	0 +x	0 + 2x			

$$\begin{aligned} \text{total pressure} &= 1.95 \text{ atm} = .750 - x + x + 2x \\ &0.60 \text{ atm} = x \end{aligned}$$

$$P_{\text{XeF}_4(\text{eq})} = .150 \text{ atm}; P_{\text{Xe}(\text{eq})} = .60 \text{ atm}; P_{\text{F}_2(\text{eq})} = 1.20 \text{ atm}$$

$$K_p = \frac{P_{\text{Xe}} \cdot P_{\text{F}_2}^2}{P_{\text{XeF}_4}} = \frac{(.6)(1.2)^2}{.150} = 5.76$$

PS8.10. The equilibrium constant, K_c, for the reaction



is 2.50×10^{-6} at a particular temperature. If the [N₂]_o = 2.00 M, the [O₂]_o = 1.00 M and the [NO]_o = 0 M, calculate the equilibrium concentration of all species.

	N₂	+	O₂	⇌	2NO	
initial	2.00 M		1.00 M		0	x = [N ₂] _{reacting}
change	-x		-x		+2x	
equilibrium	2 - x		1 - x		0 + 2x	

$$K_p = 2.5 \times 10^{-6} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(2-x)(1-x)}$$

rearranging

$$4x^2 + 7.5 \times 10^{-6}x - 5 \times 10^{-6} = 0$$

solving quadratic equation

$$x_1 = -1.12 \times 10^{-3} \text{ M}; x_2 = 1.12 \times 10^{-3} \text{ M}$$

Using the positive root $x = 1.12 \times 10^{-3} \text{ M}$

$$[\text{NO}] = 2.24 \times 10^{-3} \text{ M}; [\text{N}_2] = 2.00 \text{ M}; [\text{O}_2] = 1.00 \text{ M}$$

This problem is a lead into acid/base equilibria. The point being made in this problem is that when the magnitude of the equilibrium constant is very small, the amount reacting is very small compared to the initial amount. By making certain assumptions it will be possible to simplify this calculation eliminating the need for the quadratic equation.