

Homework 2

10. False. Equilibrium and rates of reaction (kinetics) are independent of each other. A reaction with a large equilibrium constant value may be a fast reaction or a slow reaction. The same is true for a reaction with a small equilibrium constant value. Kinetics is discussed in detail in Chapter 12 of the text.

16. No, it doesn't matter which direction the equilibrium position is reached. Both experiments will give the same equilibrium position since both experiments started with stoichiometric amounts of reactants or products.



a. $\text{HBr} \leftrightarrow \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Br}_2$ $K_p' = (P_{\text{H}_2})^{1/2} (P_{\text{Br}_2})^{1/2} / P_{\text{HBr}} = (1/K_p)^{1/2} = (1/3.5 \times 10^4)^{1/2} = 5.3 \times 10^{-3}$

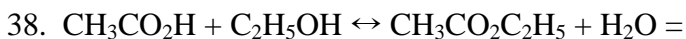
b. $2 \text{HBr} \leftrightarrow \text{H}_2 + \text{Br}_2$ $K_p'' = (P_{\text{H}_2})(P_{\text{Br}_2}) / P_{\text{HBr}}^2 = 1/K_p = 1/3.5 \times 10^4 = 2.9 \times 10^{-5}$

c. $\frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Br}_2 \leftrightarrow \text{HBr}$ $K_p''' = P_{\text{HBr}} / (P_{\text{H}_2})^{1/2} (P_{\text{Br}_2})^{1/2} = (K_p)^{1/2} = 190$

24. $K = [\text{NCl}_3]^2 / [\text{N}_2][\text{Cl}_2]^3 = (0.19)^2 / [(1.4 \cdot 10^{-3})(4.3 \cdot 10^{-4})^3] = 3.2 \cdot 10^{11}$

34. $K_p = P_{\text{H}_2}^4 / P_{\text{H}_2\text{O}}^4$; $P_{\text{tot}} = P_{\text{H}_2\text{O}} + P_{\text{H}_2}$, $36.3 \text{ torr} = 15 \text{ torr} + P_{\text{H}_2}$, $P_{\text{H}_2} = 21.3 \text{ torr}$

Since $1 \text{ atm} = 760 \text{ torr}$, $K_p = (21.3/760)^4 / (15.0/760)^4 = 4.07$



$$K = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_5\text{OH}]} = 2.2$$

a. $Q = \frac{(0.22)(0.10)}{(0.010)(0.010)} = 220 > K$; Reaction will shift left to reach equilibrium so the concentration of water will decrease

b. $Q = \frac{(0.22)(0.0020)}{(0.0020)(0.10)} = 2.2 = K$; Reaction is at equilibrium, so the concentration of water will remain the same.

c. $Q = \frac{(0.88)(0.12)}{(0.044)(6.0)} = 0.40 < K$; Since $Q < K$, the concentration of water will increase since the reaction shifts right to reach equilibrium

d. $Q = \frac{(4.4)(4.4)}{(0.88)(10.0)} = 2.2 = K$; At equilibrium, so the water concentration is unchanged

e. $K = 2.2 = \frac{(2.0)[\text{H}_2\text{O}]}{(0.10)(5.0)}$ $[\text{H}_2\text{O}] = 0.55 \text{ M}$

f. Water is a product of the reaction, but it is not the solvent. Thus, the concentration of water must be included in the equilibrium expression since it is a solute in the

reaction. Only when water is the solvent do we not include it in the equilibrium expression.



a. The initial Concentrations of H_2O and Cl_2O are:

$$1.0 \text{ g H}_2\text{O}/1.0 \text{ L} \times 1 \text{ mol}/18.02 \text{ g H}_2\text{O} = 5.5 \cdot 10^{-2} \text{ mol/L}$$

$$2.0 \text{ g Cl}_2\text{O}/1.0 \text{ L} \times 1 \text{ mol}/86.90 \text{ g Cl}_2\text{O} = 2.3 \cdot 10^{-2} \text{ mol/L}$$

	$\text{H}_2\text{O}(\text{g})$	+	Cl_2O	\leftrightarrow	$2\text{HOCl}(\text{g})$
Initial	$5.5 \cdot 10^{-2} \text{ M}$		$2.3 \cdot 10^{-2} \text{ M}$		0
	$x \text{ mol/L of H}_2\text{O reacts to reach equilibrium}$				
Change	-x		-x		+2x
Equil.	$(5.5 \cdot 10^{-2} - x) \text{ M}$		$(2.3 \cdot 10^{-2} - x) \text{ M}$		2x

$$K = 0.090 = (2x)^2/[(5.5 \cdot 10^{-2} - x)(2.3 \cdot 10^{-2} - x)] \quad \text{or}$$

$$1.14 \cdot 10^{-4} - 7.02 \cdot 10^{-3}x + 0.090 x^2 = 4x^2$$

$$3.91 x^2 + 7.02 \cdot 10^{-3} x - 1.14 \cdot 10^{-4} = 0 \quad (\text{Remember to carry extra significant figures})$$

Solving using the quadratic formula:

$$x = (-7.02 \cdot 10^{-3} \pm (4.93 \cdot 10^{-5} + 1.78 \cdot 10^{-3})^{1/2})/7.82 = 4.6 \cdot 10^{-3} \text{ or } -6.4 \cdot 10^{-3}$$

A negative answer makes no physical sense; we can't have less than nothing.

$$\text{So } x = 4.6 \cdot 10^{-3} \text{ M.}$$

$$[\text{HOCl}] = 2x = 9.2 \cdot 10^{-3} \text{ M}; [\text{Cl}_2\text{O}] = 2.3 \cdot 10^{-2} - x = 0.023 - 0.0046 = 4.6 \cdot 10^{-2} \text{ M}$$

$$[\text{H}_2\text{O}] = 5.5 \cdot 10^{-2} - x = 0.055 - 0.0046 = 5.0 \cdot 10^{-2} \text{ M}$$

	$\text{H}_2\text{O}(\text{g})$	+	Cl_2O	\leftrightarrow	$2\text{HOCl}(\text{g})$
Initial	0		0		$1.0 \text{ mol}/2.0 \text{ L} = 0.50 \text{ M}$
	$2x \text{ mol/L of HOCl reacts to reach equilibrium}$				
Change	+x		+x		-2x
Equil.	x		x		$0.50 - 2x$

$$K = 0.090 = [\text{HOCl}]^2/[\text{H}_2\text{O}][\text{Cl}_2\text{O}] = (0.50 - 2x)^2/x^2$$

The expression is a perfect square, so we can take the square root of each side:

$$0.20 = (0.50 - 2x)/x, \quad 0.30 x = 0.50 - 2x, \quad 2.30 x = 0.50$$

$$x = 0.217 \quad (\text{Remember to carry extra significant figures to the end.})$$

$$x = [\text{H}_2\text{O}] = [\text{Cl}_2\text{O}] = 0.217 = 0.22 \text{ M}, \quad [\text{HOCl}] = 0.50 - 2x = 0.50 - 0.434 = 0.07 \text{ M}$$

60. a. The moles of SO_2 will increase since the reaction will shift left to use up the added $\text{O}_2(\text{g})$.

b. Increase; Since there are fewer reactant gas molecules than product gas molecules, the reaction shifts left with a decrease in volume.

c. No effect; The partial pressures of sulfur trioxide, sulfur dioxide, and oxygen are unchanged.

d. Increase; $\text{Heat} + 2 \text{SO}_3 \leftrightarrow 2 \text{SO}_2 + \text{O}_2$; Decreasing T will remove heat, shifting the endothermic reaction to the left.

e. Decrease.

78. $\text{P}_4(\text{g}) \leftrightarrow 2 \text{P}_2(\text{g})$ $K_p = 0.200 = \frac{P_{\text{P}_2}^2}{P_{\text{P}_4}}$; $P_{\text{P}_4} + P_{\text{P}_2} = P_{\text{total}} = 1.00 \text{ atm}$, $P_{\text{P}_4} = 1.00 - P_{\text{P}_2}$

Let $y = P_{\text{P}_2}$ at equilibrium, then $y^2/(1.00 - y) = 0.100$

Solving: $y = 0.270 \text{ atm} = P_{\text{P}_2}$; $P_{\text{P}_4} = 1.00 - 0.270 = 0.73 \text{ atm}$

To solve for the fraction dissociated, we need the initial pressure of P_4 (mol \approx pressure) .

	$\text{P}_4(\text{g})$	\leftrightarrow	$2 \text{P}_2(\text{g})$	
Initial	P_0		0	$P_0 = \text{initial pressure of } \text{P}_4 \text{ in atm.}$
	$x \text{ atm of } \text{P}_4 \text{ reacts to reach equilibrium}$			
Change	$-x$	\rightarrow	$+2x$	
Equil.	$P_0 - x$		$2x$	

$P_{\text{total}} = P_0 - x + 2x = 1.00 \text{ atm} = P_0 + x$

Solving: $0.270 \text{ atm} = P_{\text{P}_2} = 2x$, $x = 0.135 \text{ atm}$; $P_0 = 1.00 - 0.135 = 0.87 \text{ atm}$

Fraction dissociation = $x/P_0 = 0.135/0.87 = 0.16$ or 16% of P_4 is dissociated to reach equilibrium.