31. Write the equilibrium expressions for the following.

(a)
$$2lCl(g) \rightleftharpoons l_2(g) + Cl_2(g)$$

(b)
$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$$

(c)
$$3O_2(g) \rightleftharpoons 2O_3(g)$$

(d)
$$2Bi^{3+}(aq) + 3 H_2S(g) \implies Bi_2S_3(s) + 6 H^+(aq)$$

(e)
$$CaCO_3(s)$$
 \longleftarrow $CaO(s) + CO_2(g)$

$$(f) \ \operatorname{CaC}_2(s) + 2\operatorname{H}_2\operatorname{O}(l) \quad \Longrightarrow \quad \operatorname{C}_2\operatorname{H}_2(g) + \operatorname{Ca}(\operatorname{OH})_2(s)$$

(g)
$$C_6H_6(l) + Br_2(l) \rightleftharpoons C_6H_5Br(l) + HBr(g)$$

(h)
$$Cu(s) + 2Ag^2(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

(i)
$$4NH_3(g) + 5 O_2(g) \iff 6 H_2O(g) + 4 NO(g)$$

(j)
$$H_2(g) + 1/2 O_2(g) \iff H_2O(l)$$

32. Write the $K_{\rm eq}$ expression for:

(a)
$$N_2O_4(g) \longrightarrow 2NO_2(g)$$
, and

(b)
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
.

Examine the relationship between the $K_{\rm eq}$ expressions for equations (a) and (b) of this question. If $K_{\rm eq}$ = 10.0 for equation (a), what would be the value of $K_{\rm eq}$ for equation (b)?

33. Write the K_{eq} expression for:

(a)
$$SO_2(g) + 1/2 O_2(g) \iff SO_3(g)$$
, and

(b)
$$2SO_2(g) + O_2(g) \iff 2SO_3(g)$$
.

Examine the which exists between the $K_{\rm eq}$ expressions for equations (a) and (b) of this question. If $K_{\rm eq}$ = 3 for equation (a), what would be the value of $K_{\rm eq}$ for equation (b)?

- 34. Which way will the equilibrium $CaCO_3(g) + CO_2(g) + H_2O(l)$ \iff $Ca^{2+}(aq) + 2 HCO_3^-(aq) + 40 kJ$ shift if
 - (a) more $CO_2(g)$ is added?
 - (b) more $CaCO_3(s)$ is added?
 - (c) $Ca^{2+}(aq)$ is removed?
 - (d) heat is added?

35. Rearrange the following equations to solve in terms of the concentrations indicated in bold.

(a)
$$\mathrm{K_{eq}} = [\mathrm{H_3O^+}]~\mathrm{[F^-]}~/~\mathrm{[HF]}$$

(b)
$$K_{eq} = [H_3O^+][F^-] / [HF]$$

(c)
$$K_{eq} = [NO_2]^2 / [NO]^2 [O_2]$$

(d)
$$K_{eq} = [NO_2]^2 / [NO]^2 [O_2]$$

(e)
$$K_{eq} = [NH_3]^2 / [N_2] [H_2]^3$$

(f)
$$K_{eq} = [N_2O_4] / [\mathbf{NO_2}]^2$$

(g)
$$K_{eq} = [NH_3]^2 / [N_2][H_2]^3$$

(h)
$$K_{eq} = [PCl_3]^4 / [P_4] [Cl_2]^6$$

- 36. Consider the following equilibria.

 - iv) $SO_2(g) + 1/2 O_2(g) \iff SO_3(g) ; K_{eq} = 110$
 - (a) Which equilibrium favours products to the greatest extent?
 - (b) Which equilibrium favours reactants to the greatest extent?

37. In the reaction $A + B \iff C + D + 100 \text{ kJ}$, what happens to the value of K_{eq} if the temperature is INCREASED?

38. If the value of K_{eq} DECREASES when the temperature DECREASES, is the reaction EXOTHERMIC or ENDOTHERMIC?

39. In the reaction $P + Q + 150 \text{ kJ} \iff R + S$, what happens to the value of K_{eq} if the temperature is DECREASED?

40. In the reaction $W + X + 100 \text{ kJ} \iff Y + Z$, what happens to the Value of K_{eq} if the [X] is INCREASED?

41. If the value of K_{eq} INCREASES when the temperature DECREASES, is the reaction EXOTHERMIC or ENDOTHERMIC?

42. In Exercises 21-23, describe the effect on Kea of the changes indicated. Write INC for increase, DEC for decrease and NC for no change.

43. In Exercise 23, assume that the bold species Sn(s) instead of $CO_2(g)$. Now redo the Exercise, describing the effect on the species in bold and the value of K_{eq} when the changes indicated occur.

44. In the equilibrium $KCl(s) + 17 \text{ kJ} \iff K^+(aq) + Cl^-(aq)$, which way will the equilibrium shift and what is the effect on the value of K_{eq} when (i) more $K^+(aq)$ is added? (ii) the temperature is decreased? (ii) more KCl(s) is added?

- 45. An equilibrium $A(aq) + 2 B(q) \implies 2 C(aq) + 2 D(aq) has K_{eq} = 0.25$ at 100°C and $K_{eq} = 0.15$ at 200°C State whether the forward reaction is endothermic or exothermic and explain why.
- 46. Examine the following graphs for the equilibrium $3O_2 \iff 2O_3$. Is the equilibrium endothermic or exothermic, as written? Explain.