Topic 5J - The Response of Equilibria to Changes in Conditions

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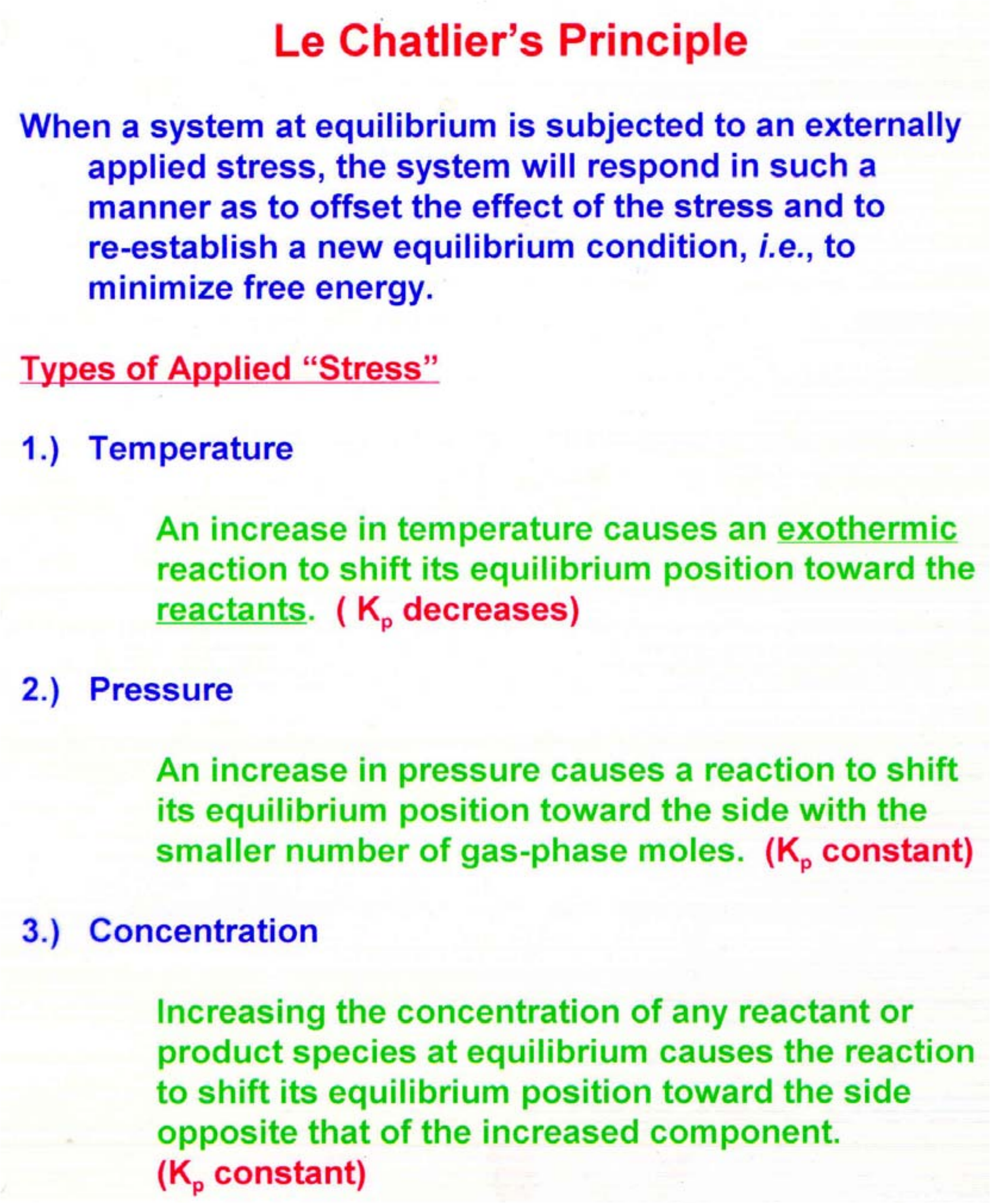


Le Chatlier's Principle

When a system at equilibrium is subjected to an externally applied stress, the system will respond in such a manner as to offset the effect of the stress and to re-establish a new equilibrium condition, *i.e.*, to minimize free energy.

Types of Applied "Stress"

1.) Temperature

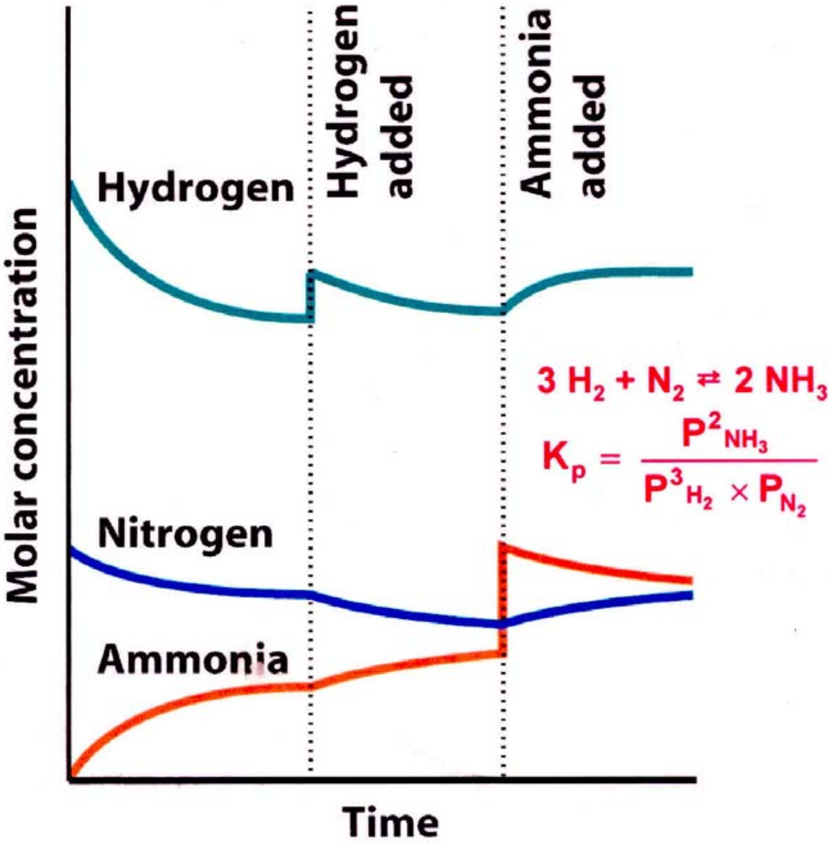
An increase in temperature causes an exothermic reaction to shift its equilibrium position toward the reactants. (K_p decreases)

2.) Pressure

An increase in pressure causes a reaction to shift its equilibrium position toward the side with the smaller number of gas-phase moles. (K_p constant)

3.) Concentration

Increasing the concentration of any reactant or product species at equilibrium causes the reaction to shift its equilibrium position toward the side opposite that of the increased component. (K_p constant)

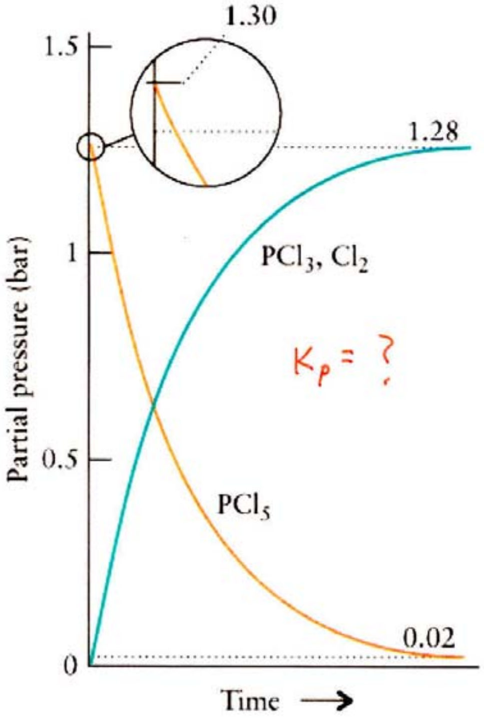


$$3\ H_2 + N_2 \rightleftarrows 2\ NH_3$$

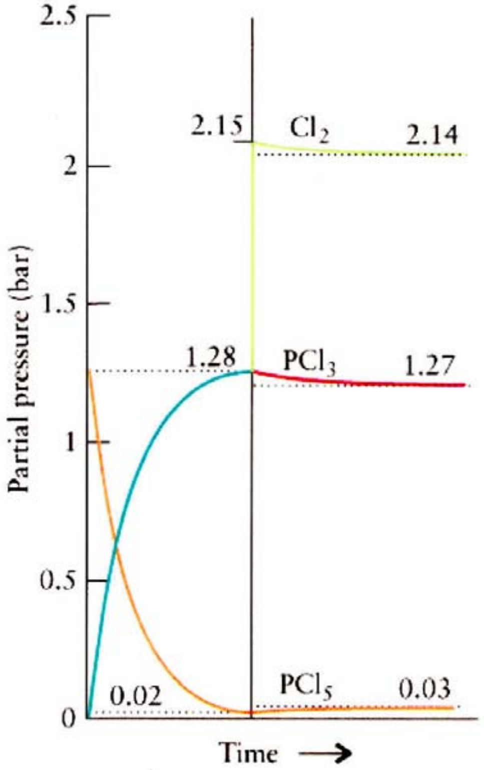
$$K_p = \frac{P^2_{NH_3}}{P^3_{H_2} \times P_{N_2}}$$

FIGURE 9.9 These graphs show the changes in composition that can be expected when additional hydrogen and then ammonia are added to an equilibrium mixture of nitrogen, hydrogen, and ammonia. Note that the addition of hydrogen results in the formation of ammonia, whereas the addition of ammonia results in the decomposition of some of the added ammonia as reactants are formed. In each case, the mixture settles into a composition in accord with the equilibrium constant of the reaction.

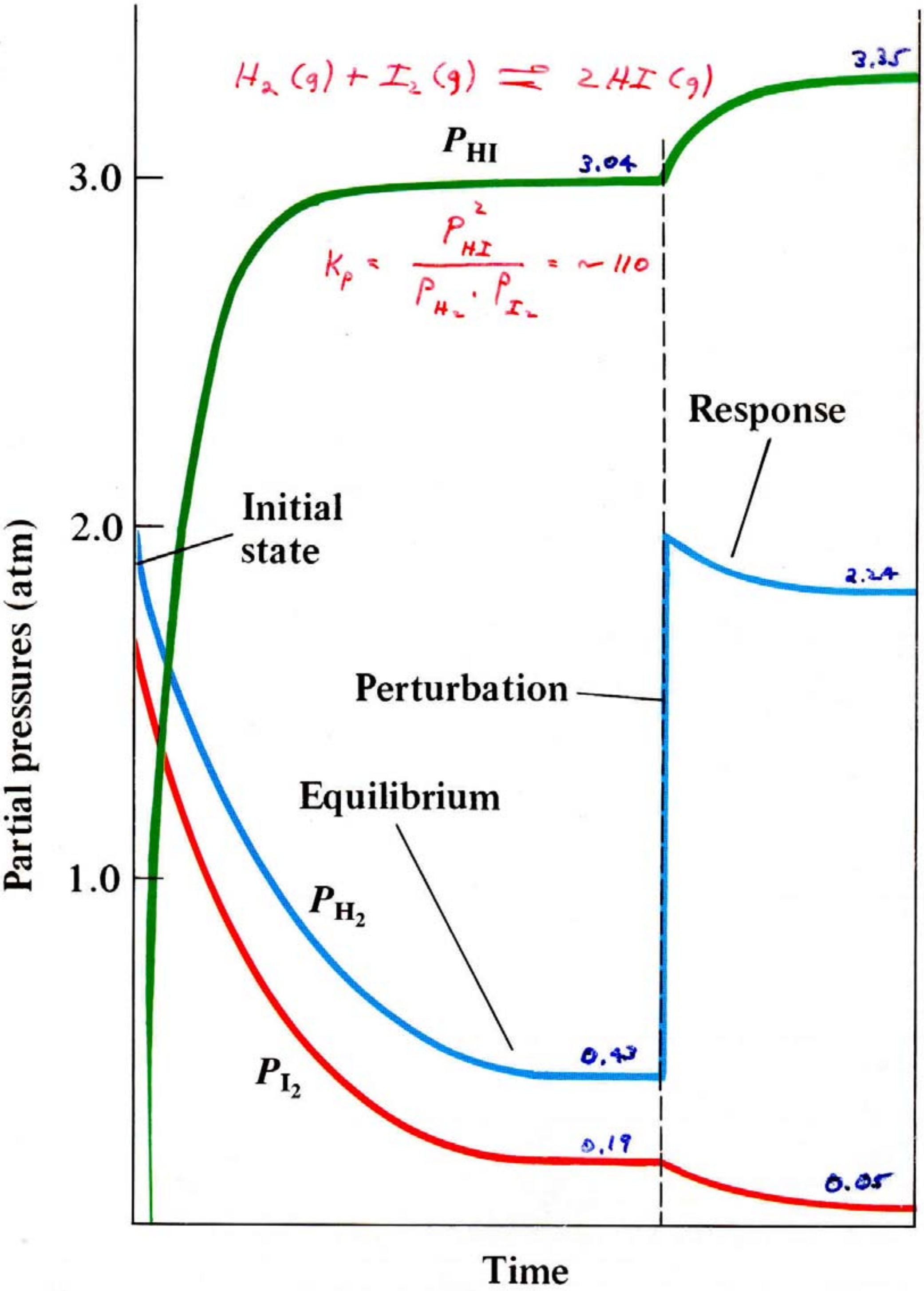
$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$



The approach of the composition of the reaction mixture to equilibrium when PCl_5 decomposes in a closed container. Note that the curves for Cl_2 and PCl_3 are superimposed, because they increase by the same amount.



Response of the equilibrium mixture to the addition of Cl_2. The curves for Cl_2 and PCl_3 are superimposed until the additional Cl_2 has been introduced.



$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \sim 110$

$$2P_{2(g)} \rightleftharpoons P_{4}\ (g)$$

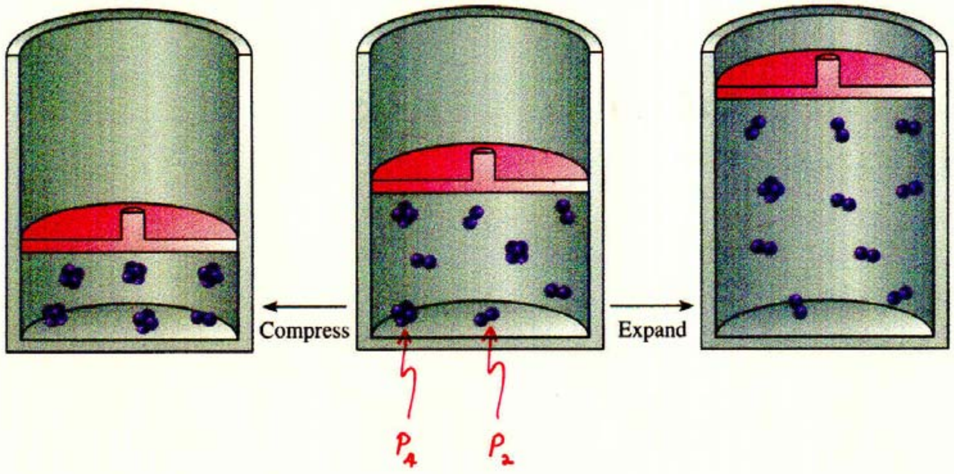
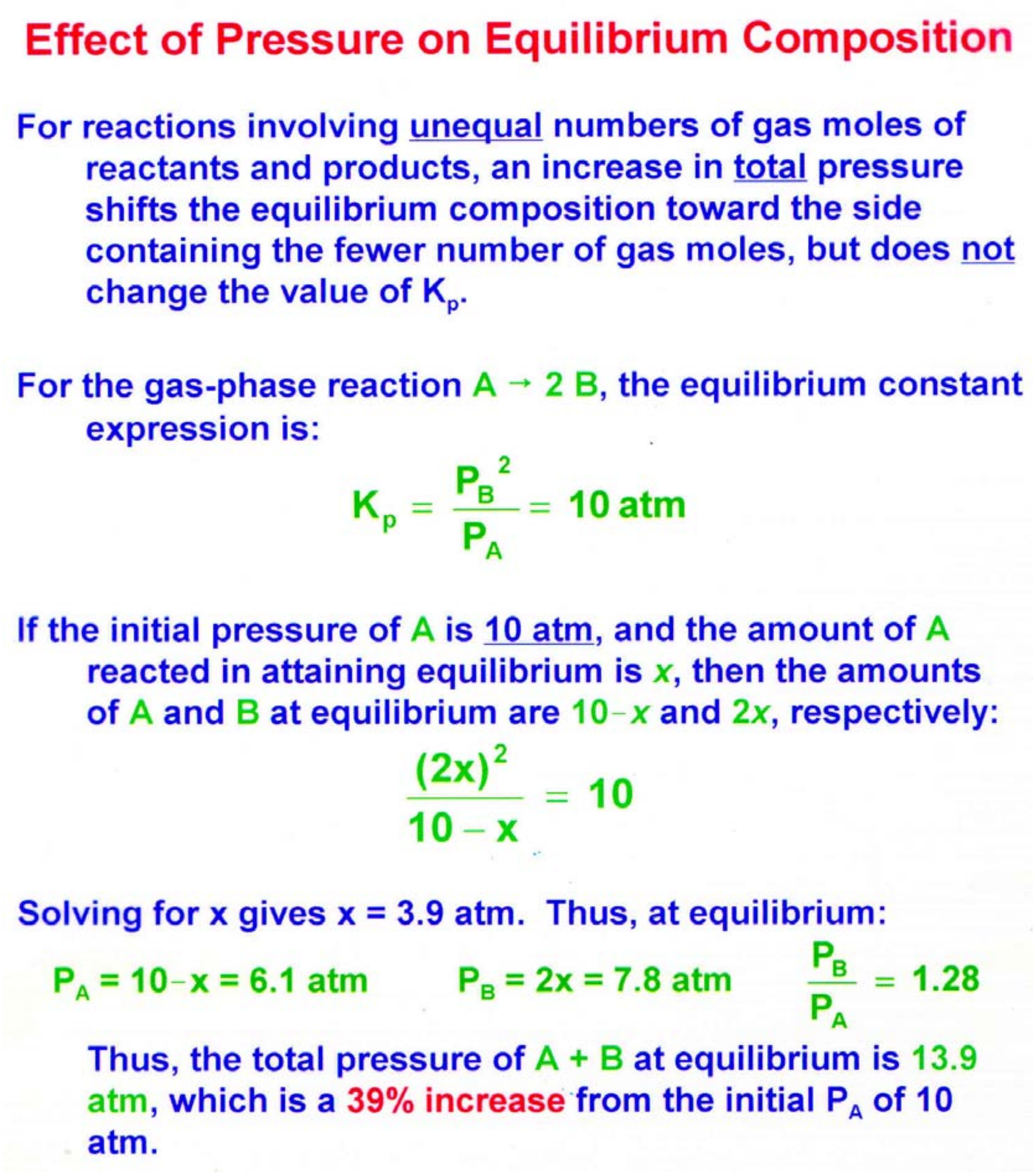


Figure 5-6
An equilibrium mixture of P_2 and P_4 (*center*) is compressed (*left*). Some P_2 molecules combine to give P_4 molecules, to reduce the total number of molecules and thus the total pressure. If the volume is increased (*right*), some P_4 molecules dissociate to pairs of P_2 molecules to increase the total number of molecules and the pressure exerted by those molecules.



Effect of Pressure on Equilibrium Composition

For reactions involving unequal numbers of gas moles of reactants and products, an increase in total pressure shifts the equilibrium composition toward the side containing the fewer number of gas moles, but does not change the value of K_p.

For the gas-phase reaction $A \rightarrow 2\,B$, the equilibrium constant expression is:

$$K_p = \frac{{P_B}^2}{P_A} = 10 \text{ atm}$$

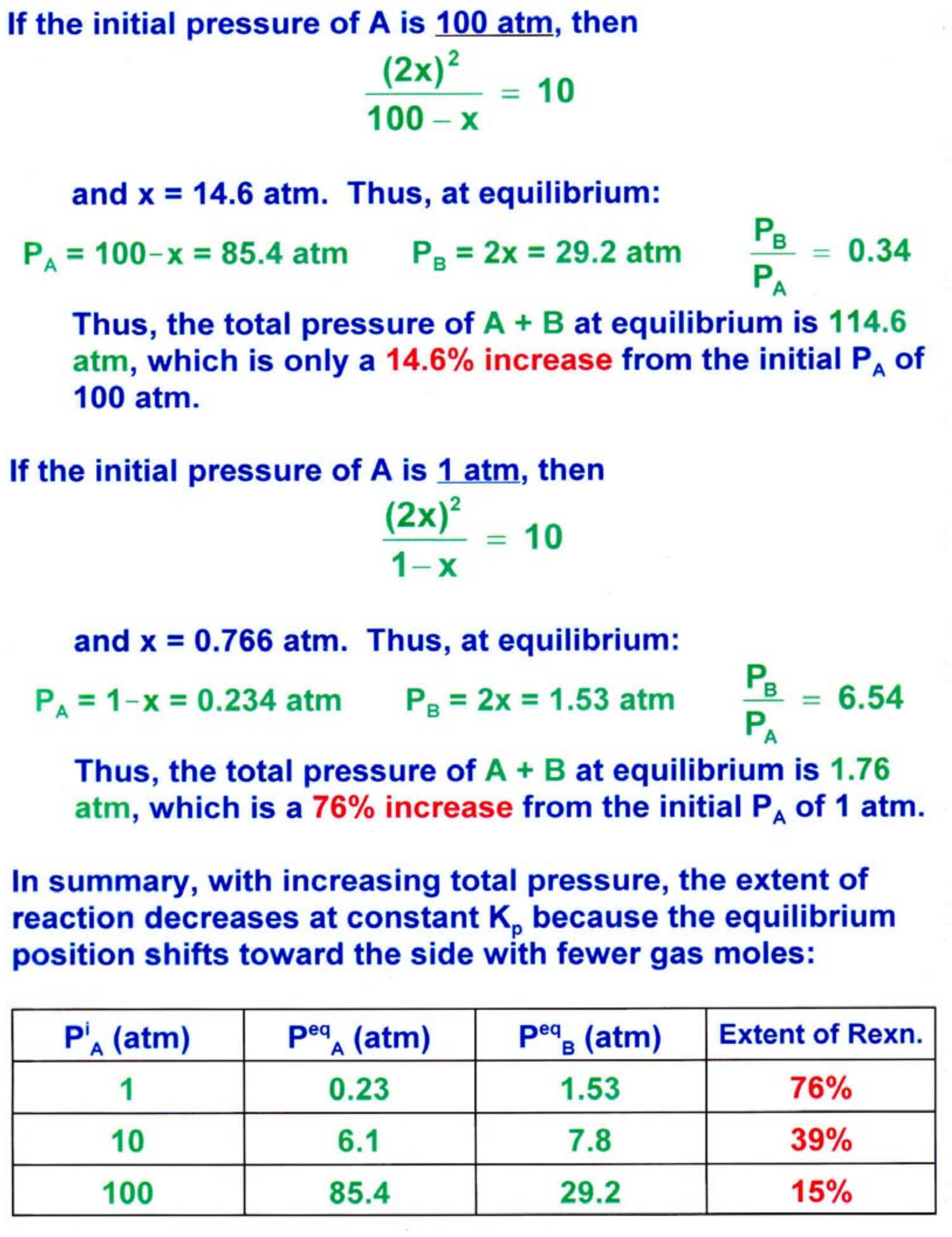
If the initial pressure of A is 10 atm, and the amount of A reacted in attaining equilibrium is *x*, then the amounts of A and B at equilibrium are $10-x$ and $2x$, respectively:

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

Solving for x gives x = 3.9 atm. Thus, at equilibrium:

$P_A = 10 - x = 6.1$ atm $\quad P_B = 2x = 7.8$ atm $\quad \dfrac{P_B}{P_A} = 1.28$

Thus, the total pressure of A + B at equilibrium is 13.9 atm, which is a 39% increase from the initial P_A of 10 atm.



If the initial pressure of A is 100 atm, then

$$\frac{(2x)^2}{100 - x} = 10$$

and x = 14.6 atm. Thus, at equilibrium:

$P_A = 100 - x = 85.4$ atm $\quad P_B = 2x = 29.2$ atm $\quad \frac{P_B}{P_A} = 0.34$

Thus, the total pressure of A + B at equilibrium is 114.6 atm, which is only a 14.6% increase from the initial P_A of 100 atm.

If the initial pressure of A is 1 atm, then

$$\frac{(2x)^2}{1 - x} = 10$$

and x = 0.766 atm. Thus, at equilibrium:

$P_A = 1 - x = 0.234$ atm $\quad P_B = 2x = 1.53$ atm $\quad \frac{P_B}{P_A} = 6.54$

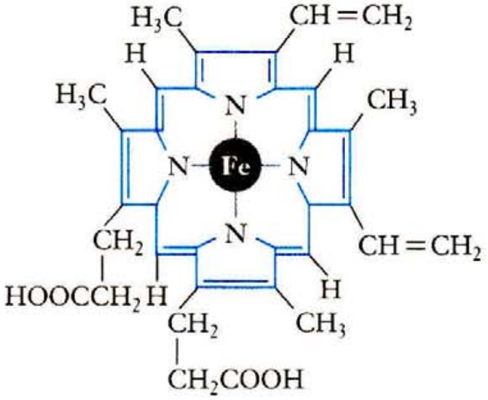
Thus, the total pressure of A + B at equilibrium is 1.76 atm, which is a 76% increase from the initial P_A of 1 atm.

In summary, with increasing total pressure, the extent of reaction decreases at constant K_p because the equilibrium position shifts toward the side with fewer gas moles:

P^i_A (atm)	P^{eq}_A (atm)	P^{eq}_B (atm)	Extent of Rexn.
1	0.23	1.53	76%
10	6.1	7.8	39%
100	85.4	29.2	15%

Example of effect of pressure on chemical reaction involving gas-liquid equilibrium:

Heme Unit:



Hemoglobin (in blood) consists of large protein (the globin) and four iron-containing heme units, each of which can bind one O_2 molecule. Consecutive equilibria are:

$$\mathrm{Hb}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)}(aq) \qquad K_1 = \frac{[\mathrm{Hb(O_2)}]}{[\mathrm{Hb}]P_{\mathrm{O_2}}} = 4.88$$

$$\mathrm{Hb(O_2)}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_2}(aq) \qquad K_2 = \frac{[\mathrm{Hb(O_2)_2}]}{[\mathrm{HbO_2}]P_{\mathrm{O_2}}} = 15.4$$

$$\mathrm{Hb(O_2)_2}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_3}(aq) \qquad K_3 = \frac{[\mathrm{Hb(O_2)_3}]}{[\mathrm{Hb(O_2)_2}]P_{\mathrm{O_2}}} = 6.49$$

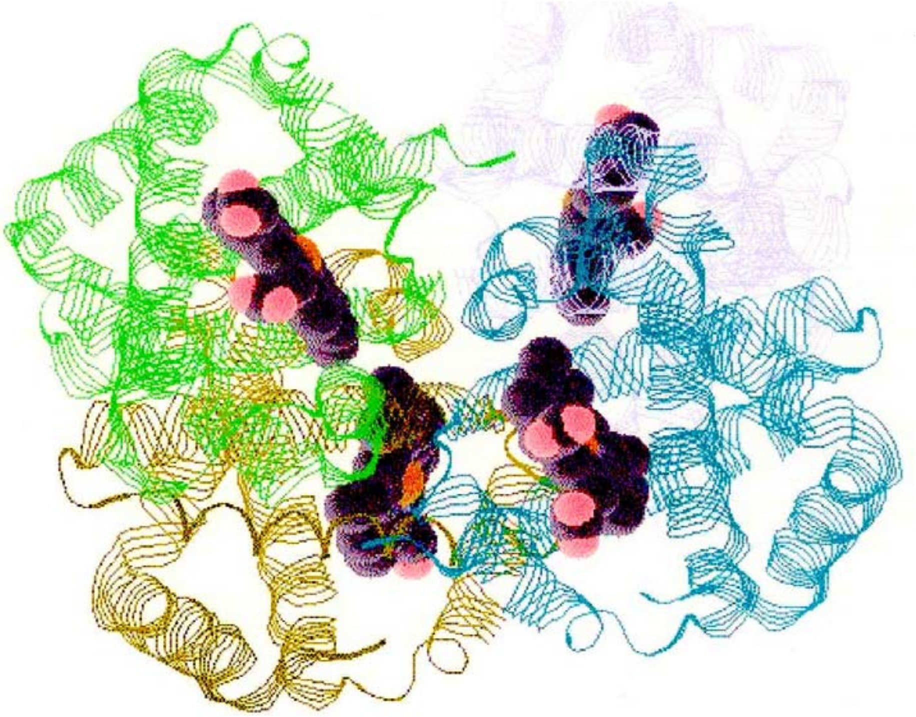
$$\mathrm{Hb(O_2)_3}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_4}(aq) \qquad K_4 = \frac{[\mathrm{Hb(O_2)_4}]}{[\mathrm{Hb(O_2)_3}]P_{\mathrm{O_2}}} = 1750$$

$$\mathbf{Hb}(aq) + \mathbf{4O_2}(g) \rightleftharpoons \mathbf{Hb(O_2)_4}(aq) \qquad \mathrm{K_T} = \frac{[\mathrm{Hb(O_2)_4}]}{[\mathrm{Hb}]\mathrm{P}^4_{\mathrm{O_2}}} = \mathrm{n} \sim 850{,}000$$

Myoglobin (in cells) contains only one heme unit

$$\mathrm{Mb}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Mb(O_2)}(aq) \qquad K = \frac{[\mathrm{Mb(O_2)}]}{[\mathrm{Mb}]P_{\mathrm{O_2}}} = 271$$

At high O_2 pressures (in arterial blood), both hemoglobin and myoglobin are saturated with O_2. At low O_2 pressures (in venous blood), equilibrium favors transfer of O_2 from hemoglobin to myoglobin.



Hemoglobin

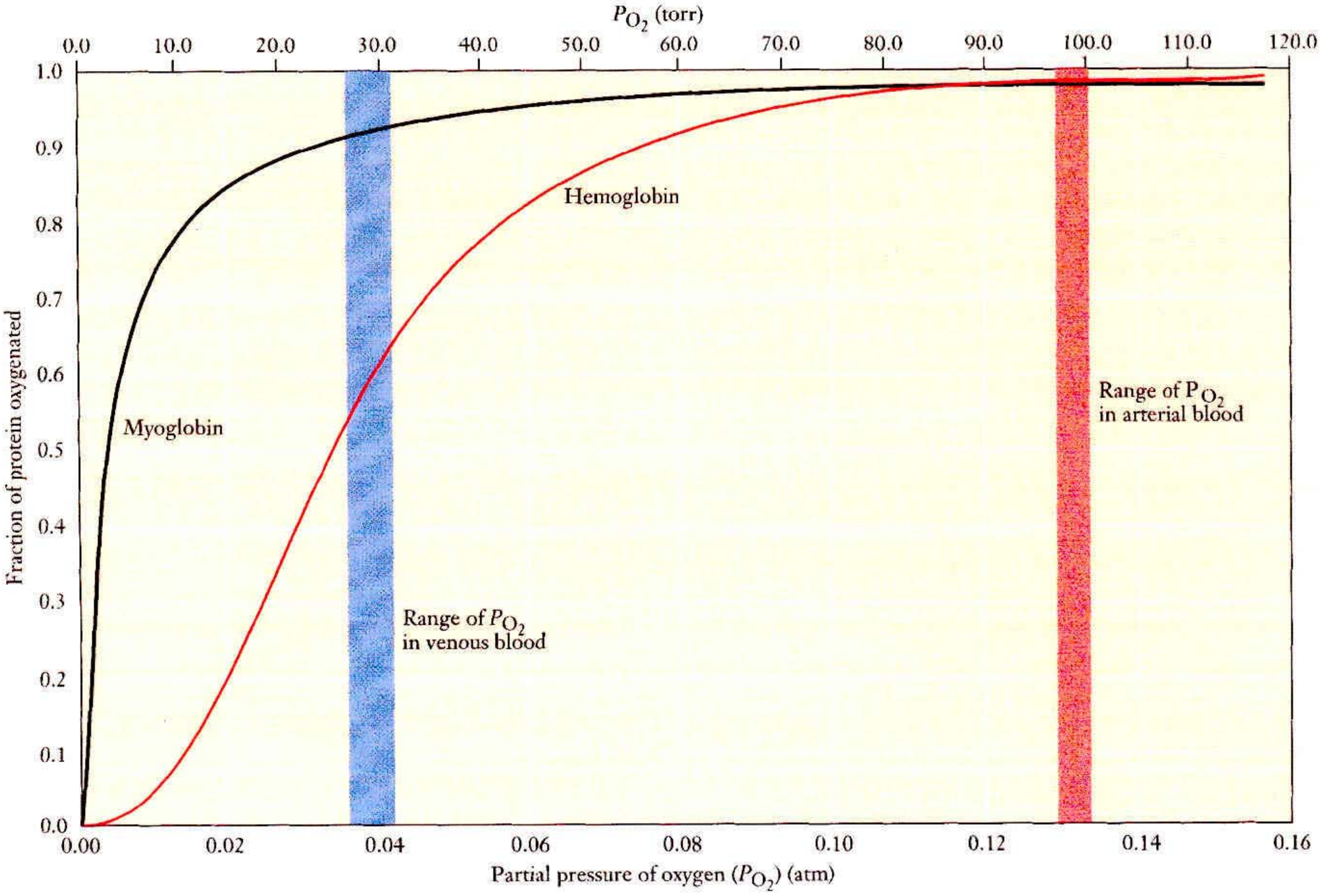
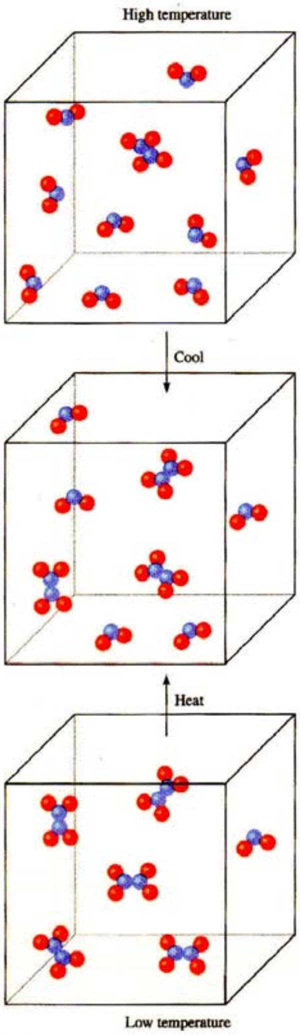


FIGURE 9.5 A plot of the fraction of the binding sites of hemoglobin (red) and myoglobin (black) that are occupied as a function of the partial pressure of O_2.

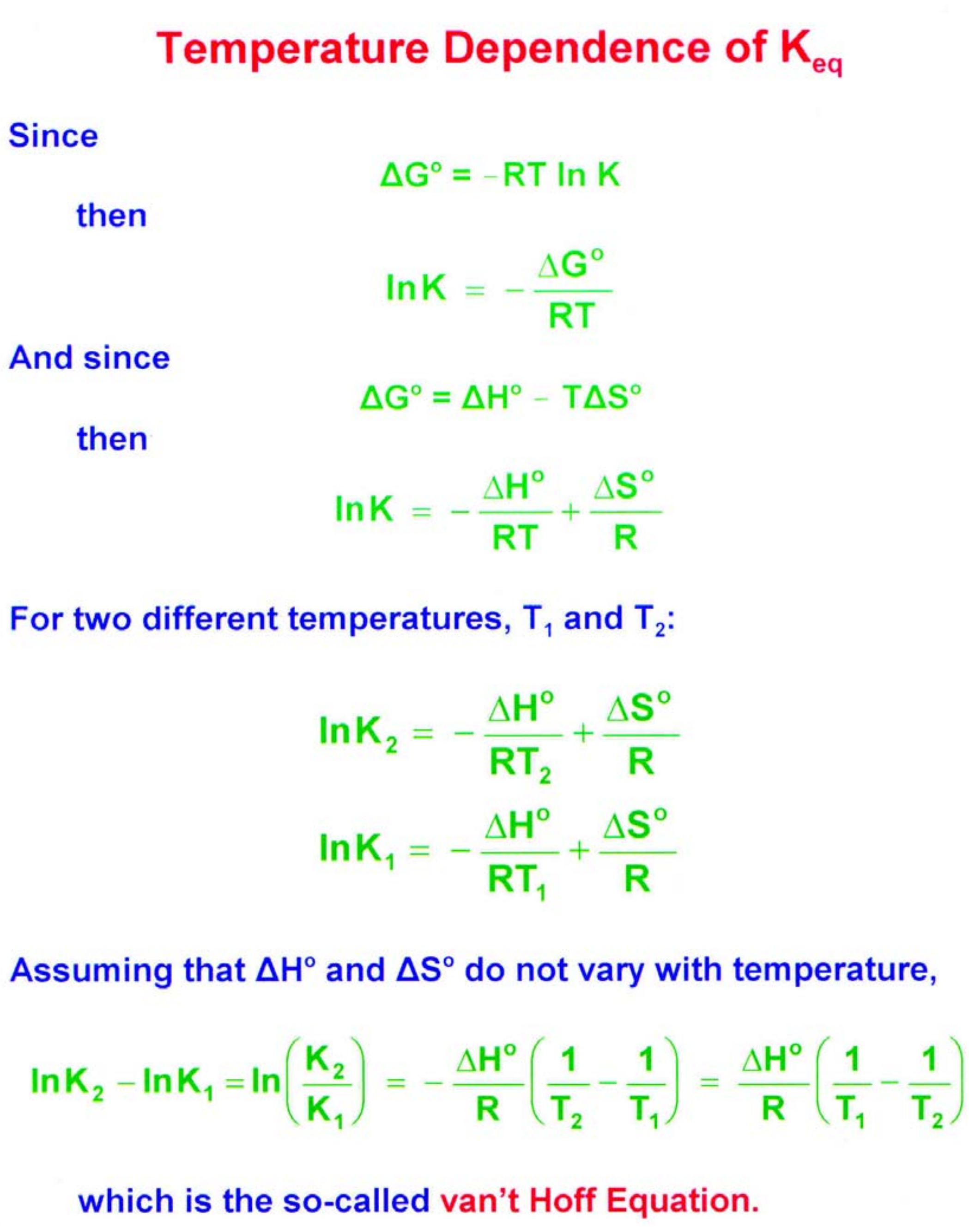
$2NO_2 \rightleftharpoons N_2O_4 + \underline{HEAT}$ $(\Delta H_r^\circ = -57\ kJ/mol)$



MORE NO_2

MORE N_2O_4

Figure 5-3
A particular equilibrium state is reached at a given temperature, regardless of whether the initial state consists of some mass of NO_2 molecules that dimerize as the gas is cooled from a high temperature, or of the same mass of N_2O_4 molecules that dissociate as the gas is heated from a low temperature.



Temperature Dependence of K_{eq}

Since

$$\Delta G^\circ = -RT \ln K$$

then

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

And since

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

then

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

For two different temperatures, T_1 and T_2:

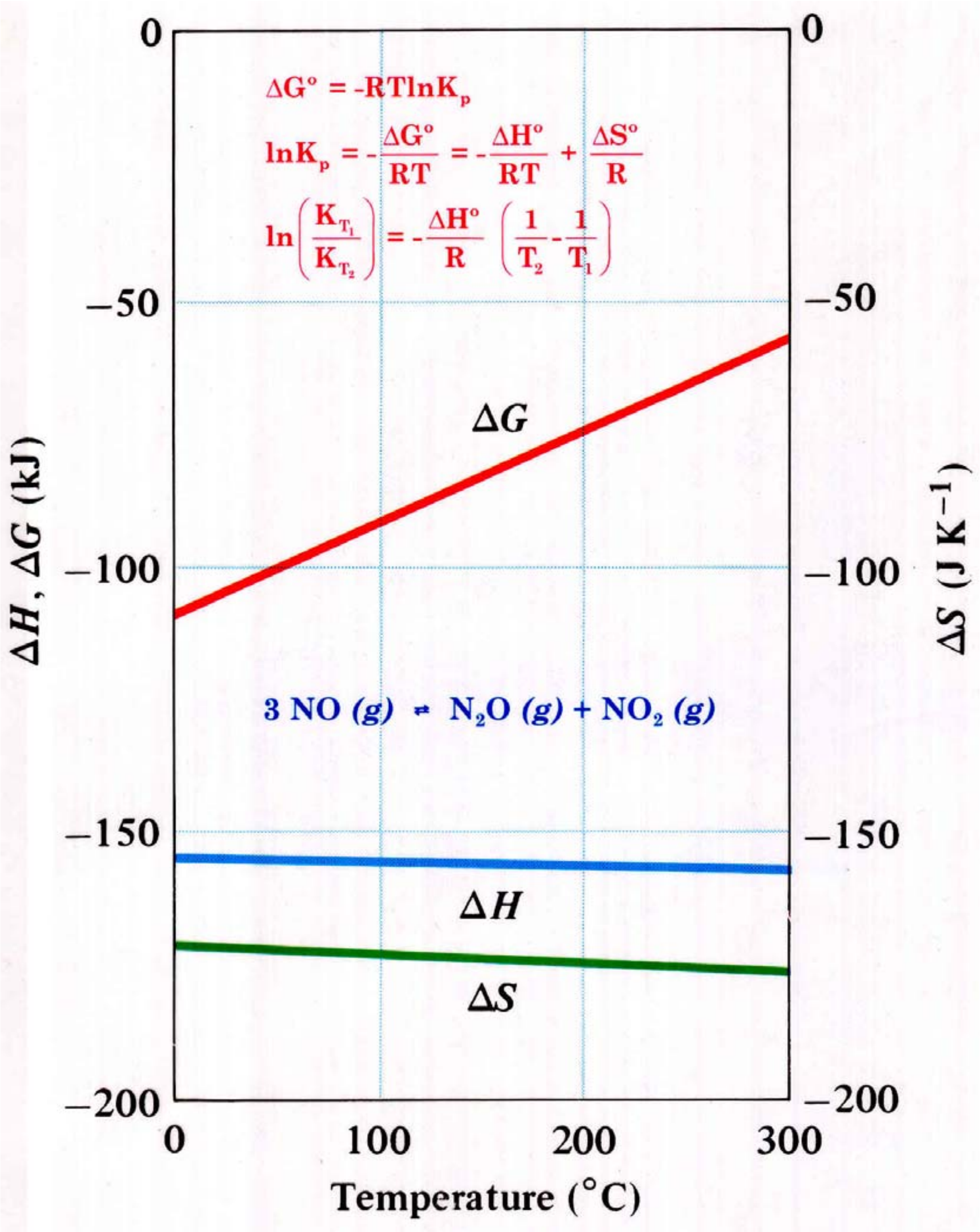
$$\ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

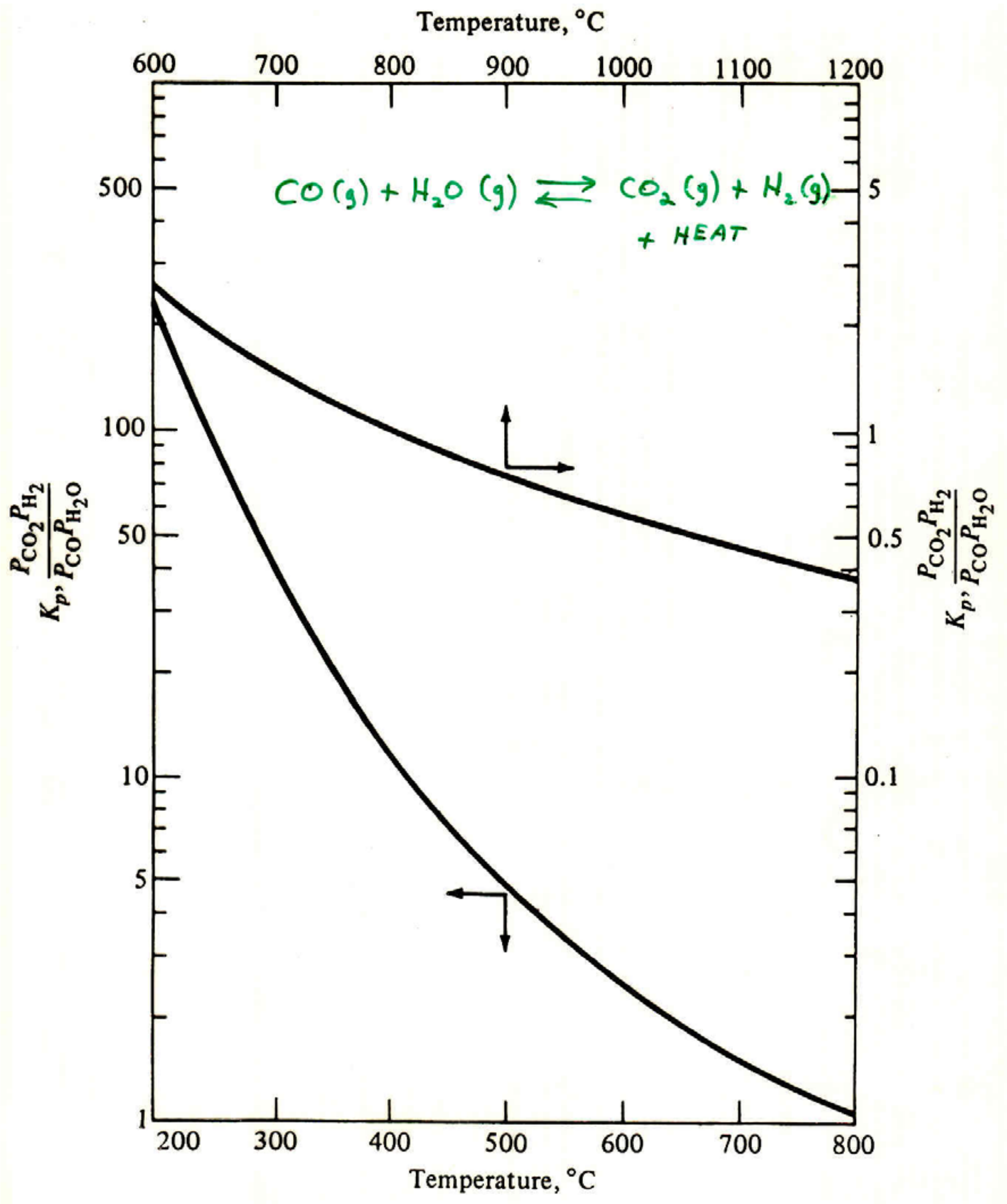
$$\ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

Assuming that ΔH° and ΔS° do not vary with temperature,

$$\ln K_2 - \ln K_1 = \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

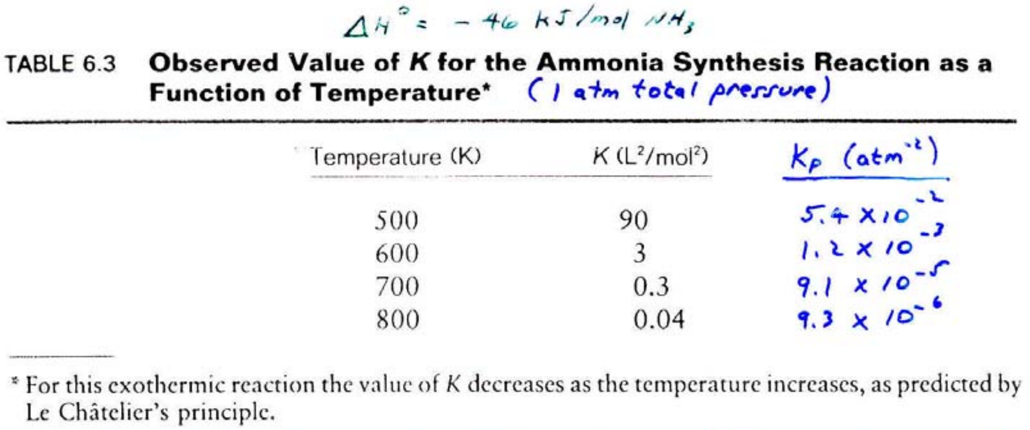
which is the so-called van't Hoff Equation.


$\Delta G° = -RT\ln K_p$
$\ln K_p = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$
$\ln\left(\frac{K_{T_1}}{K_{T_2}}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
ΔG
ΔH
ΔS
$3\,NO\,(g) \rightleftharpoons N_2O\,(g) + NO_2\,(g)$
ΔH, ΔG (kJ)
ΔS (J K⁻¹)
0
−50
−100
−150
−200
0
100
200
300
Temperature (°C)



$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$
+ HEAT

Figure 10.3 Water-gas shift equilibrium. K_p as a function of temperature.



$\Delta H^\circ = -46$ kJ/mol NH_3

TABLE 6.3 **Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*** (1 atm total pressure)

Temperature (K)	K (L^2/mol^2)	K_p (atm^{-2})
500	90	5.4×10^{-2}
600	3	1.2×10^{-3}
700	0.3	9.1×10^{-5}
800	0.04	9.3×10^{-6}

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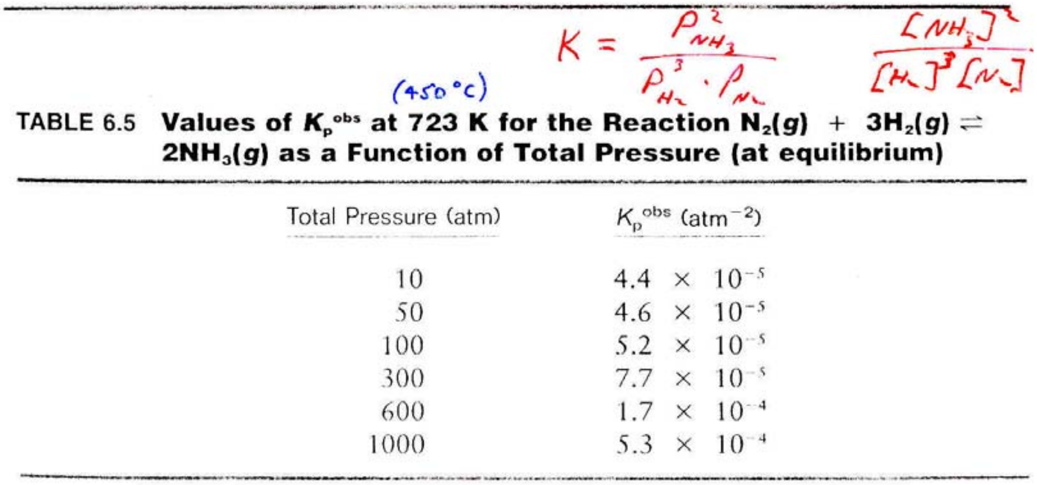
* For this exothermic reaction the value of K decreases as the temperature increases, as predicted by Le Châtelier's principle.



$$K = \frac{P_{NH_3}^2}{P_{H_2}^3 \cdot P_{N_2}} \qquad \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

(450 °C)

TABLE 6.5 **Values of K_p^{obs} at 723 K for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ as a Function of Total Pressure (at equilibrium)**

Total Pressure (atm)	K_p^{obs} (atm^{-2})
10	4.4×10^{-5}
50	4.6×10^{-5}
100	5.2×10^{-5}
300	7.7×10^{-5}
600	1.7×10^{-4}
1000	5.3×10^{-4}

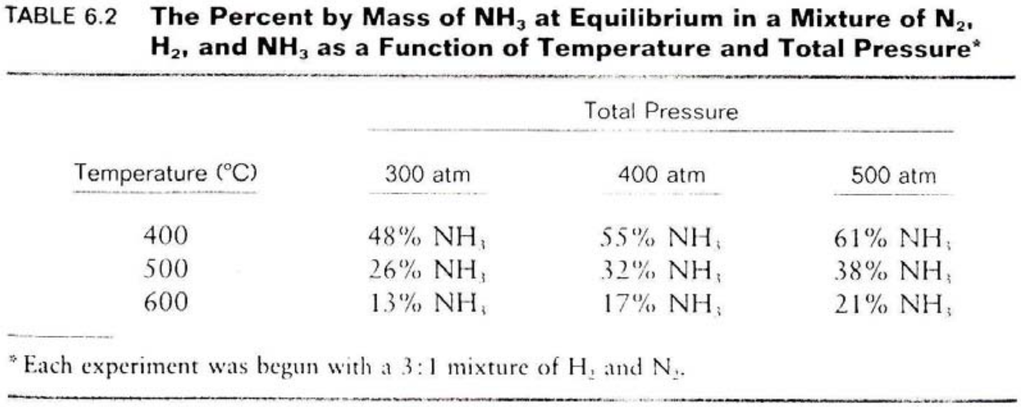


TABLE 6.2 **The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure***

	Total Pressure		
Temperature (°C)	300 atm	400 atm	500 atm
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

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* Each experiment was begun with a 3:1 mixture of H_2 and N_2.

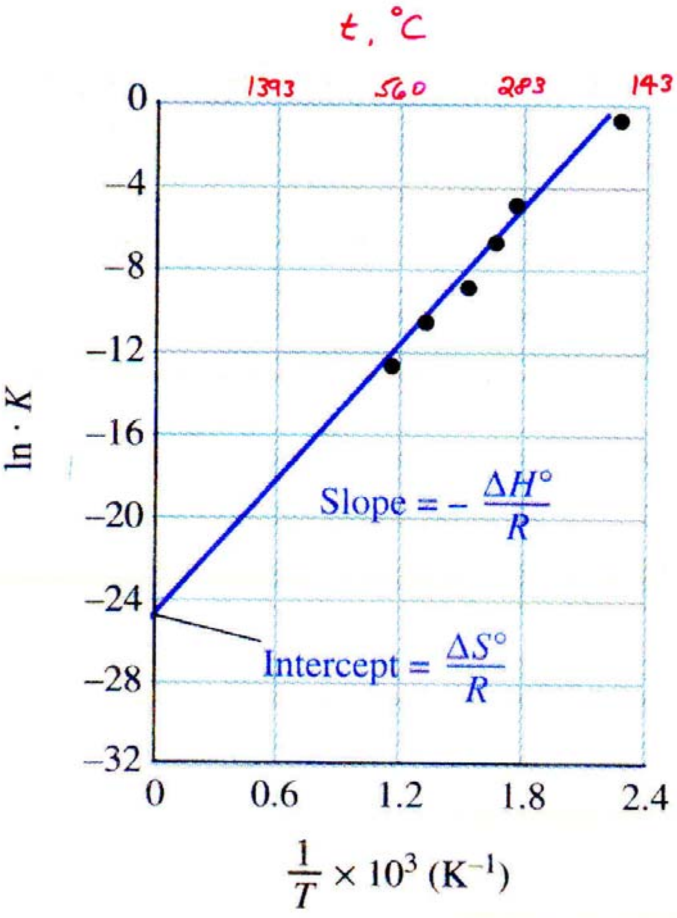
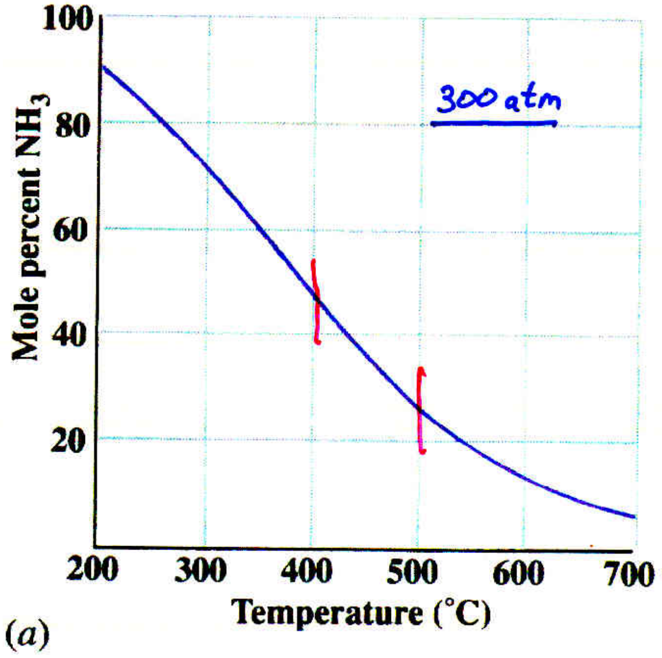


Figure 9-11

The temperature dependence of the equilibrium constant for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Experimental data are shown by points.



$3 H_2 + N_2 \rightleftarrows 2 NH_3$

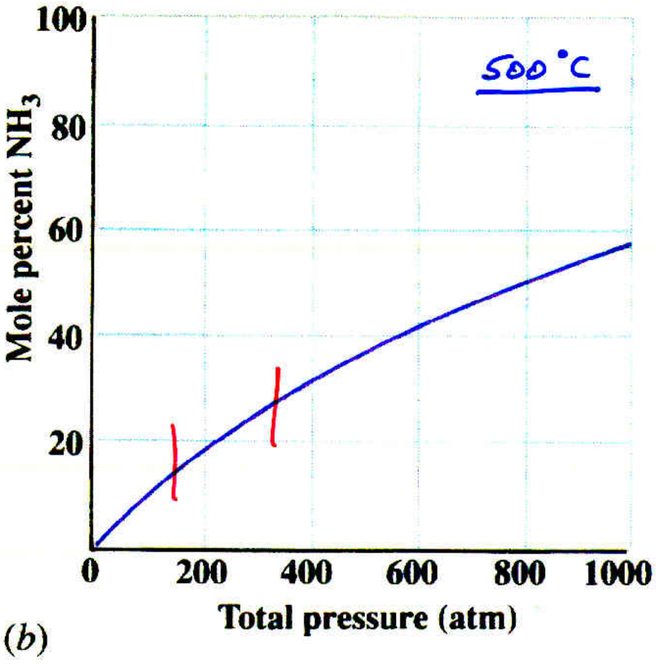


Figure 5-7

(*a*) The equilibrium mole percentage of ammonia in a 1:3 mixture of N_2 and H_2 varies with temperature; low temperatures favor high yields of NH_3. The data shown correspond to a fixed total pressure of 300 atm. (*b*) At a fixed temperature (here, 500°C), the yield of NH_3 increases with increasing total pressure.

A Deeper Look at Ammonia Synthesis

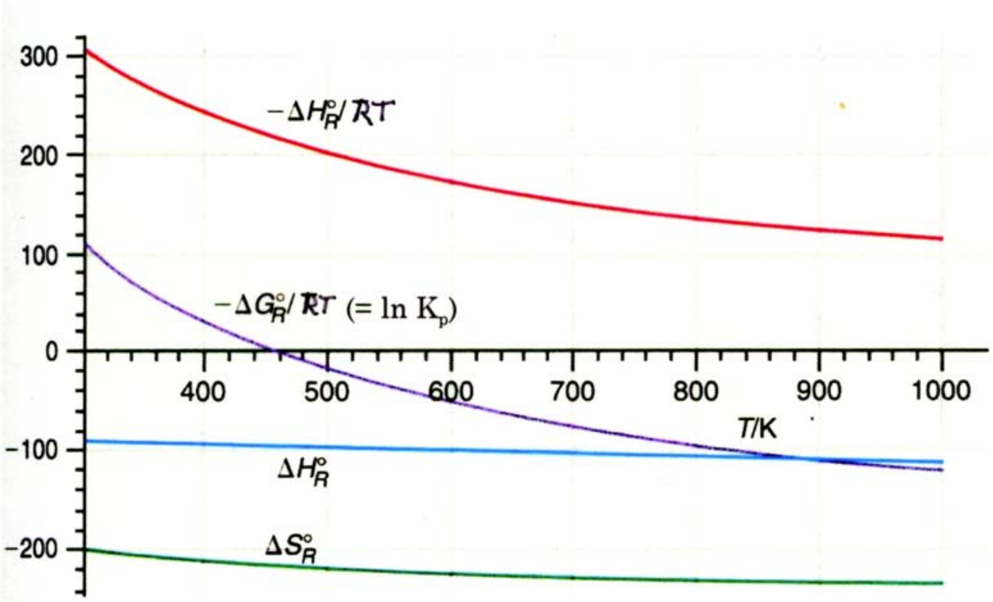
For All Chemical Reactions:

$$\Delta G_R{}^\circ = -RT \ln K_p$$

$$\ln K_p = -\Delta G_R{}^\circ/RT = -\Delta H_R{}^\circ/RT + \Delta S_R{}^\circ/R$$

Effect of Temperature on Ammonia Synthesis:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftarrows 2\,NH_3\,(g)$$



Observations:

1.) $\Delta H_R{}^\circ$ is large, negative (*i.e.*, exothermic) and only weakly dependent on temperature.

2.) Because the number of moles of gaseous species decreases as the reaction proceeds, $\Delta S_R{}^\circ$ is negative and also only weakly dependent on temperature.

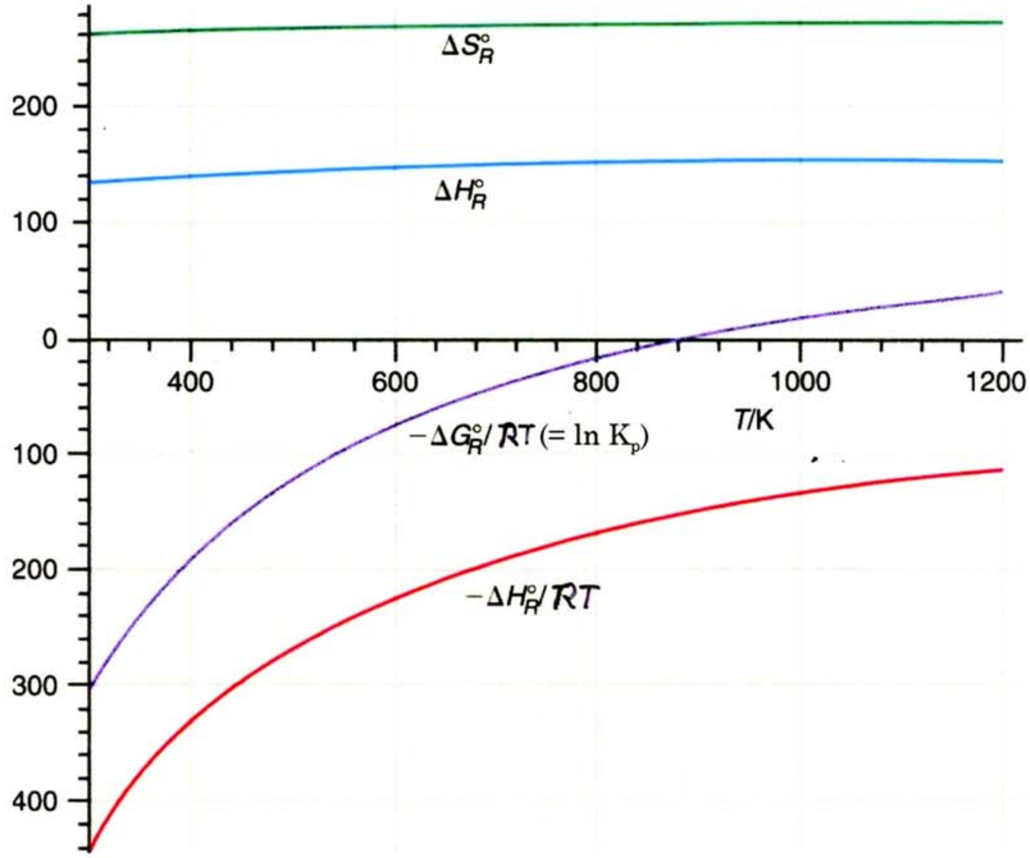
3.) The temperature dependence of $\ln K_p = -\Delta G_R{}^\circ/RT$ is determined primarily by $-\Delta H_R{}^\circ/RT$.

4.) Because $\Delta H_R{}^\circ$ is negative, K_p decreases as T increases.

5.) $K_p > 1$ for $T < 450$ K and decreases with increasing T throughout the temperature range shown.

Effect of Temperature on Coal Gasification:

$$H_2O\ (g) + C\ (s) \rightarrow CO\ (g) + H_2\ (g)$$



Observations:

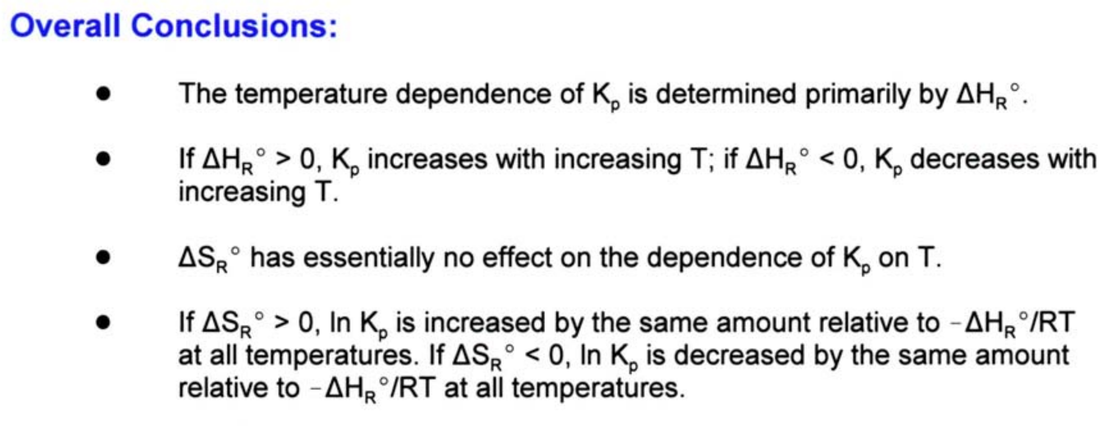
1.) ΔH_R° is large, positive (*i.e.*, endothermic) and only weakly dependent on temperature.

2.) Because the number of moles of gaseous species increases as the reaction proceeds, ΔS_R° is positive and also only weakly dependent on temperature.

3.) The temperature dependence of ln $K_p = -\Delta G_R^\circ/RT$ again is determined primarily by $-\Delta H_R^\circ/RT$.

4.) Because ΔH_R° is positive, K_p increases as T increases.

5.) $K_p < 1$ for $T <$ ~880 K and increases with increasing T throughout the temperature range shown.



Overall Conclusions:

- The temperature dependence of K_p is determined primarily by $\Delta H_R°$.
- If $\Delta H_R° > 0$, K_p increases with increasing T; if $\Delta H_R° < 0$, K_p decreases with increasing T.
- $\Delta S_R°$ has essentially no effect on the dependence of K_p on T.
- If $\Delta S_R° > 0$, ln K_p is increased by the same amount relative to $-\Delta H_R°/RT$ at all temperatures. If $\Delta S_R° < 0$, ln K_p is decreased by the same amount relative to $-\Delta H_R°/RT$ at all temperatures.

Gas-Phase Reaction of N_2 and H_2

Most chemical reactions occur *via* a sequence of elementary steps, called the reaction mechanism. For the ammonia synthesis reaction, a possible mechanism is:

$$N_2(g) \rightarrow 2N(g)$$

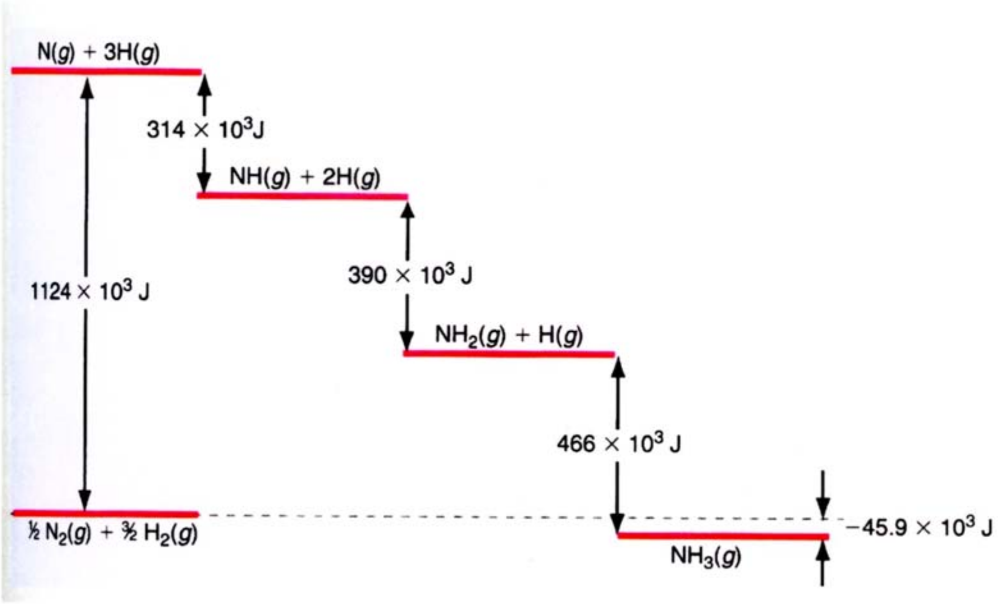
$$H_2(g) \rightarrow 2H(g)$$

$$N(g) + H(g) \rightarrow NH(g)$$

$$NH(g) + H(g) \rightarrow NH_2(g)$$

$$NH_2(g) + H(g) \rightarrow NH_3(g)$$

The first two of these steps are very endothermic, requiring large amounts of energy to break the N≡N triple bond in N_2, as well as the H–H bond in H_2, as shown in the enthalpy diagram below for this mechanism:



Heating a mixture of N_2 *(g)* and H_2 *(g)* sufficiently to dissociate an appreciable fraction of the N_2 would require such a high temperature that all of the NH_3 *(g)* formed would immediately dissociate back into N_2 and H_2 reactants. Thus, the gas-phase reaction between N_2 and H_2 appears not to be a practical route to NH_3 synthesis.

Catalyzed Reaction of N_2 and H_2

The reaction of N_2 and H_2 over a catalyst can provide an alternative pathway for the formation of NH_3, one in which the reaction is not inherently limited by the large endothermicity of N≡N and H−H bond breaking. In this approach, the presence of an appropriate solid metallic catalyst, such as Fe, results in an alternative mechanism, one in which gas-phase N_2 and H_2 molecules are spontaneously dissociated into surface-adsorbed atomic species by interaction with the metal:

$$N_2(g) + \square \rightarrow N_2(a)$$

$$N_2(a) + \square \rightarrow 2N(a)$$

$$H_2(g) + 2\square \rightarrow 2H(a)$$

$$N(a) + H(a) \rightarrow NH(a) + \square$$

$$NH(a) + H(a) \rightarrow NH_2(a) + \square$$

$$NH_2(a) + H(a) \rightarrow NH_3(a) + \square$$

$$NH_3(a) \rightarrow NH_3(g) + \square$$

Here, the symbol □ represents an ensemble of two or more neighboring Fe atoms, called surface "sites," which are capable of spontaneously dissociating N_2 and H_2 molecules. The designation *(a)* indicates that the species is adsorbed onto the Fe surface.

Because ΔH_R° is a state function, the overall enthalpy change for the reaction (−45.9 kJ) is the same whether catalyzed or uncatalyzed, but the enthalpy changes for the individual steps in the mechanism are very different for the catalyzed reaction, as shown in the enthalpy diagram below: