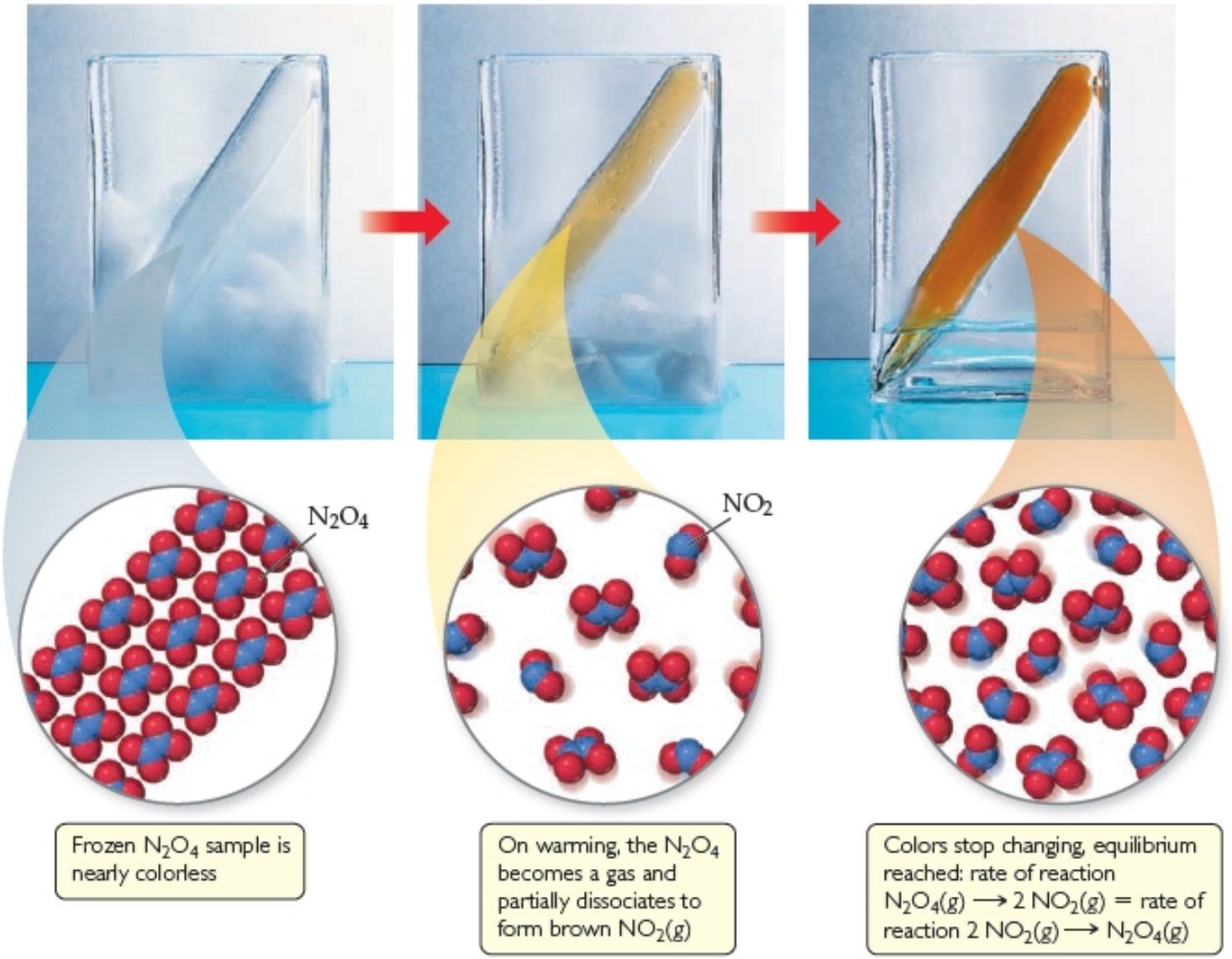
Equilíbrio Químico



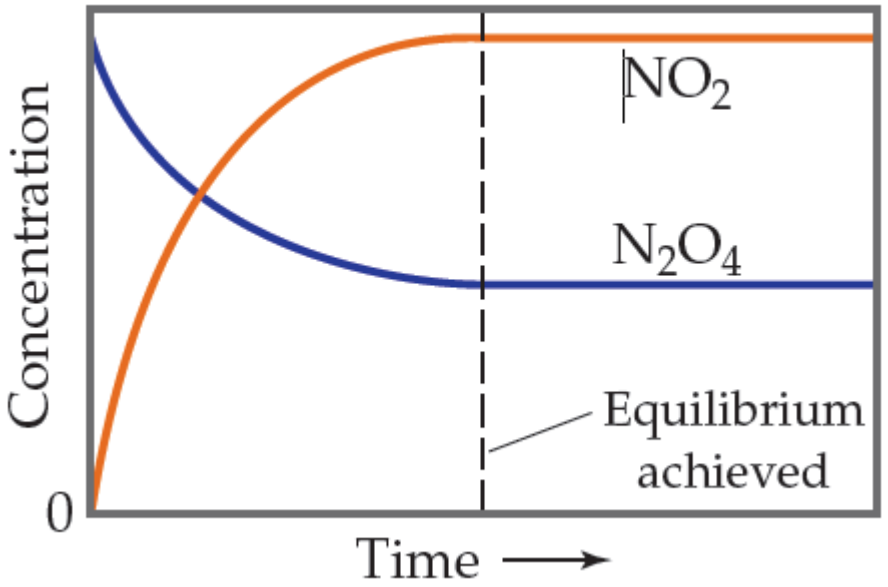
$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2(g)}$$

$$N_2O_4(g) \longrightarrow 2\,NO_2(g) \qquad \text{Rate}_f = k_f[N_2O_4]$$

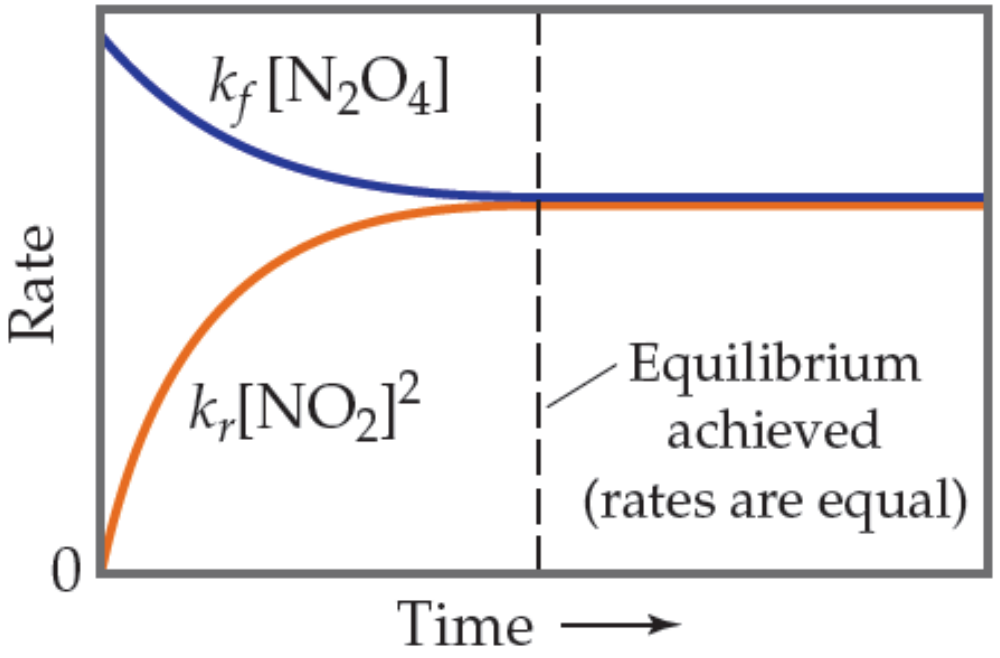
$$2\,NO_2(g) \longrightarrow N_2O_4(g) \qquad \text{Rate}_r = k_r[NO_2]^2$$

$$\underset{\text{Forward reaction}}{k_f[N_2O_4]} = \underset{\text{Reverse reaction}}{k_r[NO_2]^2}$$

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant}$$



Qual é o valor de K?

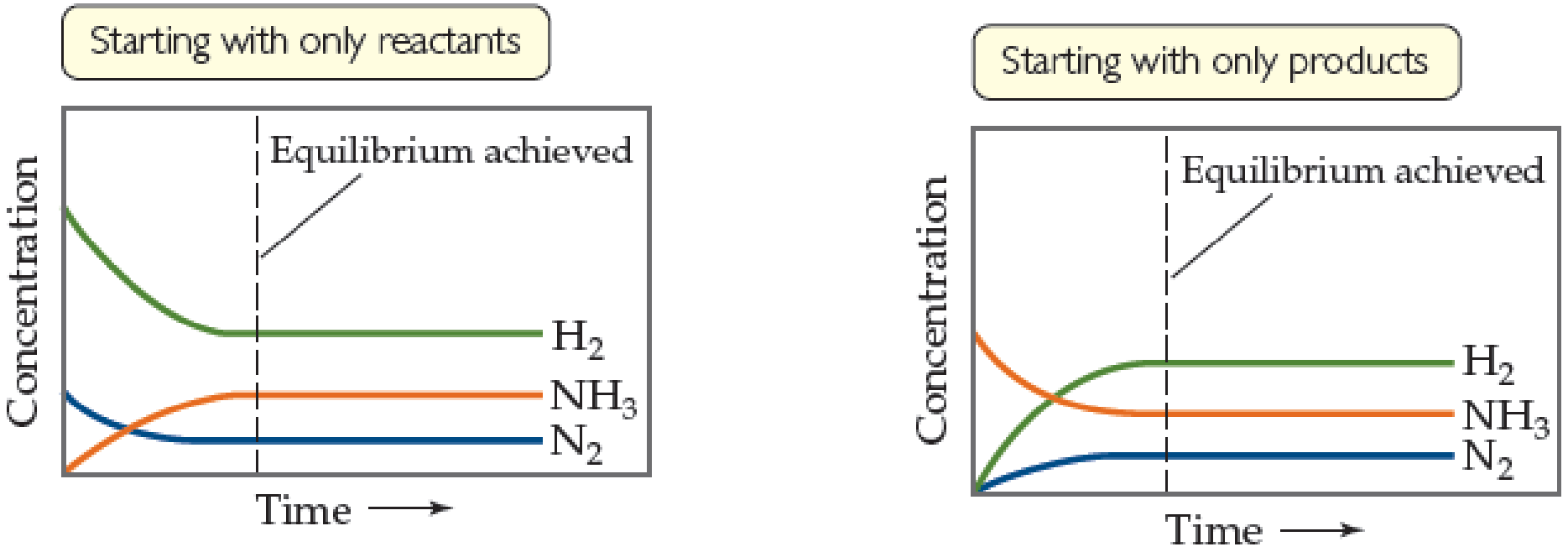


Condições observadas no equilíbrio:

As concentrações são mantidas constantes

O sistema deve ser fechado (sem fluxo de matéria)

As concentrações devem obedecer ao valor da constante de equilíbrio



▲ **Figure 15.3** **The same equilibrium is reached whether we start with only reactants (N_2 and H_2) or with only product (NH_3).**

Qual é a lei de ação das massas para esta reação?

Exercício:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Table 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

$$K_p = \frac{(P_D)^d (P_E)^e}{(P_A)^a (P_B)^b}$$

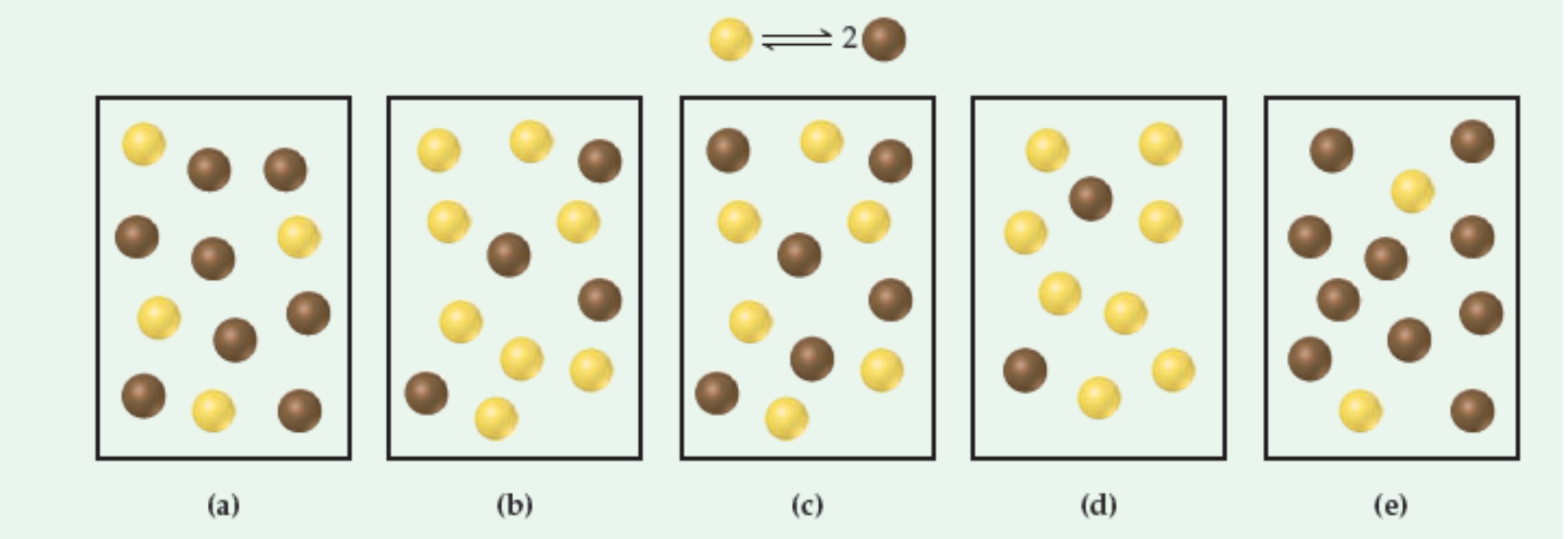
$$K_p = K_c (RT)^{\Delta n}$$

Exercício:

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

$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_c = \frac{[COCl_2]}{[CO][Cl_2]} = 4.56 \times 10^9$$



$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \quad (\text{at } 100\,^\circ\text{C})$$

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100\,^\circ\text{C})$$

$$2\,N_2O_4(g) \rightleftharpoons 4\,NO_2(g)$$

$$K_c = \frac{[NO_2]^4}{[N_2O_4]^2}$$

Qual é K_C para esta reação?

1. $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g) \quad K_{c1} = \dfrac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$

2. $Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_{c2} = \dfrac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$

$$2\,NOBr(g) + Cl_2(g) \rightleftharpoons 2\,NO(g) + 2\,BrCl(g)$$

$$\mathrm{HF}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{F^-}(aq) \qquad K_c = 6.8 \times 10^{-4}$$

$$\mathrm{H_2C_2O_4}(aq) \rightleftharpoons 2\,\mathrm{H^+}(aq) + \mathrm{C_2O_4^{2-}}(aq) \qquad K_c = 3.8 \times 10^{-6}$$

$$2\,\mathrm{HF}(aq) + \mathrm{C_2O_4^{2-}}(aq) \rightleftharpoons 2\,\mathrm{F^-}(aq) + \mathrm{H_2C_2O_4}(aq)$$

Equilíbrios Heterogêneos

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$$

$$K_c = [Pb^{2+}][Cl^-]^2$$

Exercício:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Each of these mixtures was placed in a closed container and allowed to stand:

(a) $CaCO_3(s)$

(b) $CaO(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p

(c) $CaCO_3(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p

(d) $CaCO_3(s)$ and $CaO(s)$

Determine whether or not each mixture can attain the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Participação do Solvente

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3^-(aq)$$

$$K_c = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}$$

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

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

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

A closed system initially containing 1.000×10^{-3} *M* H_2 and 2.000×10^{-3} *M* I_2 at 448 °C is allowed to reach equilibrium, and at equilibrium the HI concentration is 1.87×10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is

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

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

Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			1.87×10^{-3}

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

Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
Equilibrium concentration (*M*)	0.065×10^{-3}	1.065×10^{-3}	1.87×10^{-3}

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas} \quad K_c = 0.105$$

$$Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

$$[HI] = 2.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.0 \times 10^{-2}\,M$$
$$[H_2] = 1.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 5.0 \times 10^{-3}\,M$$
$$[I_2] = 3.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.5 \times 10^{-2}\,M$$

The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 1.45 \times 10^{-5}$, at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}\ \text{atm} = P_{NH_3}$$