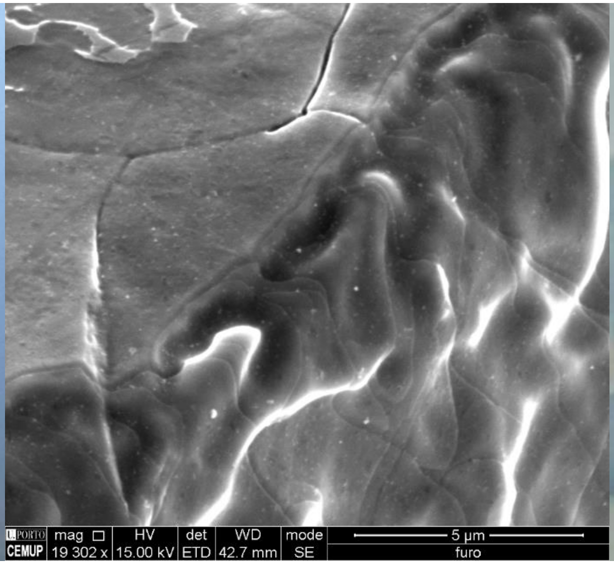
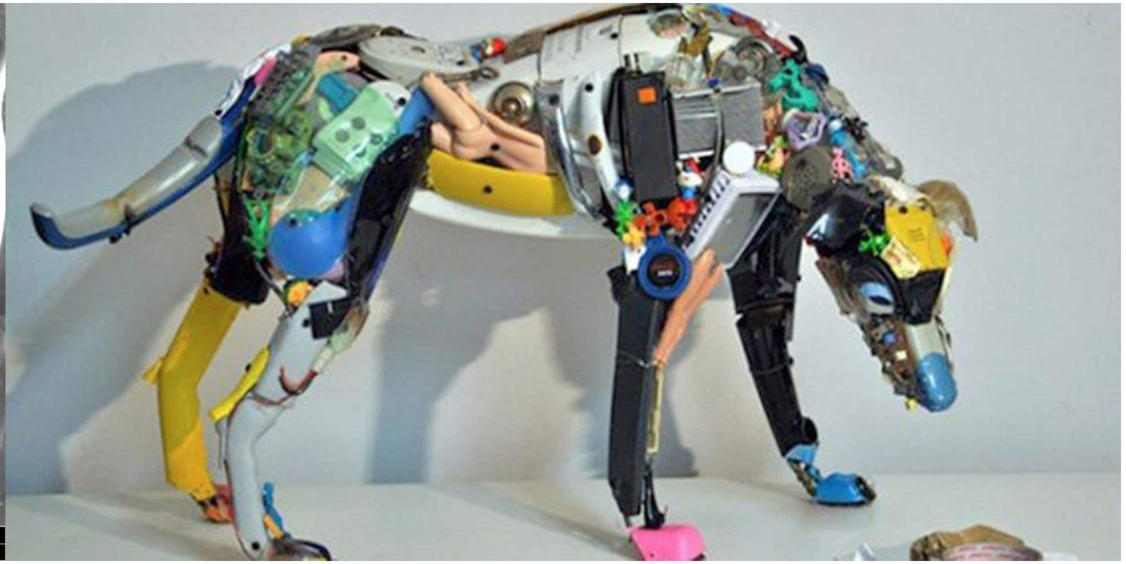
Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.





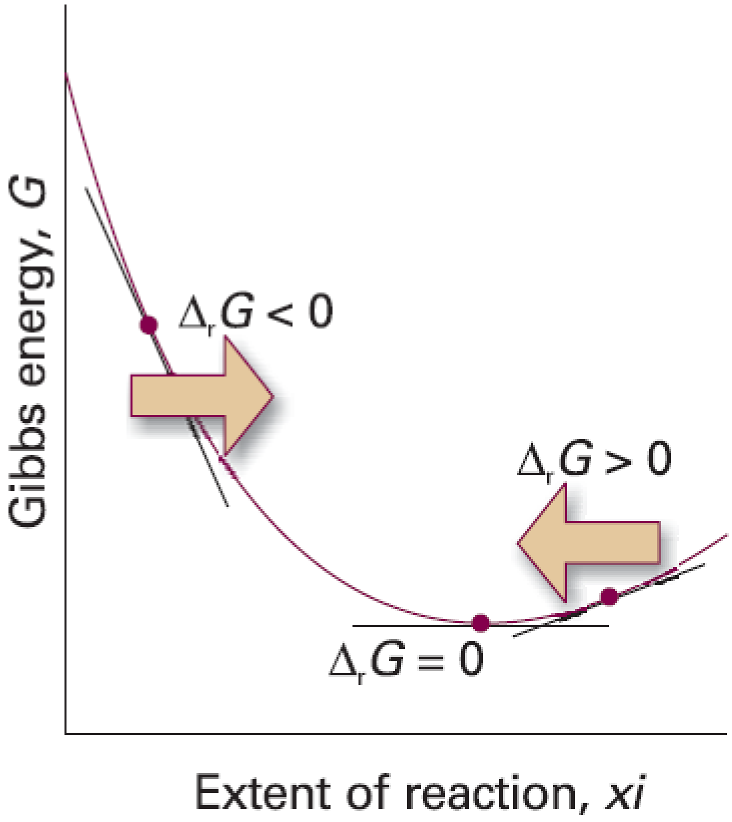
Chemical equilibrium

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

If $\Delta_r G < 0$, the forward reaction is spontaneous.
If $\Delta_r G > 0$, the reverse reaction is spontaneous.
If $\Delta_r G = 0$, the reaction is at equilibrium.

$$\Delta_r G^{\ominus} = \sum_{\text{Products}} \nu \Delta_f G^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_f G^{\ominus}$$

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$$



Chemical equilibrium

$$A + B \rightleftharpoons C + D$$

$$Q = \prod_J a_J^{\nu_J}$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}}$$

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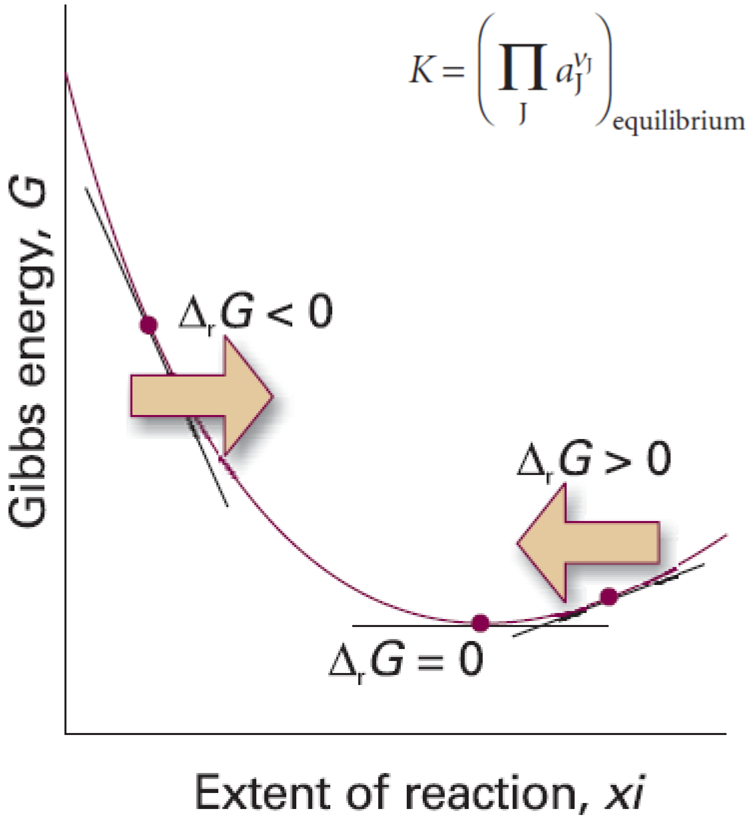

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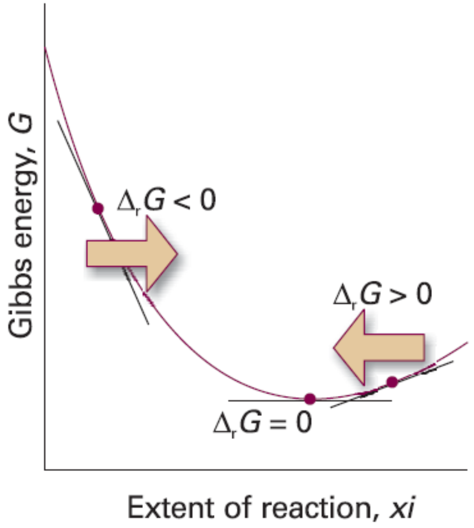

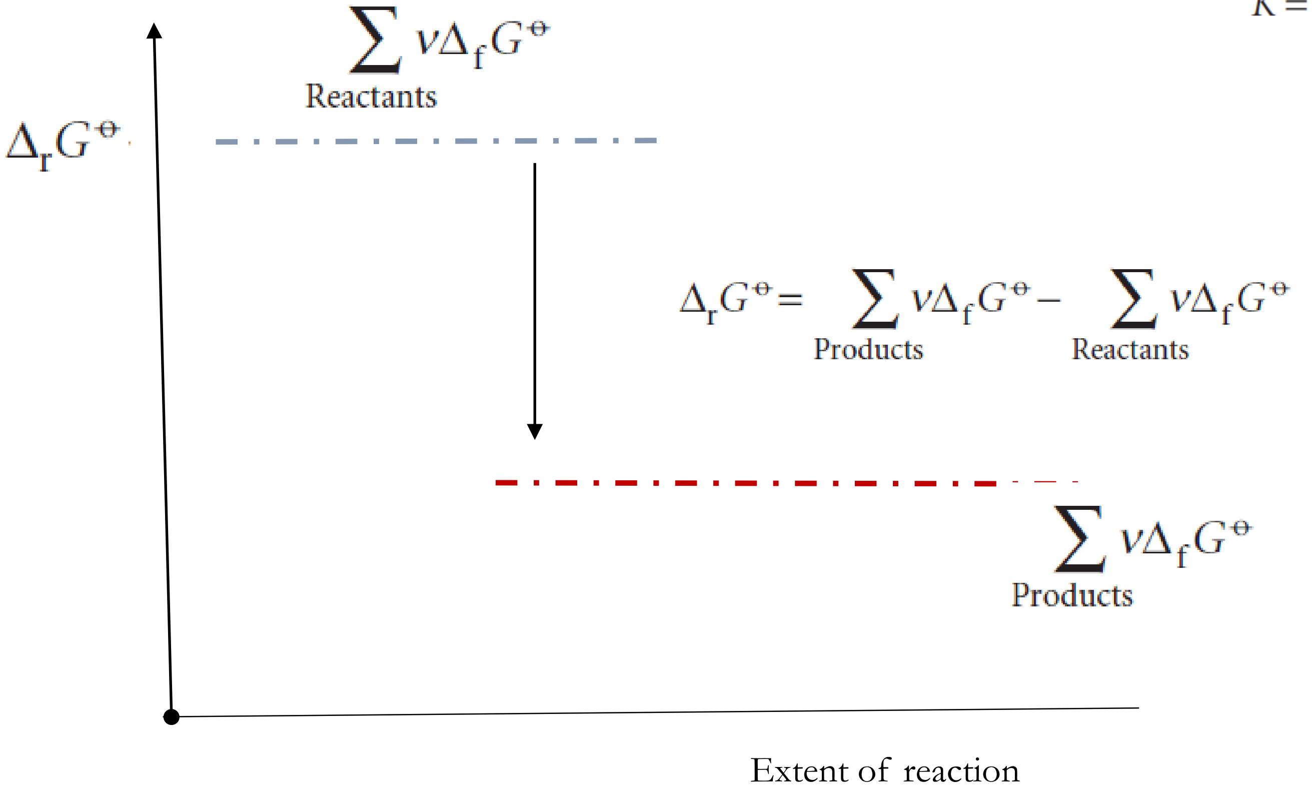

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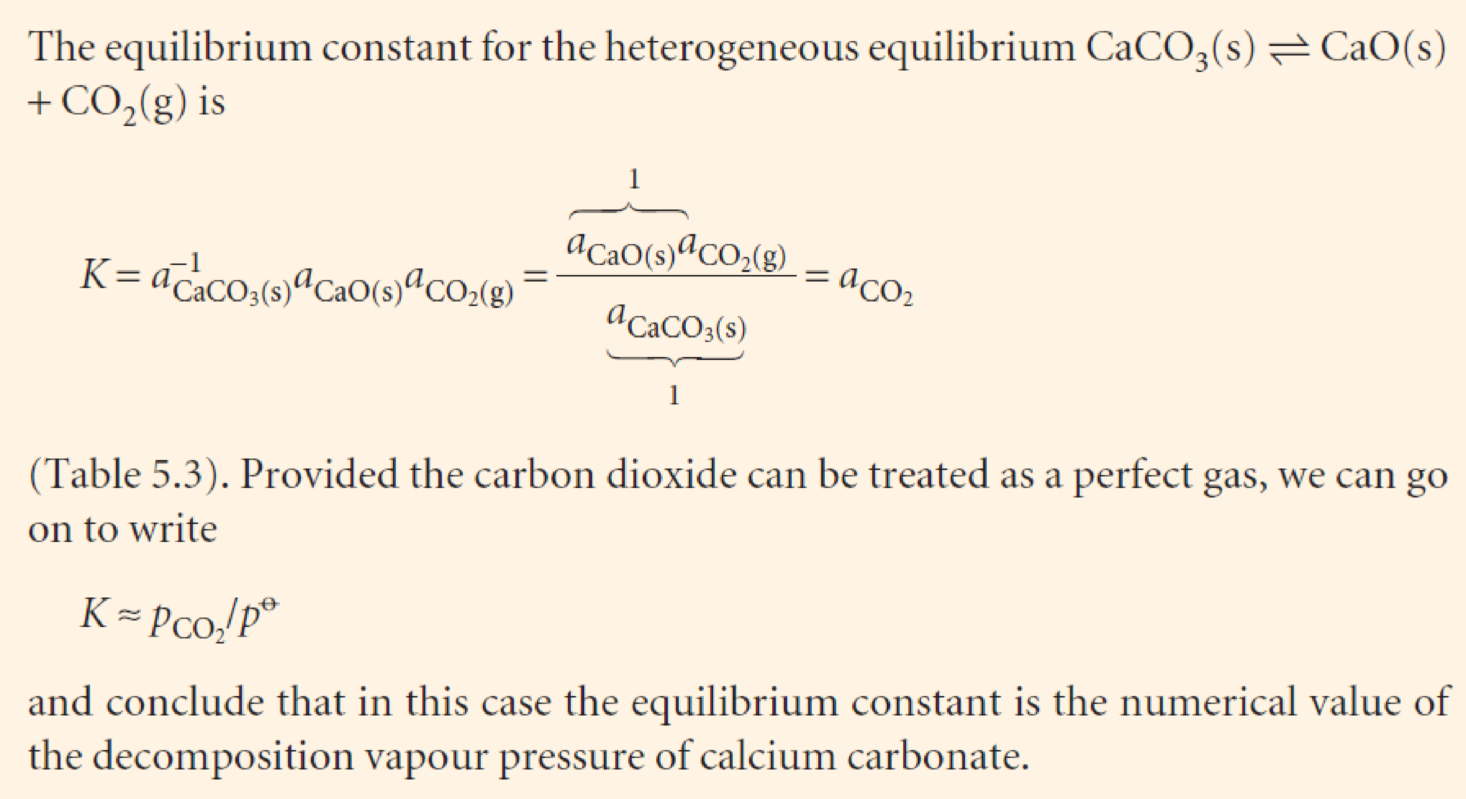
$$RT \ln K = -\Delta_r G^\ominus$$



The equilibrium constant for the heterogeneous equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is

$$K = a_{CaCO_3(s)}^{-1} a_{CaO(s)} a_{CO_2(g)} = \frac{\overbrace{a_{CaO(s)}}^{1} a_{CO_2(g)}}{\underbrace{a_{CaCO_3(s)}}_{1}} = a_{CO_2}$$

(Table 5.3). Provided the carbon dioxide can be treated as a perfect gas, we can go on to write

$$K \approx p_{CO_2}/p^\ominus$$

and conclude that in this case the equilibrium constant is the numerical value of the decomposition vapour pressure of calcium carbonate.

Chemical equilibrium

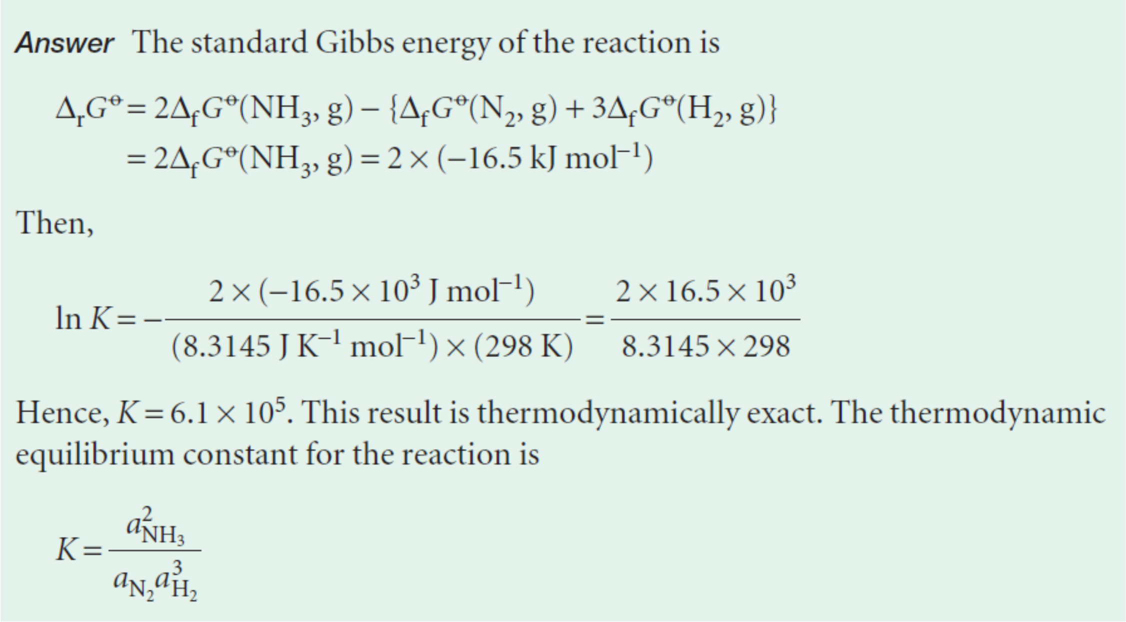
Ammonia synthesis reaction

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

$$\Delta_r G^\ominus = \sum_{\text{Products}} \nu\Delta_f G^\ominus - \sum_{\text{Reactants}} \nu\Delta_f G^\ominus$$

$$\Delta_r G = \Delta_r G^\ominus + RT\ln Q$$

$$RT\ln K = -\Delta_r G^\ominus$$



Answer The standard Gibbs energy of the reaction is

$$\begin{aligned}\Delta_r G^\ominus &= 2\Delta_f G^\ominus(NH_3, g) - \{\Delta_f G^\ominus(N_2, g) + 3\Delta_f G^\ominus(H_2, g)\}\\ &= 2\Delta_f G^\ominus(NH_3, g) = 2\times(-16.5\ \text{kJ mol}^{-1})\end{aligned}$$

Then,

$$\ln K = -\frac{2\times(-16.5\times10^3\ \text{J mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298\ \text{K})} = \frac{2\times16.5\times10^3}{8.3145\times298}$$

Hence, $K = 6.1\times10^5$. This result is thermodynamically exact. The thermodynamic equilibrium constant for the reaction is

$$K = \frac{a_{NH_3}^2}{a_{N_2}a_{H_2}^3}$$

$$K = \frac{(p_{NH_3}/p^\ominus)^2}{(p_{N_2}/p^\ominus)(p_{H_2}/p^\ominus)^3} = \frac{p_{NH_3}^2 p^{\ominus 2}}{p_{N_2}p_{H_2}^3}$$

Chemical equilibrium

Ammonia synthesis reaction

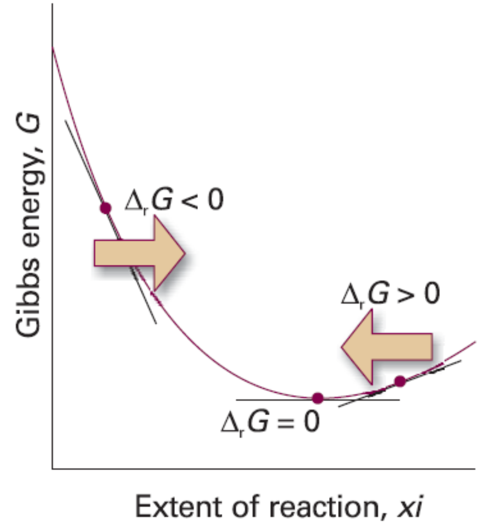
$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3\,(g)$$

$$RT \ln K = -\Delta_r G^{\ominus}$$

$$\ln K = -\frac{\Delta_r G^{\ominus}}{RT}$$

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \frac{b_C b_D}{b_A b_B} = K_\gamma K_b$$

Activity coefficients **Debye–Hückel**



Chemical equilibrium

Ammonia synthesis reaction

Predicting the effect of compression

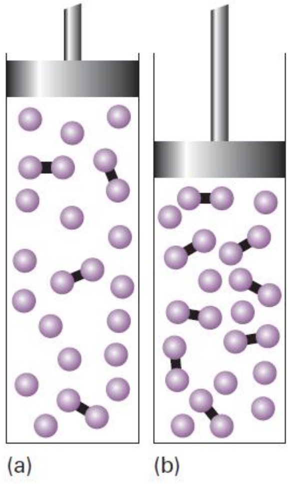


Fig. 7.6 When a reaction at equilibrium is compressed (from *a* to *b*), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the linked spheres).

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

H_2

N_2

NH_3

$$p = p_{NH_3} + p_{H_2} + p_{N_2}$$

Equilibrium constant

$$K = \frac{p_{NH_3}^2\,p^{\ominus 2}}{p_{N_2}\,p_{H_2}^3}$$

$$p_{NH_3}^2 = x_{NH_3}^2 \cdot p^2$$

$$p_{H_2}^3 = x_{H_2}^3 \cdot p^3$$

$$p_{N_2} = x_{N_2} \cdot p$$

$$= \frac{x_{NH_3}^2\,p^2\,p^{\ominus 2}}{x_{N_2}\,x_{H_2}^3\,p^4}$$

$$= \frac{K_x\,p^{\ominus 2}}{p^2}$$

$$K_x = \frac{x_{NH_3}^2}{x_{N_2} . x_{H_2}^3}$$

$$K = \frac{x_{NH_3}^2}{x_{N_2} . x_{H_2}^3} \cdot \frac{p^{\emptyset\,2}}{p^4}$$

Therefore, **doubling** the pressure must increase K_x by a factor of 4 **to preserve the value of *K*.**

Chemical equilibrium

Ammonia synthesis reaction

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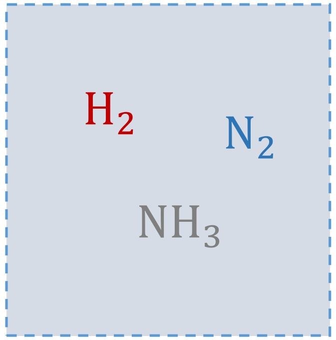

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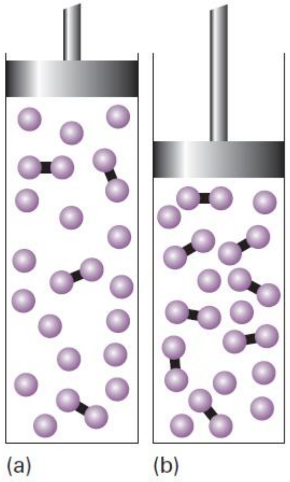
$$K = \frac{p_{NH_3}^2\, p^{\ominus 2}}{p_{N_2}\, p_{H_2}^3}$$

$$p = p_{NH_3} + p_{H_2} + p_{N_2}$$



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$$K = \frac{x_{NH_3}^2}{x_{N_2}\,.\,x_{H_2}^3} \cdot \frac{p^{\emptyset\,2}}{p^2}$$

$$K_x = \frac{x_{NH_3}^2}{x_{N_2}\,.\,x_{H_2}^3}$$

Therefore, **doubling** the pressure must increase K_x by a factor of 4 **to preserve the value of** $\boldsymbol{K}$.