Statistical Molecular Thermodynamics

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Video 12.4

Determining Equilibrium Constants

Equilibrium Constants from G°

$$\Delta_r G^\circ(T) = -RT \ln \boxed{K_P(T)}$$

One can calculate the equilibrium constant from the standard Gibbs energy of reaction, which is related to the difference in chemical potentials of reactants and products,

$$\Delta_r G^\circ(T) = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$$

One can derive $\Delta_r H^o$ from tabulated enthalpies of formation $\Delta_f H^o$, and similarly we've seen tabulated values for ΔS^o (cf. videos 5.10 and 7.6)

$$\Delta_f G^\circ = \Delta_f H^\circ - T\Delta_f S^\circ$$ (or directly tabulated $\Delta_f G^o$ values)

For $\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$

$$\Delta_r G^\circ(T) = \nu_Y \Delta_f G^\circ[Y] + \nu_Z \Delta_f G^\circ[Z] - \nu_A \Delta_f G^\circ[A] - \nu_B \Delta_f G^\circ[B]$$

MEASURING G

Consider a simple reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Reaction proceeds to extent: $1-\xi$ $\quad$ 2ξ $\quad$ $(0 \le \xi \le 1)$

The Gibbs energy of the reaction mixture,

$$G(\xi) = \underline{(1-\xi)\overline{G}_{N_2O_4}} + \underline{2\xi\overline{G}_{NO_2}}$$

$$= \underline{(1-\xi)G^\circ_{N_2O_4}} + \underline{2\xi G^\circ_{NO_2}} + \underline{(1-\xi)RT\ln P_{N_2O_4}} + \underline{2\xi RT\ln P_{NO_2}}$$

Use: $P_{N_2O_4} = \dfrac{1-\xi}{1+\xi}P_{total}$ $\quad$ $P_{NO_2} = \dfrac{2\xi}{1+\xi}P_{total}$ $\quad$ $\text{total moles} = (1-\xi) + 2\xi = 1+\xi$

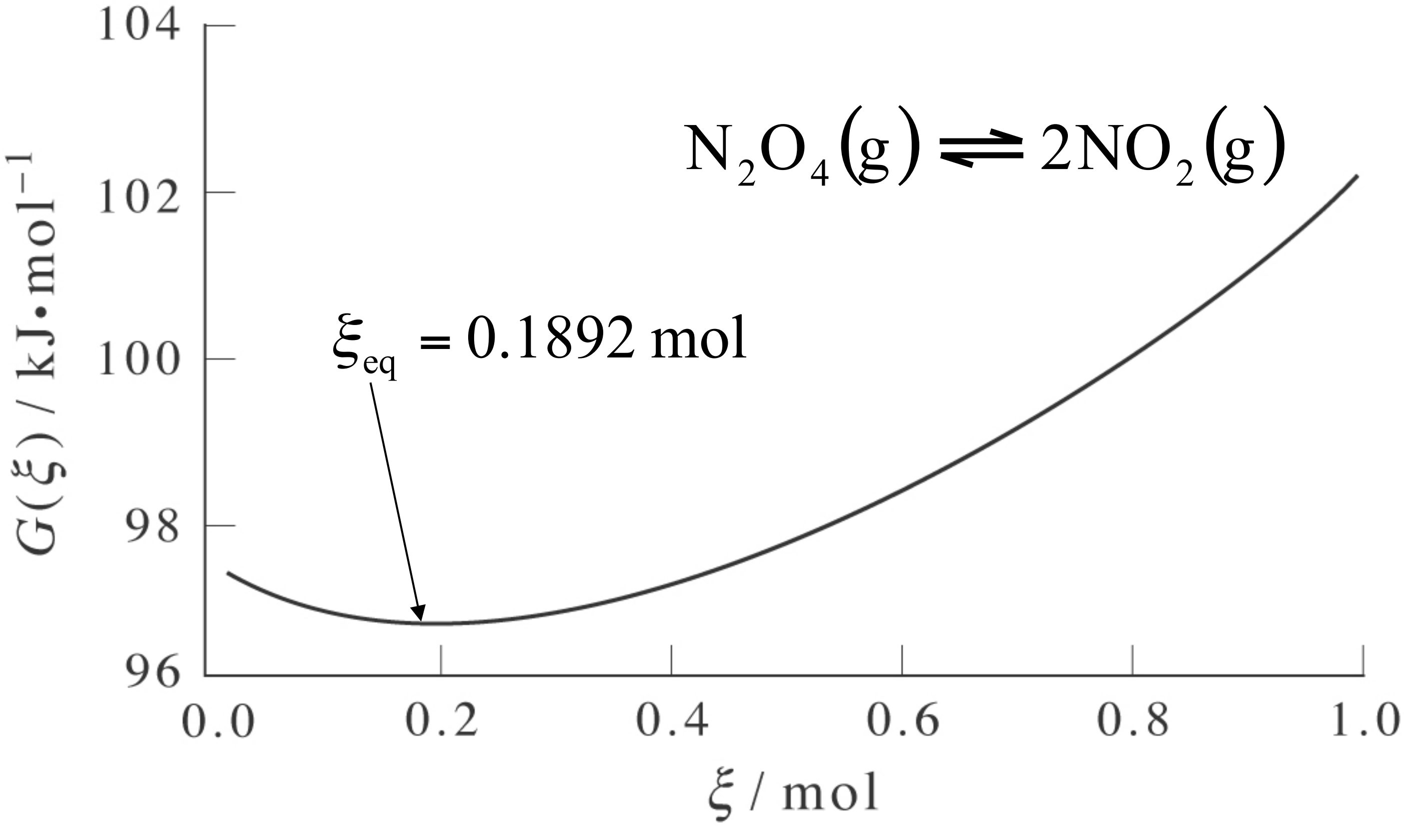
$P_{total} = 1$ bar (externally fixed)

choose standard states so that: $G^\circ_{N_2O_4} = \Delta_f G^\circ_{N_2O_4}$ $\quad$ $G^\circ_{NO_2} = \Delta_f G^\circ_{NO_2}$

$$\boxed{G(\xi) = (1-\xi)\Delta_f G^\circ_{N_2O_4} + 2\xi\Delta_f G^\circ_{NO_2} + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi}}$$

G As Function of Reaction Extent

$$G(\xi) = (1-\xi)\Delta_f G^\circ_{N_2O_4} + 2\xi\Delta_f G^\circ_{NO_2} + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi}$$



298.15 K / 1 bar:

$\Delta_f G^\circ_{N_2O_4} = 97.79\ \text{kJ}\cdot\text{mol}^{-1}$

$\Delta_f G^\circ_{NO_2} = 51.26\ \text{kJ}\cdot\text{mol}^{-1}$

$RT = 2.479\ \text{kJ}\cdot\text{mol}^{-1}$

Self-assessment

$$G(\xi) = (1-\xi)\Delta_f G^\circ_{N_2O_4} + 2\xi\Delta_f G^\circ_{NO_2} + (1-\xi)RT\ln\frac{1-\xi}{1+\xi} + 2\xi RT\ln\frac{2\xi}{1+\xi}$$

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

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Given that G is minimized (stationary) at equilibrium, how else might ξ_{eq} be determined rather than graphically?

Self-assessment Explained

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Given that G is minimized (stationary) at equilibrium, how else might ξ_{eq} be determined rather than graphically?

Stationary implies $dG/d\xi_{eq} = 0$, so one simply takes the derivative of the left hand side, inserts the necessary constants, and solves for ξ_{eq}. The verification that one obtains 0.1892 is left to the calculusly eager.

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Next: Reaction Quotient Redux