Statistical Molecular Thermodynamics
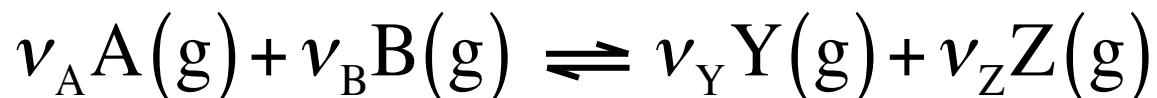
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Video 12.7

Determining *K* from *Q* (the *other Q*)

K FROM Q (THE PARTITION FUNCTION!)

For the general reaction:

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

At constant T and V, (by analogy to video 12.1 for T and P)

$$dA = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \quad (\text{constant } T \text{ and } V)$$

At equilibrium (cf. video 12.1 for T and P):

$$\Delta_r A = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0 \quad (\text{constant } T \text{ and } V)$$

And now if we can relate the chemical potential to the partition function we can get K from Q… (note that one just must be careful to keep the partition function "Q" straight from the reaction quotient "Q")

Chemical Potential in the Mixture

$$\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$$
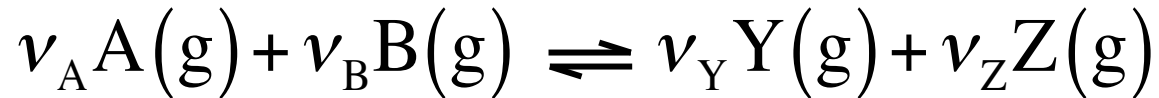
For a mixture of ideal gases, the constituents are *independent* and so the system partition function is *separable*,

$$Q(N_A, N_B, N_Y, N_Z, V, T) = Q(N_A, V, T)Q(N_B, V, T)Q(N_Y, V, T)Q(N_Z, V, T)$$

$$Q(N_A, N_B, N_Y, N_Z, V, T) = \frac{q_A(V,T)^{N_A}}{N_A!} \frac{q_B(V,T)^{N_B}}{N_B!} \frac{q_Y(V,T)^{N_Y}}{N_Y!} \frac{q_Z(V,T)^{N_Z}}{N_Z!}$$
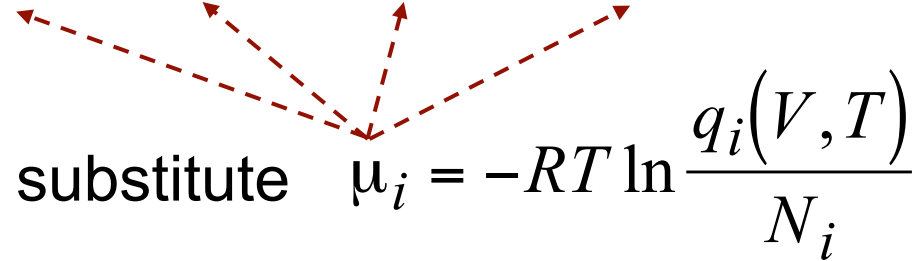
Recall for each constituent,

$$\mu_i = -RT\left(\frac{\partial \ln Q}{\partial N_i}\right)_{N_j, V, T} = -RT \ln \frac{q_i(V,T)}{N_i}$$

where Stirling's approximation has been used for $N_i!$ (cf. video 9.7)

Connecting to K_c

$$\nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0 \quad (\text{constant } T \text{ and } V)$$

substitute $\quad \mu_i = -RT \ln \dfrac{q_i(V,T)}{N_i}$

Self-assessment: Show that the indicated substitution leads to

$$\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}}$$

Self-assessment Explained

$$\nu_Y\mu_Y + \nu_Z\mu_Z - \nu_A\mu_A - \nu_B\mu_B = 0 \qquad \mu_i = -RT\ln\frac{q_i(V,T)}{N_i}$$

$$-RT\left[\nu_Y\ln\frac{q_Y(V,T)}{N_Y} + \nu_Z\ln\frac{q_Z(V,T)}{N_Z} - \nu_A\ln\frac{q_A(V,T)}{N_A} - \nu_B\ln\frac{q_B(V,T)}{N_B}\right] = 0$$

$$\ln q_Y(V,T)^{\nu_Y} - \ln N_Y^{\nu_Y} + \ln q_Z(V,T)^{\nu_Z} - \ln N_Z^{\nu_Z} + \ln q_A(V,T)^{\nu_A}$$

$$- \ln N_A^{\nu_A} + \ln q_B(V,T)^{\nu_B} - \ln N_B^{\nu_B} = 0$$

$$\ln\frac{q_Y(V,T)^{\nu_Y} q_Z(V,T)^{\nu_Z}}{q_A(V,T)^{\nu_A} q_B(V,T)^{\nu_B}} - \ln\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = 0 \qquad \textit{rearrange and exponentiate}$$

$$\frac{q_Y(V,T)^{\nu_Y} q_Z(V,T)^{\nu_Z}}{q_A(V,T)^{\nu_A} q_B(V,T)^{\nu_B}} = \frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} \qquad \text{Q.E.D.}$$

Connecting to K_c (cont.)

Division of N by V gives number density, ρ, which is concentration, giving an expression for K_c

$$\frac{N_Y^{\nu_Y} N_Z^{\nu_Z}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_Y^{\nu_Y} q_Z^{\nu_Z}}{q_A^{\nu_A} q_B^{\nu_B}}$$

$$K_c = \frac{c_Y^{\nu_Y} c_Z^{\nu_Z}}{c_A^{\nu_A} c_B^{\nu_B}} = \frac{\rho_Y^{\nu_Y} \rho_Z^{\nu_Z}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{\left(N_Y/V\right)^{\nu_Y} \left(N_Z/V\right)^{\nu_Z}}{\left(N_A/V\right)^{\nu_A} \left(N_B/V\right)^{\nu_B}} = \frac{\left(q_Y/V\right)^{\nu_Y} \left(q_Z/V\right)^{\nu_Z}}{\left(q_A/V\right)^{\nu_A} \left(q_B/V\right)^{\nu_B}}$$

$$K_c = \frac{\left(q_Y/V\right)^{\nu_Y} \left(q_Z/V\right)^{\nu_Z}}{\left(q_A/V\right)^{\nu_A} \left(q_B/V\right)^{\nu_B}}$$

The equilibrium constant from molecular partition functions!

Specific Example

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

$$K_c = \frac{\left(q_{HI}/V\right)^2}{\left(q_{H_2}/V\right)\left(q_{I_2}/V\right)} = \frac{q_{HI}^2}{q_{H_2}q_{I_2}}$$

For ideal diatomics, we have (cf. video 4.6)

$$q(V,T) = \left(\frac{2\pi(m_1 + m_2)k_B T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma\Theta_{rot}} \cdot \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \cdot g_{e1} e^{(D_0 + h\nu/2)/k_B T}$$
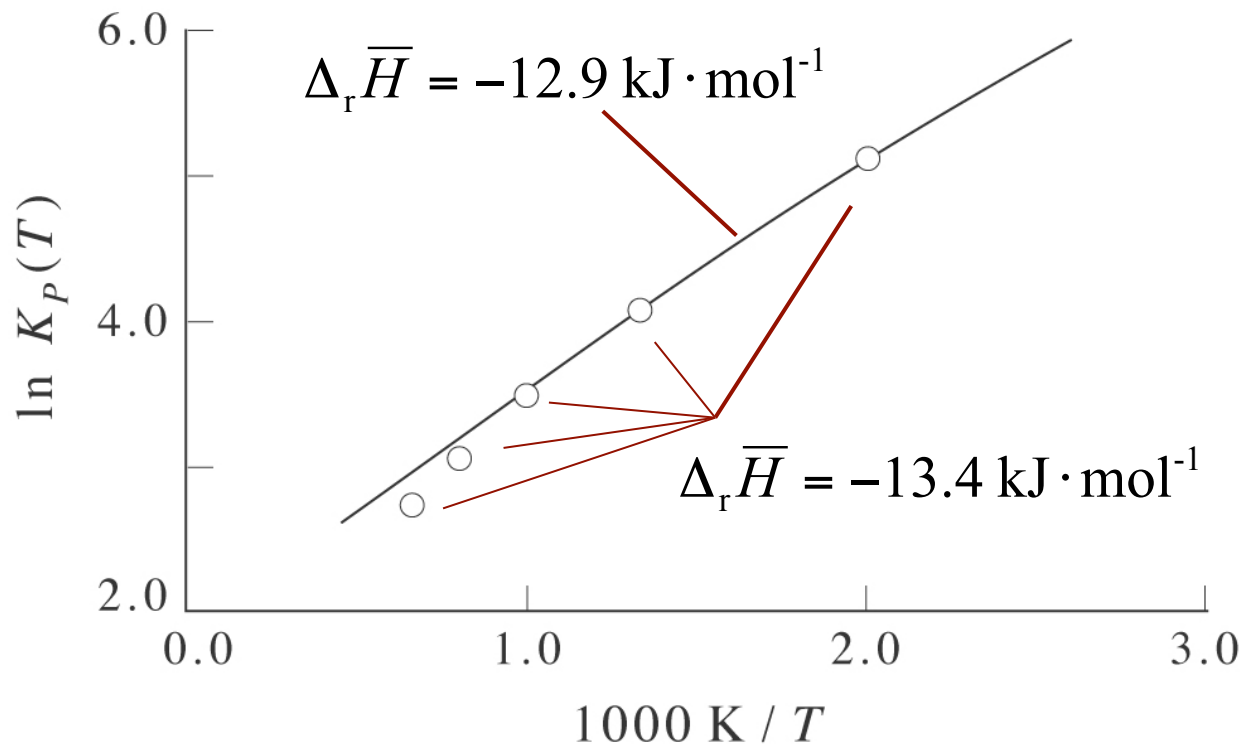
$$K(T) = \left(\frac{m_{HI}^2}{m_{H_2}m_{I_2}}\right)^{3/2} \cdot \left(\frac{4\Theta_{rot}^{H_2}\Theta_{rot}^{I_2}}{\left(\Theta_{rot}^{HI}\right)^2}\right) \cdot \frac{\left(1 - e^{-\Theta_{vib}^{H_2}/T}\right)\left(1 - e^{-\Theta_{vib}^{I_2}/T}\right)}{\left(1 - e^{-\Theta_{vib}^{HI}/T}\right)^2} \cdot \exp\left(\frac{2D_0^{HI} - D_0^{H_2} - D_0^{I_2}}{RT}\right)$$
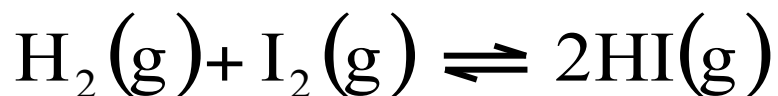
K directly from quantized molecular energy levels!!

VALIDATION

$$K(T) = \left(\frac{m_{HI}^2}{m_{H_2}m_{I_2}}\right)^{3/2} \cdot \left(\frac{4\Theta_{rot}^{H_2}\Theta_{rot}^{I_2}}{\left(\Theta_{rot}^{HI}\right)^2}\right) \cdot \frac{\left(1-e^{-\Theta_{vib}^{H_2}/T}\right)\left(1-e^{-\Theta_{vib}^{I_2}/T}\right)}{\left(1-e^{-\Theta_{vib}^{HI}/T}\right)^2} \cdot \exp\left(\frac{2D_0^{HI}-D_0^{H_2}-D_0^{I_2}}{RT}\right)$$

Predicted (curve) vs. measured (points)

$\Delta_r \overline{H} = -12.9 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta_r \overline{H} = -13.4 \text{ kJ} \cdot \text{mol}^{-1}$

At high T (left) the rigid rotor and harmonic oscillator approximations in the partition functions begin to fail

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

Next: Review of Module 12