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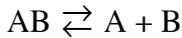
5.62 Physical Chemistry II  
Spring 2008

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## 5.62 Lecture #17: Chemical Equilibrium. II. Examples

Readings: Hill, pp. 182-187  
 Maczek, pp. 83-92  
 Metiu, pp. 191-196

### 2 Dissociation of a Diatomic Molecule



$$K_p = \frac{(q_A^*/N)(q_B^*/N)}{(q_{AB}^*/N)} e^{+\Delta D_0^0/RT} \text{ [unitless]} = \frac{(p_A/p^\circ)(p_B/p^\circ)}{(p_{AB}/p^\circ)}$$

$$K_p = \frac{(q_{\text{trans},B}/N)(q_{\text{trans},A}/N)}{(q_{\text{trans},AB}/N)} \frac{g_{0,B}g_{0,A}}{g_{0,AB}} \frac{q_{\text{rot},B}q_{\text{rot},A}}{q_{\text{rot},AB}} \frac{q_{\text{vib},B}^*q_{\text{vib},A}^*}{q_{\text{vib},AB}^*} e^{+\Delta D_0^0/RT}$$

$$K_p = \frac{(2\pi m_B)^{3/2} (kT)^{5/2}}{h^3 p} \frac{(2\pi m_A)^{3/2} (kT)^{5/2}}{h^3 p} \frac{h^3 p}{(2\pi m_{AB})^{3/2} (kT)^{5/2}} \\ \times \frac{g_{0,B}g_{0,A}}{g_{0,AB}} \cdot 1 \cdot 1 \cdot \frac{\sigma_{\text{rot},AB}}{T} \cdot 1 \cdot 1 \cdot (1 - e^{-\theta_{\text{vib},AB}/T}) e^{+\Delta D_0^0/RT}$$

$p$  is in units of bar because the standard state  $p^\circ = 1 \text{ bar} = 10^5 \text{ pascal}$ . But all terms in statistical mechanical expression for  $K_p$  are evaluated in S. I. units. Be careful!

$$K_p = \frac{(2\pi\mu)^{3/2} (kT)^{5/2}}{h^3 p} \frac{g_{0,B}g_{0,A}}{g_{0,AB}} \frac{\sigma_{\text{rot}}}{T} (1 - e^{-\theta_{\text{vib}}/T}) e^{+\Delta D_0^0/RT}$$

where  $\mu = \frac{m_A m_B}{m_A + m_B} = \frac{m_A m_B}{m_{AB}}$  reduced mass  
 ↑  
 kg/molecule for SI

$$I_2 \rightleftharpoons 2I \quad K_p = \frac{p_I^2}{p_{I_2}} \quad [p\text{'s in bar}]$$

$$m_I = 0.1269 \text{ kg mol}^{-1}$$

$$g_{0,I} = 4 \quad g_{0,I_2} = 1$$

$$\omega_e = 214.5 \text{ cm}^{-1}$$

$$B_e = 0.03737 \text{ cm}^{-1}$$

$$\mu_{I_2} = 0.06345 \text{ kg mol}^{-1}$$

$$\sigma_{I_2} = 2$$

$$\theta_{\text{vib}} = 308.6 \text{ K}$$

$$\theta_{\text{rot}} = 0.05377 \text{ K}$$

$$D_0^0, I_2 = 12440 \text{cm}^{-1} = 17889 \text{K} \quad (\text{determined by laser spectroscopy!})$$

[Be careful about units here!]

$$\Delta D_0^0 = \sum_p (D_0^0) - \sum_r (D_0^0) = 0 - (17889 \text{K}) = -17889 \text{K}$$

$$K_p = \frac{(2\pi \cdot 0.0634 / 6 \cdot 10^{23})^{3/2} (kT)^{5/2}}{h^3 \cdot 10^5} \frac{\sigma_{\text{vib}} \sqrt{\theta_{\text{rot}}}}{1 \cdot T} (1 - e^{-308.6/T}) e^{-17889/T}$$

$$1 \text{ bar} = 10^5 \text{ pascal. } 1 \text{ pascal} = 1 \text{N/m}^2. \quad 1 \text{N} = 1 \text{kg m s}^{-2}$$

$$K_p = (13.115 T^{5/2}) (16) \frac{0.1074}{T} (1 - e^{-308.6/T}) e^{-17889/T}$$

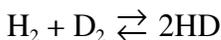
$$K_p = 22.537 T^{3/2} (1 - e^{-308.6/T}) e^{-17889/T}$$

T[K]	$K_p(\text{calc})$	$K_p(\text{expt})$	% error
1274	0.1761	0.170±0.001	3%
1173	4.9999 · 10 <sup>-2</sup>	(4.68±0.03) · 10 <sup>-2</sup>	2.6%
1073	1.14 · 10 <sup>-2</sup>	1.10 · 10 <sup>-2</sup>	3%
973	1.93 · 10 <sup>-3</sup>	1.82 · 10 <sup>-3</sup>	5.4%
872	2.13 · 10 <sup>-4</sup>	(1.84±0.17) · 10 <sup>-4</sup>	-14%

probably more accurate than expt because  $K_p$  is so small at low T, that partial pressure of dissociated I atoms is too small to measure accurately

M. J. Perlman and G. K. Rollefson, *J. Chem. Phys.* **9**, 362 (1941)

3 Isotope Exchange Reaction



$$K_p = \left[ \frac{(q_{\text{HD}}^*/N)^2}{(q_{\text{H}_2}^*/N)(q_{\text{D}_2}^*/N)} \right] e^{+\Delta D_0^0/RT}$$

$$K_p = \frac{(q_{\text{trans,HD}}/N)^2}{(q_{\text{trans,H}_2}/N)(q_{\text{trans,D}_2}/N)} \frac{g_{0,\text{HD}}^2}{g_{0,\text{H}_2} g_{0,\text{D}_2}} \frac{q_{\text{vib,HD}}^{*2}}{q_{\text{vib,H}_2}^* q_{\text{vib,D}_2}^*} \frac{q_{\text{rot,HD}}^2}{q_{\text{rot,H}_2} q_{\text{rot,D}_2}} e^{+\Delta D_0^0/RT}$$

$$K_p = \frac{(2\pi m_{\text{HD}})^3 (kT)^5}{h^6 p^2} \frac{h^3 p}{(2\pi m_{\text{H}_2})^{3/2} (kT)^{5/2}} \frac{h^3 p}{(2\pi m_{\text{D}_2})^{3/2} (kT)^{5/2}} \frac{g_{0,\text{HD}}^2}{g_{0,\text{H}_2} g_{0,\text{D}_2}}$$

$$\frac{(1 - e^{-\theta_{\text{vib,H}_2}/T})(1 - e^{-\theta_{\text{vib,D}_2}/T})}{(1 - e^{-\theta_{\text{vib,HD}}/T})^2} \left( \frac{kT}{hcB_e^{\text{HD}} \sigma_{\text{HD}}} \right)^2 \left( \frac{hcB_e^{\text{H}_2} \sigma_{\text{H}_2}}{kT} \right) \left( \frac{hcB_e^{\text{D}_2} \sigma_{\text{D}_2}}{kT} \right) e^{+\Delta D_0^0/RT}$$

$$m_{\text{H}_2} = 2 \text{ amu} \quad \sigma_{\text{H}_2} = 2 \quad g_0(\text{H}_2) = 1 \quad D_0^0(\text{H}_2) = 36,100 \text{ cm}^{-1}$$

$$m_{\text{HD}} = 3 \text{ amu} \quad \sigma_{\text{HD}} = 1 \quad g_0(\text{HD}) = 1 \quad D_0^0(\text{HD}) = 36,394 \text{ cm}^{-1}$$

$$m_{\text{D}_2} = 4 \text{ amu} \quad \sigma_{\text{D}_2} = 2 \quad g_0(\text{D}_2) = 1 \quad D_0^0(\text{D}_2) = 36,742 \text{ cm}^{-1}$$

$$\omega_e(\text{H}_2) = 4401 \text{ cm}^{-1} \quad \theta_{\text{vib}}^{\text{H}_2} = 6337 \text{ K} \quad B_e(\text{H}_2) = 60.8 \text{ cm}^{-1}$$

$$\omega_e(\text{HD}) = 3813 \text{ cm}^{-1} \quad \theta_{\text{vib}}^{\text{HD}} = 5419 \text{ K} \quad B_e(\text{HD}) = 45.7 \text{ cm}^{-1}$$

$$\omega_e(\text{D}_2) = 3116 \text{ cm}^{-1} \quad \theta_{\text{vib}}^{\text{D}_2} = 4487 \text{ K} \quad B_e(\text{D}_2) = 30.4 \text{ cm}^{-1}$$

$$\Delta D_0^0 = \sum_p(D_0) - \sum_r(D_0)$$

$$\begin{aligned} \Delta D_0^0 &= 2(36,394) - [36,100 + 36,742] \\ &= -54 \text{ cm}^{-1} = -78\text{K} \end{aligned}$$

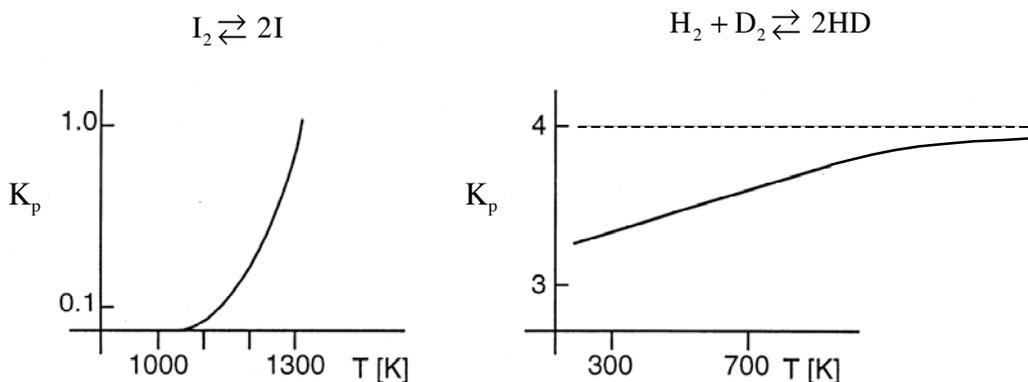
What is  $K_p$  at  $T = 298\text{K}$ ?

$$K_p = \frac{m_{\text{HD}}^3}{m_{\text{H}_2}^{3/2} m_{\text{D}_2}^{3/2}} \frac{g_{0,\text{HD}}^2}{g_{0,\text{H}_2} g_{0,\text{D}_2}} \frac{(1 - e^{-\theta_{\text{vib}}^{\text{H}_2}/T})(1 - e^{-\theta_{\text{vib}}^{\text{D}_2}/T})}{(1 - e^{-\theta_{\text{vib}}^{\text{HD}}/T})^2} \frac{B_e^{\text{H}_2} B_e^{\text{D}_2}}{(B_e^{\text{HD}})^2} \frac{\sigma_{\text{H}_2} \sigma_{\text{D}_2}}{\sigma_{\text{HD}}} e^{+\Delta D_0^0/RT}$$

$$K_p = \frac{(0.003/6 \cdot 10^{23})^3}{(0.002/6 \cdot 10^{23})^{3/2} (0.004/6 \cdot 10^{23})^{3/2}} \frac{1^2 (1 - e^{-4487/298})}{1 \cdot 1 (1 - e^{-5419/298})^2} \\ \times (1 - e^{-6337/298}) \frac{(60.8)(30.4) 2 \cdot 2}{(45.7)^2} \frac{1}{1} e^{-78/298} = 3.27$$

T[K]	$K_p$ [CALC]	$K_p$ [EXP]
298	3.27	3.28
383	3.47	3.50
741	3.82	3.75

### DEPENDENCE OF $K_p$ ON T



**Qualitative difference in behaviors:**

$$\text{I}_2 \rightleftharpoons 2\text{I}$$

$$K_p \approx \frac{q_{\text{trans-I}}^2}{q_{\text{trans-I}_2} q_{\text{rot}} q_{\text{vib}}} e^{+\Delta D_0^0/RT}$$

$$\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$$

$$K_p \approx \frac{q_{\text{trans,HD}}^2 q_{\text{rot,HD}}^2 q_{\text{vib,HD}}^2 e^{+\Delta D_0^0/RT}}{q_{\text{trans,H}_2} q_{\text{trans,D}_2} q_{\text{rot,H}_2} q_{\text{vib,H}_2} q_{\text{rot,D}_2} q_{\text{vib,D}_2}}$$

$q_{\text{trans 1}} \approx q_{\text{trans 2}}$   
(ignore factor of 2 in mass)

$$\left. \begin{array}{l} \text{ignoring} \\ \text{mass} \\ \text{functions} \end{array} \right\} \begin{cases} q_{\text{trans,HD}} \approx q_{\text{trans,H}_2} \approx q_{\text{trans,D}_2} \\ \left[ \frac{3^2}{2 \cdot 4} \right]^{3/2} \approx 1 \\ q_{\text{rot,H}_2} \approx q_{\text{rot,D}_2} \approx q_{\text{rot,HD}} \\ \left[ \frac{\mu_{\text{HD}}^2}{\mu_{\text{H}_2} \mu_{\text{D}_2}} \right] = \frac{(2/3)^2}{(1/2)(1)} \approx 1 \\ q_{\text{vib,H}_2} \approx q_{\text{vib,D}_2} \approx q_{\text{vib,HD}} \end{cases}$$

$$K_p \propto \frac{q_{\text{trans}}}{q_{\text{rot}} q_{\text{vib}}} e^{+\Delta D_0^0 / RT}$$

$$q_{\text{trans}} \approx 10^{30}, q_{\text{rot}} \approx 10^3, q_{\text{vib}} \approx 1, \Delta D_0^0 \approx -18,000\text{K}$$

$$K_p \propto 10^{27} e^{-18,000/T}$$

$$K_p \propto \sigma^2 e^{+\Delta D_0^0 / RT}$$

$$\Delta D_0^0 \approx -78\text{K}$$

$$K_p \propto 4e^{-78/T}$$

- \* large T dependence and large  $K_p$  because of  $10^{27}$  factor — gain in translational entropy due to change in number of moles
- \* results in shift of equilibrium toward separated atoms at high T
- \* actually  $q_{\text{trans}} \propto T^{5/2}$ ,  $\frac{1}{q_{\text{rot}}} \propto \frac{1}{T}$ , the pre-exponential factor is T-dependent
- \* as T increases, both pre-exponential and exponential factors increase and shift equilibrium toward dissociation.

“Small” values of  $K_p$ :

- \* no gain in entropy except for symmetry # (factor of 4)
- \*  $K_p \rightarrow 4$  at modest T because of small difference in zero point energy.

Recall from 5.60:

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T \Delta S^\circ(T) = -RT \ln K(T)$$

$$K(T) = \underbrace{e^{\Delta S^\circ(T)/R}}_{\text{pre-exponential factor}} e^{-\Delta H^\circ(T)/RT}$$

This gives us an intuitive understanding of the T-dependence of equilibrium constants. Mostly,  $\Delta S^\circ(T)$  is determined by change in number of moles (strong T-dependence), secondarily in changes in floppiness (approximately T-independent). Mostly  $\Delta H^\circ(T)$  is determined by bond energies (or differences in dissociation energies), but if you want to compute  $K(T)$  from microscopic quantities, use  $K(T) = e^{-\Delta G^\circ/RT}$  and use statistical mechanics to calculate  $\Delta G^\circ(T)$  directly, not both  $\Delta H^\circ(T)$  and  $\Delta S^\circ(T)$  separately.

In using statistical mechanics to compute equilibrium constants, it is computationally most compact and intuitively most instructive to assemble the relevant factors in

$$\frac{(q_C^*/N)^c (q_D^*/N)^d}{(q_A^*/N)^a (q_B^*/N)^b}$$

by assembling all of the relevant information factored according to degree of freedom

(translation)(electronic)(vibration)(rotation)

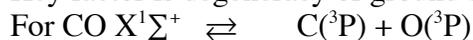
### Translation

Key factors are

- \* does the number of moles change
- \* the only species-specific quantity is mass

### Electronic

Key factor is degeneracy of ground state



g: 1                       $3 \times 3$      $3 \times 3$

The electronic factor is usually negligibly T-dependent, unless there are low-lying states. For C, the  $^3\text{P}$  state is “regular” and  $J = 0$  is lowest. For O, the  $^3\text{P}$  state is “inverted” and  $J = 2$  is lowest. So at low-T the degeneracies are 1 and 5, not 9 and 9, but at T where atoms have appreciable population,  $kT \gg$  spin-orbit splittings for atoms from the first three rows of the periodic table.

### Vibration

Atoms have  $q_{\text{vib}}^* = 1$  (no vibrational d/f). For polyatomic molecules, the lowest frequency vibrations result in small but dominant T-dependence. It is easy to guess whether a molecule has low-frequency vibrations.

### Rotation

Atoms have  $q_{\text{rot}} = 1$  (no rotational d/f). Generally, all rotations are in the high-T limit. Thus  $q_{\text{rot}} \propto T^{3/2}$  (non-linear polyatomic) or  $T^1$  (linear molecule).

For isotope effects in a diatomic molecule:  $q_{\text{vib}}$ ,  $q_{\text{rot}}$ , and zero-point energy

$$\omega_e \propto [\mu]^{-1/2}$$

$$B_e \propto [\mu]^{-1}$$

In a polyatomic molecule, the relationships between atomic masses and  $\omega_{e_i}$  ( $1 \leq i \leq 3N - 6$ ) and A, B, C are more complicated.