5.62 Physical Chemistry II
Spring 2008

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Dissociation of a Diatomic Molecule

\[ \text{AB} \rightleftharpoons \text{A} + \text{B} \]

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

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

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

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

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

where \( \mu = \frac{m_A m_B}{m_A + m_B} = \frac{m_A m_B}{m_{AB}} \) reduced mass

\[ \text{kg/molecule for SI} \]

\[ \text{I}_2 \rightleftharpoons 2\text{I} \quad K_p = \frac{p_1^2}{p_2} \quad \text{[p’s in bar]} \]

\[ m_1 = 0.1269 \text{ kg mol}^{-1} \quad \mu_{\text{I}_2} = 0.06345 \text{ kg mol}^{-1} \]

\[ g_o, I = 4 \quad g_o, I_2 = 1 \quad \sigma_{\text{I}_2} = 2 \]

\[ \omega_e = 214.5 \text{ cm}^{-1} \quad \theta_{\text{vib}} = 308.6K \]

\[ B_e = 0.03737 \text{ cm}^{-1} \quad \theta_{\text{rot}} = 0.05377K \]
\[ D_0^0, I_2 = 12440 \text{cm}^{-1} = 17889 \text{K} \quad \text{(determined by laser spectroscopy!)} \]

[Be careful about units here!]

\[ \Delta D_0^0 = \sum_p p(D_0^0) - \sum_r r(D_0^0) = 0 - (17889 \text{K}) = -17889 \text{K} \]

\[
K_p = \frac{(2\pi0.0634/6\cdot10^{21})^{3/2}(kT)^{5/2}}{h^3\cdot10^5} \frac{\sigma\sqrt{\nu}}{T} \left(1 - \exp\left(-\frac{308.6}{T}\right)\right) \exp\left(-\frac{17889}{T}\right)
\]

1 bar = \(10^5\) pascal. 1 pascal = 1N/m\(^2\). 1N = 1kg m s\(^{-2}\)

\[
K_p = (13.115 T^{5/2})(16) \frac{0.1074}{T} \left(1 - \exp\left(-\frac{308.6}{T}\right)\right) \exp\left(-\frac{17889}{T}\right)
\]

\[
K_p = 22.537 T^{3/2} \left(1 - \exp\left(-\frac{308.6}{T}\right)\right) \exp\left(-\frac{17889}{T}\right)
\]

<table>
<thead>
<tr>
<th>T[K]</th>
<th>(K_p) (calc)</th>
<th>(K_p) (expt)</th>
<th>% error</th>
</tr>
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<tbody>
<tr>
<td>1274</td>
<td>0.1761</td>
<td>0.170±0.001</td>
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</tr>
<tr>
<td>1173</td>
<td>4.9999 \cdot 10^{-2}</td>
<td>(4.68±0.03) \cdot 10^{-2}</td>
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</tr>
<tr>
<td>1073</td>
<td>1.14 \cdot 10^{-2}</td>
<td>1.10 \cdot 10^{-2}</td>
<td>3%</td>
</tr>
<tr>
<td>973</td>
<td>1.93 \cdot 10^{-3}</td>
<td>1.82 \cdot 10^{-3}</td>
<td>5.4%</td>
</tr>
<tr>
<td>872</td>
<td>2.13 \cdot 10^{-4}</td>
<td>(1.84±0.17) \cdot 10^{-4}</td>
<td>-14%</td>
</tr>
</tbody>
</table>

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

Isotope Exchange Reaction

\[ \text{H}_2 + \text{D}_2 \overset{\text{r}}\rightarrow 2\text{HD} \]

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

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

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

\[ \frac{(1 - e^{-\theta_{\text{vib,H}_2}/T})(1 - e^{-\theta_{\text{vib,D}_2}/T})}{(1 - e^{-\theta_{\text{vib,HD}}/T})^2} \left( \frac{kT}{hcB_e \sigma_{\text{HD}}} \right) \left( \frac{hcB_e H_2 \sigma_{\text{H}_2}}{kT} \right) \left( \frac{hcB_e D_2 \sigma_{\text{D}_2}}{kT} \right) e^{\Delta D_0^0/RT} \]

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

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

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

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

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

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

\[ \Delta D_0^0 = \sum_p p(D_0) - \sum_r r(D_0) \]

\[ \Delta D_0^0 = 2(36,394) - [36,100 + 36,742] \]

\[ = -54 \text{ cm}^{-1} = -78 \text{ K} \]
What is $K_p$ at $T = 298$K?

$$K_p = \frac{m_{HD}^3}{m_{H_2}^3 m_{D_2}^3} \left( \frac{g_{0,HD}^2}{g_{0,H_2} g_{0,D_2}} \right) \left( 1 - e^{-\theta_{vib}^H / T} \right) \left( 1 - e^{-\theta_{vib}^D / T} \right) \frac{B_e^2 B_e D_2^2}{(B_{e}^H)^2} \frac{\sigma_{H_2} \sigma_{D_2}}{\sigma_{HD}} e^{+\Delta D_0^0 / RT}$$

$$K_p = \frac{(0.003 / 6 \cdot 10^{23})^3}{(0.002 / 6.10^{23})^{3/2}} \frac{1^2 (1 - e^{-4487/298})}{(0.004 / 6.10^{23})^{3/2}} \frac{1 \cdot 1 (1 - e^{-5419/298})^2}{2} \times (1 - e^{-6337/298}) \frac{(60.8)(30.4)}{(45.7)^2} \frac{2 \cdot 2}{1} e^{-78/298} = 3.27$$

<table>
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<tr>
<td>298</td>
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<td>3.28</td>
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<tr>
<td>383</td>
<td>3.47</td>
<td>3.50</td>
</tr>
<tr>
<td>741</td>
<td>3.82</td>
<td>3.75</td>
</tr>
</tbody>
</table>

**DEPENDENCE OF $K_p$ ON $T$**

$I_2 \not\approx 2I$

$$K_p \approx \frac{q_{trans - I_2}^2}{q_{trans - 2I_2} q_{rot} q_{vib}} e^{+\Delta D_0^0 / RT}$$

$H_2 + D_2 \not\approx 2HD$

$$K_p \approx \frac{q_{trans,H_2}^2 q_{rot,H_2}^2 q_{vib,H_2}^2}{q_{trans,D_2} q_{rot,D_2} q_{vib,D_2}^2} e^{+\Delta D_0^0 / RT}$$

Qualitative difference in behaviors:

$I_2 \not\approx 2I$

$H_2 + D_2 \not\approx 2HD$
\[ q_{\text{trans}} \approx q_{\text{trans}} \]
(ignoring factor of 2 in mass)

\[
\begin{align*}
q_{\text{trans}, \text{HD}} & = q_{\text{trans}, \text{H}_2} = q_{\text{trans}, \text{D}_2} \\
\begin{bmatrix}
\frac{2^2}{3^2} \\
\frac{2}{4}
\end{bmatrix} & = 1 \\
\begin{bmatrix}
\mu_{\text{HD}} \\
\mu_{\text{H}_2} \mu_{\text{D}_2}
\end{bmatrix} & = \left(\frac{2}{3}\right)^2 (1/2)(1) = 1 \\
q_{\text{vib}, \text{H}_2} & = q_{\text{vib}, \text{D}_2} = q_{\text{vib}, \text{HD}}
\end{align*}
\]

\[ K_p \propto \frac{q_{\text{trans}}}{q_{\text{rot}} q_{\text{vib}}} e^{\Delta D_0^0 / RT} \]
\[ q_{\text{trans}} = 10^{30}, q_{\text{rot}} = 10^3, q_{\text{vib}} = 1, \Delta D_0^0 = -18,000K \]
\[ K_p = 10^{27} e^{-18,000 / T} \]

* 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.

Recall from 5.60:
\[
\Delta G^\circ(T) = \Delta H^\circ(T) - T \Delta S^\circ(T) = -RT \ln K(T)
\]
\[ K(T) = e^{\Delta S^\circ(T) / R} e^{-\Delta H^\circ(T) / RT} \]

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 \( K(T) = e^{-\Delta G^\circ(T) / RT} \) 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

$$\left(\frac{q^*_C/N}{q^*_D/N}\right)^c \left(\frac{q^*_B/N}{q^*_A/N}\right)^d$$

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

For CO $X^1\Sigma^+ \leftrightarrow C(3P) + O(3P)$

<table>
<thead>
<tr>
<th>g</th>
<th>$3 \times 3$</th>
<th>$3 \times 3$</th>
</tr>
</thead>
</table>

The electronic factor is usually negligibly T-dependent, unless there are low-lying states. For C, the $3P$ state is “regular” and $J = 0$ is lowest. For O, the $3P$ 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 $q_{vib}^* = 1$ (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 $q_{rot} = 1$ (no rotational d/f). Generally, all rotations are in the high-T limit. Thus $q_{rot} \propto T^{3/2}$ (non-linear polyatomic) or $T^1$ (linear molecule).

For isotope effects in a diatomic molecule: $q_{vib}$, $q_{rot}$, 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 $\omega_{ei}$ ($1 \leq i \leq 3N - 6$) and A, B, C are more complicated.

revised 1/10/08 12:55 PM