Temperature effects

\[ k(T) = \exp \left( -\frac{\Delta G^0_{rxn}}{RT} \right) = \exp \left( -\frac{\Xi v_i h_i^0}{RT} \right) \]

\[ \frac{d\ln k}{dT} = \frac{d}{dT} \left[ -\frac{\Delta G^0_{rxn}}{RT} \right] = \frac{\Delta H^0_{rxn}}{RT^2} \text{ van't Hoff relationship} \]

Proof \[ \partial (G/T) = \frac{1}{T} \partial G - \frac{G}{T^2} = \frac{S}{T} \cdot \frac{G}{T} = \frac{T S - G}{T^2} = \frac{\Delta H^0}{T^2} \]

\[ \Delta H^0_{rxn} (T=298 \, K) \text{ obtained from } \Delta H^0_{form} (T=298 \, K) \]

as described in App. I from the WebBook

\[ \Delta H^0_{rxn} > 0 \text{ endothermic } \text{rxn} \text{ K↑ as } T↑ \]

\[ \Delta H^0_{rxn} < 0 \text{ exothermic } \text{rxn} \text{ K↓ as } T↑ \]

Le Châtelier's Principle: systems shift their equilibrium to counteract external changes

\[ \text{If } \frac{\Delta H^0_{rxn}}{RT^2} \text{ n const. with } T, \text{ integrate} \]

\[ \ln \frac{k(T_2)}{k(T_1)} = -\frac{\Delta H^0_{rxn}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

In general,

\[ \Delta H^0_{rxn} (T_i) = \Delta H^0_{rxn} (T_o) + \int_{T_o}^{T_i} \Delta C_p^0 (T) dT \]

where \[ \Delta C_p = \sum_i \frac{v_i}{E_i} v_i C_p^0 \]
Pressure effects

Liquid and solid fugacities are approximately independent of pressure.

Gas fugacities at low pressures are

\[ \phi_i = P_i = y_i P \]

For an all-gas reaction,

\[ y_1 v_1 + y_2 v_2 + \cdots + y_n v_n \cdot P = k(T) \]

\[ \Rightarrow \quad y_1^{v_1} y_2^{v_2} \cdots y_n^{v_n} = \frac{k(T)}{P^{\Sigma v_i}} \]

as \( P \uparrow \) if \( \Sigma v_i > 0 \) (reaction produces a net mole gain) "effective" constant \( \uparrow \)

If \( \Sigma v_i < 0 \) (net mole loss) \( \Rightarrow \) effective constant \( \uparrow \)

\( \Sigma v_i = 0 \) no effect

Example 10.3: NH₃ synthesis

\[ \text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3 \quad \text{ : fertilizers!} \]

Conversion from stoichiometric mixture for \( P = 5-\)20 bar,

Even though pressures are moderately high, assume ideal gas

\( P^\circ \) for ideal gas state from Shomate Equ.,

\[ P^\circ = a + b \left( \frac{T}{1000} \right) + c \left( \frac{T}{1000} \right)^2 + d \left( \frac{T}{1000} \right)^3 + e \left( \frac{1000}{T} \right)^2 \]

Constants \( a, b, c, d, e \) from Webbook
Instead of integrating van't Hoff equation, obtain

\[
\Delta H^\circ_{\text{form}} (T_2) = \Delta H^\circ_{\text{form}} (T_1) + \int_{T_1}^{T_2} \frac{C_p^\circ}{T} \, dT
\]

\[
S^\circ (T_2) = S^\circ (T_1) + \int_{T_1}^{T_2} \frac{C_p^\circ}{T} \, dT
\]

Shomate equation for \( C_p^\circ \) and \( C_p^\circ / T \) readily integrated. Integration constants at \( T_\phi = 298 \, \text{K} \) listed directly in WebBook.

\[
\Delta H^\circ_{\text{form}} (T) = \Delta H^\circ_{\text{form}} (298 \, \text{K}) + a + b \frac{t^2}{2} + c \frac{t^4}{4} + \frac{d}{t^2} + e + f
\]

\[
S^\circ (T) = S^\circ (298 \, \text{K}) + a \ln t + b t + \frac{c t^2}{2} + \frac{d t^3}{3} - \frac{e}{t^2} + g
\]

\[
\Delta G^\circ_{\text{rxn}} (T) = \Delta H^\circ_{\text{rxn}} (T) - T \sum_{i=1}^{n} V_i S_i^\circ = \sum_{i=1}^{n} V_i \left( \frac{\Delta H^\circ_{\text{form}}}{T} - T S_i^\circ \right)
\]

<table>
<thead>
<tr>
<th>Species</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>1 - ( \frac{2}{3} )</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>3 - ( \frac{3}{3} )</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>( \frac{2}{3} )</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>( 4 - \frac{2}{3} )</td>
</tr>
</tbody>
</table>

\[
K = e^{\frac{-\Delta G^\circ_{\text{rxn}}}{RT}} = \frac{\delta N_{\text{H}_3}}{\delta N_{\text{N}_2} \delta N_{\text{H}_2}}
\]

\[
(2\frac{1}{3})^2 \left(4 - \frac{2}{3}\right)^2 \frac{1}{(1 - \frac{2}{3})(3 - \frac{3}{3})^3} = p^2 K
\]

Solve using Excel’s Goal Seek

<table>
<thead>
<tr>
<th>Core</th>
<th>( T/K )</th>
<th>( P/\text{kPa} )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>500</td>
<td>20</td>
<td>0.631</td>
</tr>
<tr>
<td>b</td>
<td>600</td>
<td>20</td>
<td>0.309</td>
</tr>
<tr>
<td>c</td>
<td>500</td>
<td>5</td>
<td>0.429</td>
</tr>
<tr>
<td>d</td>
<td>700</td>
<td>200</td>
<td>0.466</td>
</tr>
</tbody>
</table>

Le Chatelier’s rule:

Exothermic reaction, consumes 

Le Chatelier’s rule:
As $T \uparrow$ at const $P$, conversion ↓
As $P \uparrow$ at const $T$, conversion ↑

Commercial production: Haber-Bosch process, (Nobel 1918, 1931) operates at 300-550 °C (570-820 K), $P = 150-250$ bar.

At lower $T$ equilibrium is favorable, but rates are too slow!
At high $P$ both rates and equilibrium more favorable.

Why not even higher $P$? → Cost of equipment + power for compression.