

Temperature effects

$$k(T) = \exp\left(-\frac{\Delta G_{rxn}^{\circ}}{RT}\right) = \exp\left(-\frac{\sum_i \nu_i \mu_i^{\circ}}{RT}\right)$$

$$\frac{d \ln k}{dT} = \frac{d}{dT} \left[-\frac{\Delta G_{rxn}^{\circ}}{RT} \right] = \frac{\Delta H_{rxn}^{\circ}}{RT^2} \quad \text{van't Hoff relationship}$$

$$\text{Proof } \frac{\partial(G/T)}{\partial T} = \frac{1}{T} \frac{\partial G}{\partial T} - \frac{G}{T^2} = \frac{S}{T} - \frac{G}{T^2} = \frac{TS - G}{T^2} = \frac{H}{T^2}$$

ΔH_{rxn}° ($T=298\text{K}$) obtained from ΔH_{form}° ($T=298\text{K}$) as described in App. I from the webBook

$\Delta H_{rxn}^{\circ} > 0$ endothermic rxn $k \uparrow$ as $T \uparrow$

$\Delta H_{rxn}^{\circ} < 0$ exothermic rxn $k \downarrow$ as $T \uparrow$

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

If $\frac{\Delta H_{rxn}^{\circ}}{RT^2} \sim \text{const.}$ with T , integrate

$$\ln \frac{k(T_2)}{k(T_1)} = -\frac{\Delta H_{rxn}^{\circ}}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

In general,

$$\Delta H_{rxn}^{\circ}(T_1) = \Delta H_{rxn}^{\circ}(T_0) + \int_{T_0}^{T_1} \Delta C_p^{\circ}(T) dT$$

$$\text{where } \Delta C_p^{\circ} = \sum_{i=1}^n \nu_i C_{p,i}^{\circ}$$

Pressure effects

Liquid and solid fugacities are approximately independent of pressure.

Gas fugacities at low pressures are

$$f_i = P_i = y_i P$$

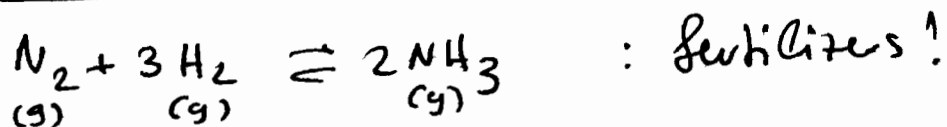
for an all-gas reaction, $y_1^{v_1} y_2^{v_2} \dots y_n^{v_n} \cdot P^{\sum v_i} = k(T)$

$$\Rightarrow y_1^{v_1} y_2^{v_2} \dots y_n^{v_n} = \frac{k(T)}{P^{\sum v_i}}$$

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

if $\sum v_i < 0$ (net mole loss) \rightarrow
effective constant \uparrow

$\sum v_i = 0$ no effect

Example 10.3: NH_3 synthesis

conversion from stoich. mixture for $P = 5-20 \text{ bar}$,
 $T = 500, 600 \text{ K}$

Even though pressures are moderately high, assume ideal gases

C_p° for ideal gas state from Shomate Equ.,

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

constants a, b, c, d, e from WebBook

Instead of integrating van't Hoff equation, obtain

$$\Delta H_{\text{form}}^{\circ}(T_2) = \Delta H_{\text{form}}^{\circ}(T_1) + \int_{T_1}^{T_2} C_p^{\circ} dT$$

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

Shomate equation for C_p° and C_p°/T readily integrated. / Integration constants at $T_0 = 298 \text{ K}$ listed directly in webBook.

See
webBook

$$\Delta H_{\text{form}}^{\circ}(T) = \Delta H_{\text{form}}^{\circ}(298\text{K}) + at + b \frac{t^2}{2} + c \frac{t^3}{3} + d \frac{t^4}{4} + \frac{e}{t} + f$$

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

$t = T/1000$ & constants listed

$$\Delta G_{\text{rxn}}^{\circ}(T) = \Delta H_{\text{rxn}}^{\circ}(T) - T \sum_{i=1}^{\nu} \nu_i S_i^{\circ} = \sum_{i=1}^{\nu} \nu_i \left[\Delta H_{\text{form},i}^{\circ} - T S_i^{\circ} \right]$$

See
Excel
work
sheet

Species	Amount
N_2	1-3
H_2	3-33
NH_3	23
total	4-23

$$k = e^{-\frac{\Delta G_{\text{rxn}}^{\circ}}{RT}} = \frac{f_{NH_3}^2}{f_{N_2} f_{H_2}^3} \Rightarrow$$

$$\Rightarrow \frac{(23)^2 (4-23)^2}{(1-3)(3-33)^3} = P^2 K$$

→ Solve using Excel's Goal Seek

Case	T/K	P/bar	ξ
a	500	20	0.671
b	600	20	0.309
c	500	5	0.429
d	700	200	0.466

Le Chatelier's rule:

Exothermic reaction,
consumes moles

CBE 246 T and P effects on reactions (4)

As $T \uparrow$ at const P , conversion \downarrow

As $P \uparrow$ at const T , conversion \uparrow

Commercial production: Haber-Bosch process,
(Nobel 1918, 1931) operates at $300-550^\circ\text{C}$
($570-820\text{ K}$), $P = 150-250\text{ bar}$

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 ? \rightarrow Cost of
equipment + power
for compression