

Thermodynamics: Phenomenology

- Work and other forms of energy
 - Transfer and dissipation
- 1. & 2. Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
 - Technological applications, cyclic engines
- **Free energy in chemical reactions**
- Real gases equation of state
 - Technological applications
- Phase equilibria

Reading Assignments
Weeks 13&14

LN V-VI:

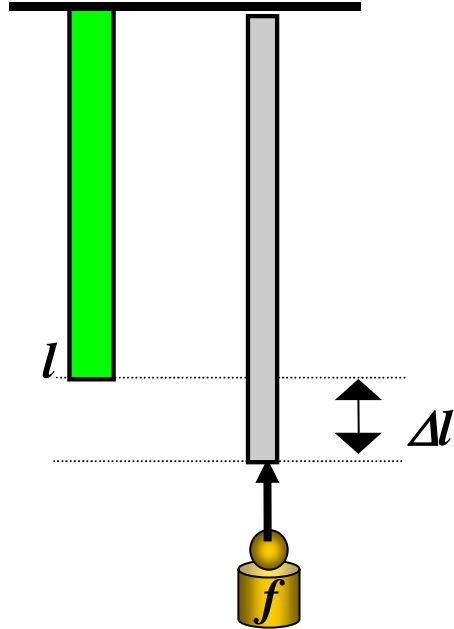
Kondepudi Ch. 6 & 7

McQuarrie & Simon
Ch. 12

1

Free Energy and Work

Rubber Contraction



Gibbs' free energy: work potential of system (other than trivial pV work) at **constant p, T**. Can be made very large at high T and $\Delta S < 0$

Reversible contraction process:

$$\Delta G = \Delta H - T \cdot \Delta S = \Delta (H - T \cdot S) = w_{\text{rev}} < 0$$

reversible work recovers 100% of G!

Irreversible contraction:

$$\Delta G < w < 0$$

Less than 100% of the potential ΔG is converted into useful work, waste heat!

Use sign convention consistently!

Even if $\Delta H > 0$ (endoth.), the system can be in equilibrium.

With $\Delta G < 0$, additional work can be done $w_{\text{rev}} < w_{\text{irrev}}$.

Free Energy of an Ideal Gas

$$n \text{ moles} : dF = -SdT - pdV; \quad S = \frac{5}{2}nR + nR \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right]$$

$$\left(\frac{\partial F}{\partial T} \right)_v = -s = -\frac{5}{2}R - R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right]$$

$$\left(\frac{\partial F}{\partial v} \right)_T = -p = -\frac{RT}{v}$$

$$dF = - \left[\frac{5}{2}R + R \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right] dT - \left[\frac{RT}{v} \right] dv$$

$$F = -nRT \left\{ 1 + \ln \left[\frac{v}{v_0} \left(\frac{T}{T_0} \right)^{3/2} \right] \right\}$$

Natural Variables of the Free Energy

$$G = H - T \cdot S = (U + p \cdot V) - T \cdot S$$

$$\begin{aligned} dG &= dU + p dV + V dp - T dS - S dT = \\ &= [T dS - p dV] + p dV + V dp - T dS - S dT \\ &= V \cdot dp - S \cdot dT \end{aligned}$$

$$\underline{G = G(p, T)}$$

Similar for Helmholtz energy

$$\underline{F = F(V, T)}$$

Thermodynamical Potential Energies

- $dU = T \cdot dS - p \cdot dV + \mu \cdot dN$ Internal Energy
- $dF = -S \cdot dT - p \cdot dV + \mu \cdot dN$ Helmholtz FE
- $dH = T \cdot dS + V \cdot dp + \mu \cdot dN$ Enthalpy
- $dG = -S \cdot dT + V \cdot dp + \mu \cdot dN$ Gibbs' FE

Integrals

Isothermal: $dT = 0$

$$dG = V \cdot dp$$

ideal gas : $dG = nRT \cdot dp/p$

$$\rightarrow \underline{G(p) = G(p_0) + nRT \cdot \ln(p/p_0)}$$

$G(p_0, T_0) = G^\circ$ Standard Free Energy

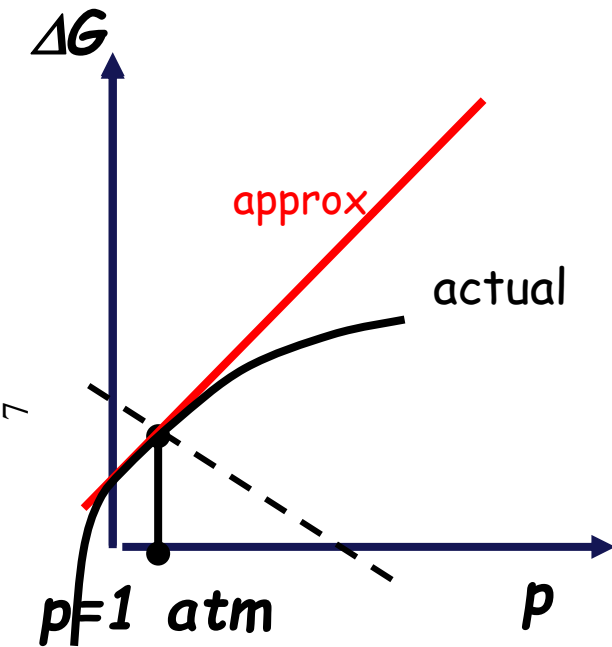
Isobaric: $dp = 0$

$$dG = -S \cdot dT \quad (\Delta G/\Delta T)_p = -S$$

ideal gas : $G = H + T \cdot (\Delta G/\Delta T)_p$

$$\rightarrow \underline{G(T)/T = G(T_0)/T_0 + \Delta [H(T)/T^2]dT}$$

p-Dependence of the Free Energy



Tabulated values: $\Delta G^\circ(T=298\text{K}, p=1\text{atm})$ p-dependence for T-const.:

$$\begin{aligned}\Delta G &= \Delta[H - T \cdot S] = \Delta U + \Delta[p \cdot V] - T \cdot \Delta S = \\ &= q - p \cdot \Delta V + [p \cdot \Delta V + \Delta p \cdot V] - T \cdot \Delta S \\ &= V \cdot \Delta p\end{aligned}$$

For an ideal gas 1 \rightarrow 2:

$$\begin{aligned}G(p_2) - G(p_1) &= \int_{p_1}^{p_2} V(p) dp = \\ &= \int_{p_1}^{p_2} \frac{nRT}{p} dp = nRT \cdot \ln\left(\frac{p_2}{p_1}\right)\end{aligned}$$

If V independent of pressure: $G(p_2) - G(p_1) = V (p_2 - p_1)$
(solid, liquid)

Example: p Dependence of G

Nitrogen at $T = 298 \text{ K}$, $p = 1 \text{ atm}$: standard free energy
 0 J/mol .

$$G = G^0 =$$

Calculate $G(10 \text{ atm}, 298\text{K})$ and $G(0.2 \text{ atm}, 298\text{K})$

Ideal gas $1(298\text{K}, 1\text{atm}) \rightarrow 2(298\text{K}, 10\text{atm})$:

$$G(298\text{K}, 10\text{atm}) = G(298\text{K}, 1\text{atm}) + RT \cdot \ln(10) =$$

$$= 0 + 8.31 \frac{\text{J}}{\text{Kmol}} 298\text{K} \cdot 2.303 =$$

$$= 5.71 \frac{\text{kJ}}{\text{mol}}$$

Example: p Dependence of G

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 0 J/mol .

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Calculate $G(10 \text{ atm}, 298\text{K})$ and $G(0.2 \text{ atm}, 298\text{K})$

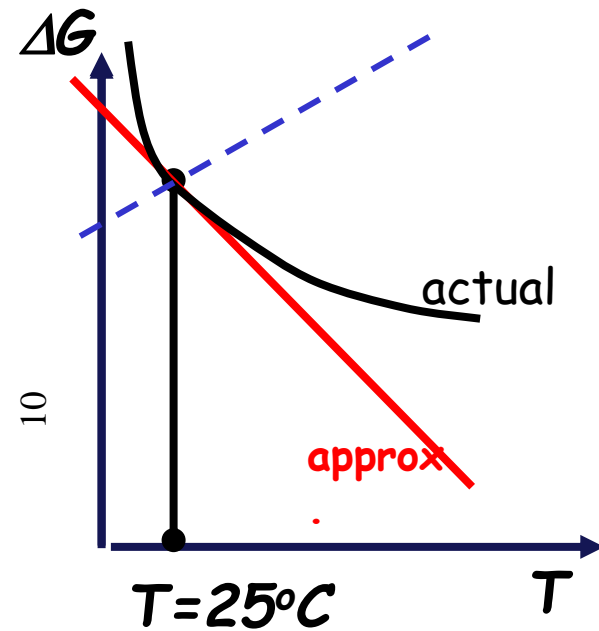
Ideal gas $1(298\text{K}, 1\text{atm}) \rightarrow 2(298\text{K}, 0.2\text{atm})$:

$$G(298\text{K}, 10\text{atm}) = G(298\text{K}, 1\text{atm}) + RT \cdot \ln(10) =$$

$$= 0 + 8.31 \frac{\text{J}}{\text{Kmol}} 298\text{K} \cdot (-1.61)$$

$$= - 3.99 \frac{\text{kJ}}{\text{mol}}$$

T-Dependence of the Free Energy



Even if $\Delta H = \text{const}$ and $\Delta S = \text{const.}$,
 $\rightarrow \Delta G = \Delta G(T)$

$$\Delta G(T) = \Delta H(25^\circ\text{C}) - T \cdot \Delta S(25^\circ\text{C})$$

use:

$$\Delta G(T) - \Delta G(25^\circ\text{C}) = -(T - 298\text{K}) \cdot \Delta S(25^\circ\text{C})$$

Sign of ΔS indicates whether ΔG increases or decreases with T : If $\Delta S > 0$, then ΔG decreases and reaction becomes easier.

$$\frac{\Delta G(T)}{T} - \frac{\Delta G(298\text{K})}{298\text{K}} = \left(\frac{1}{T} - \frac{1}{298\text{K}} \right) \Delta H(298\text{K})$$

if ΔS or ΔH strongly T -dependent:

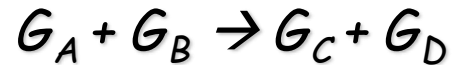
Gibbs – Helmholtz Eqn.

$$\boxed{\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = - \int_{T_1}^{T_2} \frac{\Delta H(T)}{T^2} dT}$$

Extensive Energy Variables

- All energy variables are extensive (1 LTD)

Reactions:

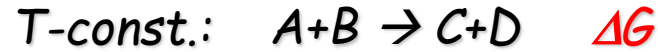
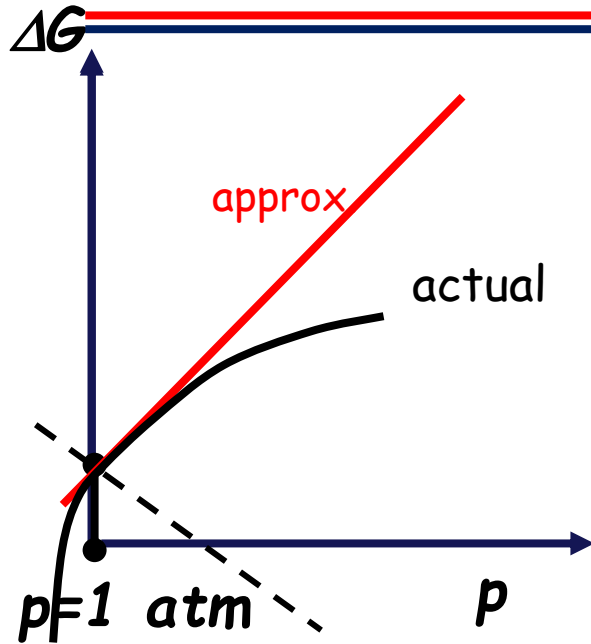


$$\Delta G = (G_C + G_D) - (G_A + G_B)$$

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Free Energy

Free Energy in Reactions



for reactants and products

$$\Delta G = G_C + G_D - G_A - G_B$$

all reactants solids or liquids: $V = \text{const}$

$$G(p_2) - G(p_1) = V \cdot (p_2 - p_1)$$

$$\Delta G(p_2) - \Delta G(p_1) = \Delta V \cdot (p_2 - p_1)$$

Sign of ΔV determines response of system(process) to pressure changes: If the process leads to expansion ($\Delta V > 0$), increasing the pressure increases ΔG (makes it less negative) and hinders the process. A process leading to compression of the system is aided by increasing the pressure. ("System tries to adapt to new environment.")

Example

Example: $C(\text{graphite}) \rightarrow C(\text{diamond})$ (all solids)

$V(\text{graphite}) = 5.33 \text{ cm}^3/\text{mole}$ $V(\text{diamond}) = 3.42 \text{ cm}^3/\text{mole}$

$\Delta G(p) = - \Delta G(1 \text{ atm}) + \Delta V \cdot (p - 1 \text{ atm}) =$ (at 25 °C)

$$= 2.84 \text{ kJ/mol} + (3.42 - 5.33) \cdot (p - 1 \text{ atm}) \text{ cm}^3/\text{mole}$$

$$\Delta G(p) = 2.84 \text{ kJ/mol} - 1.94 \cdot 10^{-4} \cdot (p - 1) \text{ kJ/mole} \quad (p \text{ in atm})$$

Q: At what pressure is equilibrium established between graphite and diamond production?

A:

Example

Example:

?

?

$$\Delta G(p) = 2.84 \text{ kJ/mol} - 1.94 \cdot 10^{-4} (p-1) \text{ kJ/mole}$$

Q: At what pressure is equilibrium established between graphite and diamond production?

A: The free energy decreases with increasing pressure, shifting the process towards more diamond production.

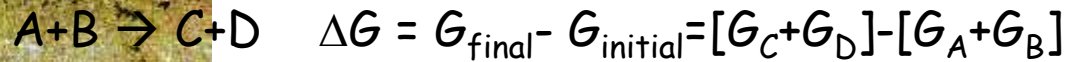
At $\Delta G(p) = 0$ equilibrium is reached,

$$2.84 \text{ kJ/mol} = 1.94 \cdot 10^{-4} \cdot (p-1) \text{ kJ/mol} \rightarrow$$

$$p-1 = (2.84/1.94) \cdot 10^4 \quad p = 15000 \text{ atm}$$

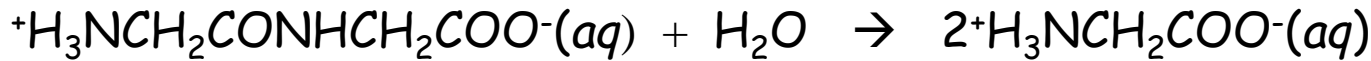
Free Energy in Reactions

($p, T: \text{const}$), otherwise G has no simple meaning



Q: Are proteins in aqueous solution (at 25°C) unstable against decay into their constituent amino acids?

Example: Glycylglycine \rightarrow 2x glycine, spontaneous at STP?



A: (G° : look up in Table)

$$\begin{aligned} \Delta G^\circ &= 2G^\circ(\text{glycine}, s) - G^\circ(\text{glycylglycine}, s) - G^\circ(\text{H}_2\text{O}, l) = \\ &= 2(-377.7) - (-490.6) - (-237.2) \text{ kJ/mol} \\ &= -27.6 \text{ kJ/mol} < 0 \end{aligned}$$

Protein is unstable (25°C). How to stabilize against hydrolysis?

Free Energy in Chemical Reactions

For reactions in the (ideal) gas phase ($V = \text{const.}$):

$$G(p_2) - G(p_1) = nRT \cdot \ln\left(\frac{p_2}{p_1}\right) \quad \text{reversible process}$$

$$\text{standard } G^0 = G(T = 25^\circ \text{C}; p = 1 \text{ atm})$$

$$G(p) = G^0 + nRT \cdot \ln(p)$$

$$\text{Reaction } A + B \rightarrow C + D \quad \Delta G = [G_C + G_D] - [G_A + G_B]$$

$$\Delta G = \Delta G^0 + RT \cdot [n_C \ln(p_C) + n_D \ln(p_D) - n_A \ln(p_A) - n_B \ln(p_B)]$$

$$\underline{\underline{\Delta G}} = \Delta G^0 + RT \cdot \ln \left[\frac{(p_C)^{n_C} \cdot (p_D)^{n_D}}{(p_A)^{n_A} \cdot (p_B)^{n_B}} \right] = \underline{\underline{\Delta G^0 + RT \cdot \ln Q}}$$

Q:
reaction
quotient

Free Energy in Chemical Reactions



$\Delta G = \Delta G^0 + RT \cdot \ln Q$ Q: reaction quotient

In Equilibrium: $\Delta G = 0 \rightarrow$

$\Delta G^0 = -RT \cdot \ln K_p$ Equilibrium Constant $K_p = Q_{equ}$

$K_p = e^{-\frac{\Delta G^0}{RT}}$ $K_p \begin{cases} < 1 \text{ not spontaneous (reverse is spontaneous)} \\ = 1 \text{ equilibrium in standard state} \\ > 1 \text{ spontaneous in standard state} \end{cases}$

$\Delta G = \Delta G^0 + RT \cdot \ln Q = -RT \cdot \ln K_p + RT \cdot \ln Q$

$\Delta G = RT \cdot \ln \frac{Q}{K_p}$ *Very important practically*

Example: Reaction Quotient and Equilibrium Constant

Calculate the free energy and equilibrium constant for the reaction



at $T = 298\text{K}$ from the reaction quotient Q , for all $p_i = 100\text{atm}$.

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First, calculate

$$K_p = e^{-\frac{\Delta G_{rxn}^0}{RT}} = \exp \left\{ + \frac{32.9 \frac{\text{kJ}}{\text{mol}}}{8.315 \frac{\text{J}}{\text{Kmol}} \cdot 298\text{K}} \right\} = e^{13.28} = 5.84 \cdot 10^5$$

Then, calculate the reaction quotient

$$Q = \frac{p^2(NH_3)}{p(N_2) \cdot p^3(H_2)} = \frac{100^2}{100 \cdot 100^3} = 10^{-4}$$

Example: Reaction Quotient and Equilibrium Constant

Calculate the free energy and equilibrium constant for the reaction



at $T = 298\text{K}$ from the reaction quotient Q , for all $p_i = 100\text{atm}$.

First, calculate

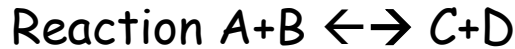
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and

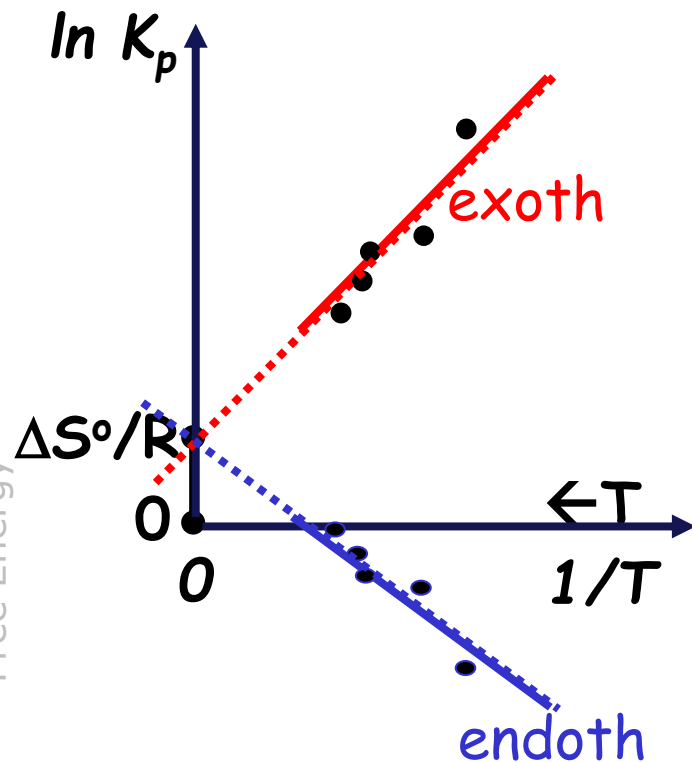
$$\Delta G_{rxn} = \Delta G_{rxn}^0 + RT \cdot \ln Q = -32.9 \frac{\text{kJ}}{\text{mol}} + 2.479 \frac{\text{kJ}}{\text{mol}} \cdot \ln(10^{-4}) = -55.7 \frac{\text{kJ}}{\text{mol}}$$

$\Delta G_{rxn} < 0$ *Reaction is spontaneous at these pressures*

T-Dependence of Equilibrium



T dependence of G derives from its components, H and S



$$RT \cdot \ln K_p = -\Delta G^0 = -\Delta H^0 + T\Delta S^0$$

$$\ln K_p = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

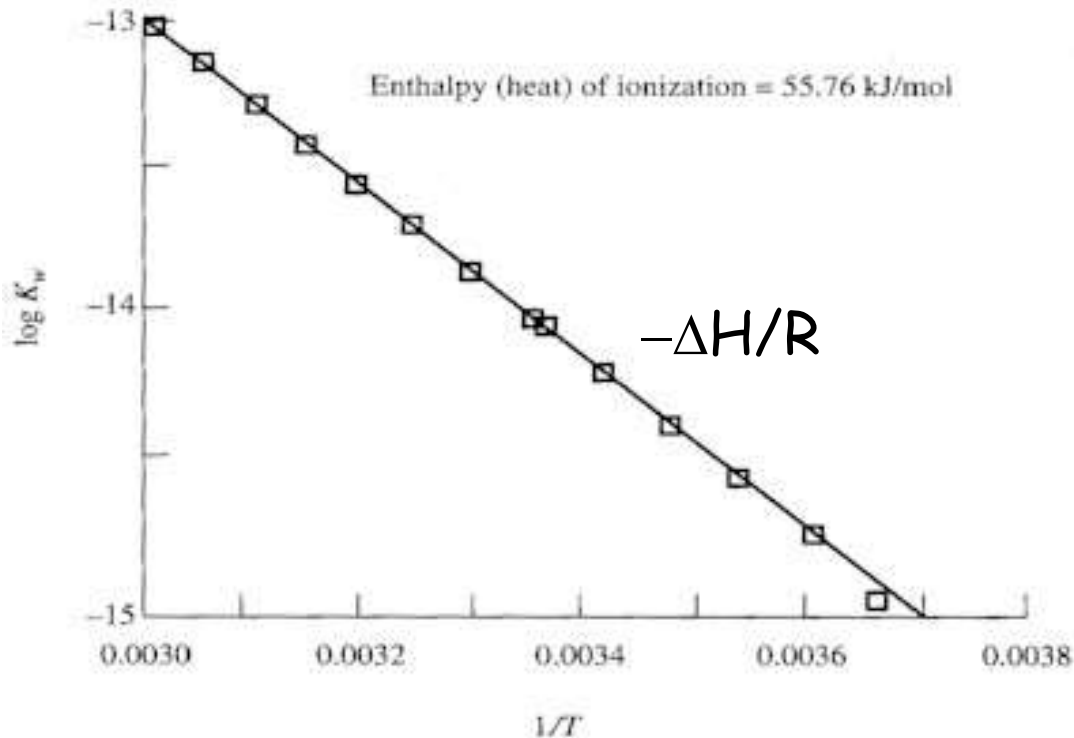
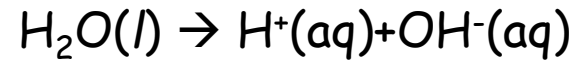
$$\ln K_p(T) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T}$$

Appr. linear function, sign ΔH^0 determines sign of slope.

Increasing T shifts equilibrium for exoth. ($\Delta H < 0$) reaction to reactants: **System adapts to environment (Least Resistance) LeChatelier.**

Ionization Constant of Water

Van 't Hoff Plot for Water



$$\ln K_w(T) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T}$$

Slope is negative:

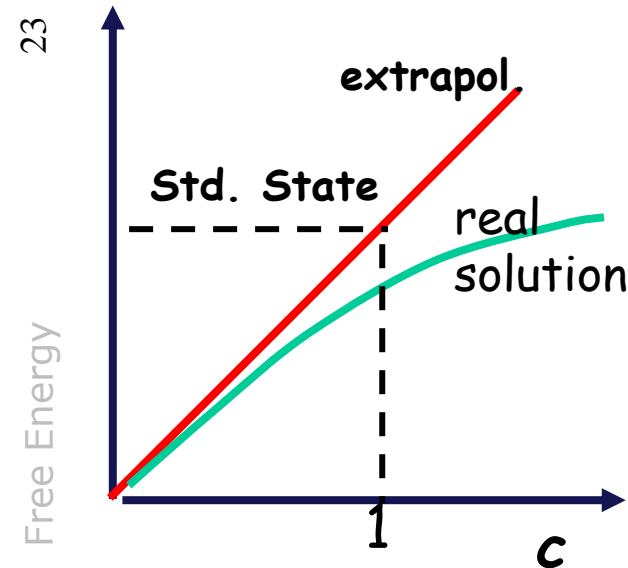
$\Delta H > 0$ endothermic

$\Delta H = 55.76 \text{ kJ/mol}$

Free Energy for Real Gases, Liquids, and Solids

Non-ideal behavior of gases (at high pressures) and of solutions.

Effective quantities simulating pressure of an ideal gas and all the associated laws.



$$\text{Activity } a: G(a) = G^{\circ} + nRT \cdot \ln(a)$$

$$G^{\circ} = G(\text{standard state}) \quad 1M$$

$$\text{ideal gas } a = p / 1\text{atm}$$

$$\text{real gas } a = \gamma \cdot p \quad \gamma = \text{activity coefficient}$$

$$\text{pure solids or liquids } a = 1$$

$$\text{solutions } a = \gamma \cdot c \quad c = \text{concentration (mol / L)}$$