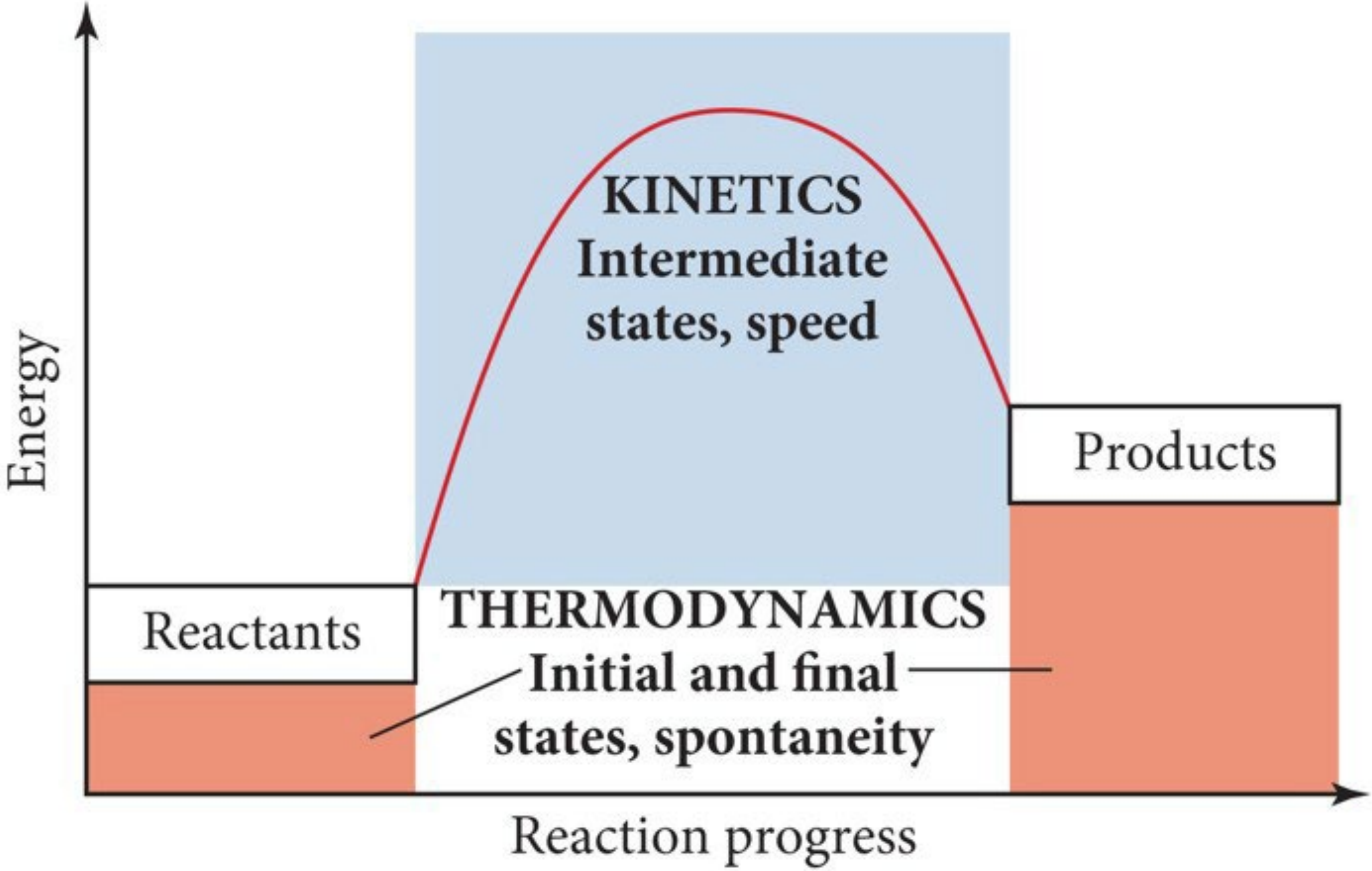
Thermodynamics versus Kinetics



Ch 103 Enthalpy ΔH

$\Delta H < 0$ exotherm

$\Delta H > 0$ endothermi

Is a reaction exo or endothermic?

heat

ΔH enthalpy

Ch 104 thermodynamics (spontaneity) will a reaction happen as written?

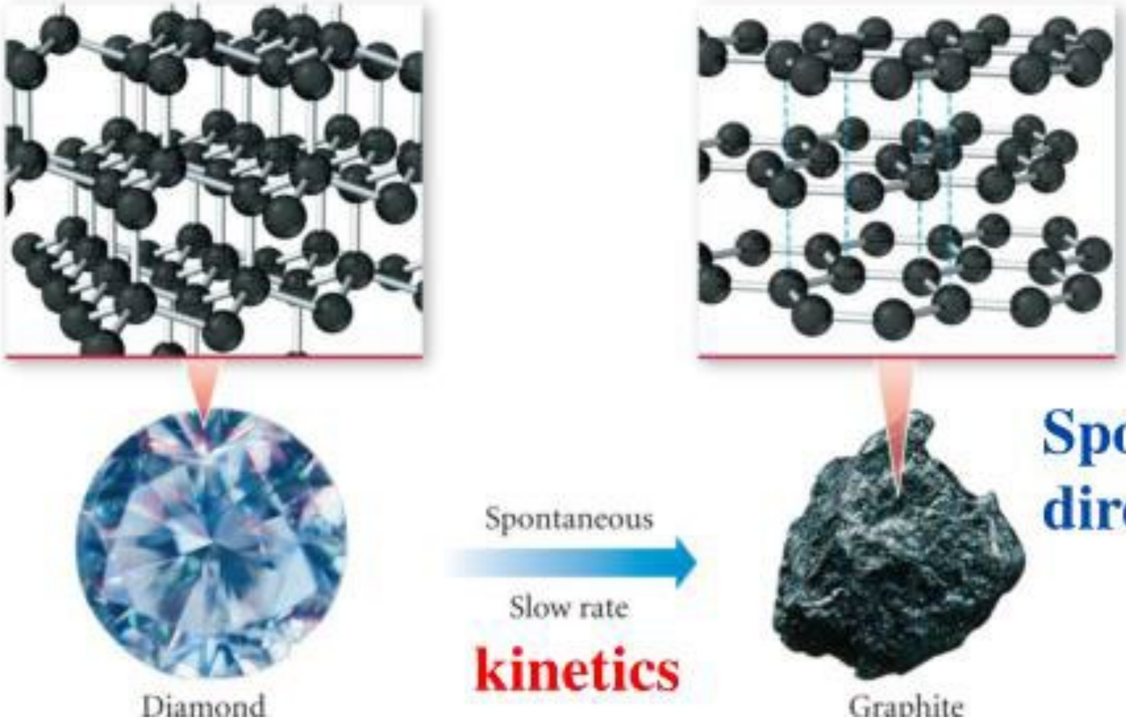
ΔH enthalpy "heat"

ΔS entropy "disorder"

Example

Diamond → Graphite

kinetics:
how fast



Spontaneity:
direction & extent

Entropy

measure of disorder of the system or surroundings

- **Entropy** is a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components increases, S.
- $S = k \ln W$, $\Delta S = k\ln(W_f/W_i)$
  - k = Boltzmann constant = 1.38×10^{-23} J/K
  - W is the number of energetically equivalent ways a system can exist.
    - Unitless

surroundings: everything else

System is the chemical reaction or process studying in lab 4

Ch103 1st law thermodynamics

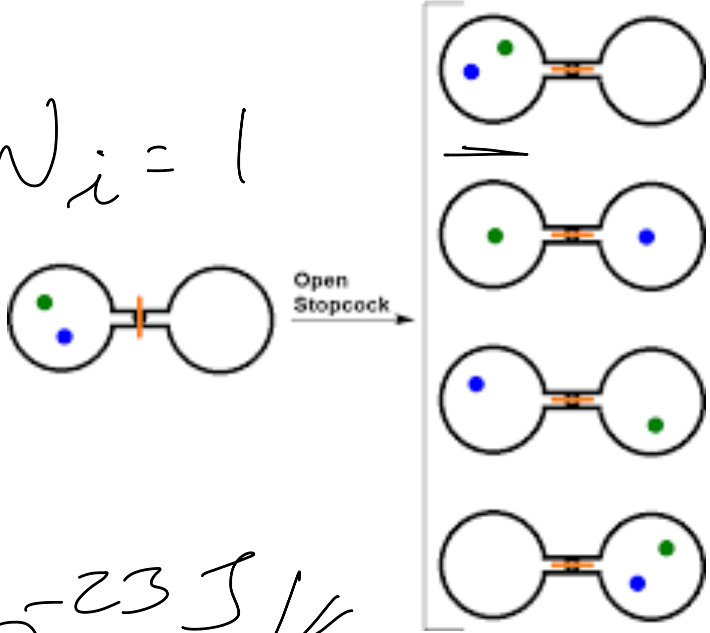
$q_{sys} + q_{surr} = 0$

energy is conserved

$\Delta H_{sys} + \Delta H_{surr} = 0$

How many microstates?

$W_i = 1$



$W_f = 4$

$\Delta S = 1.38 \times 10^{-23} \cdot \ln\left(\frac{4}{1}\right)$

$1.38 \times 10^{-23}\ J/K$

What is the ΔS?

$+\Delta S$ increased entropy

$\Delta S = K \ln\left(\frac{W_f}{W_i}\right)$

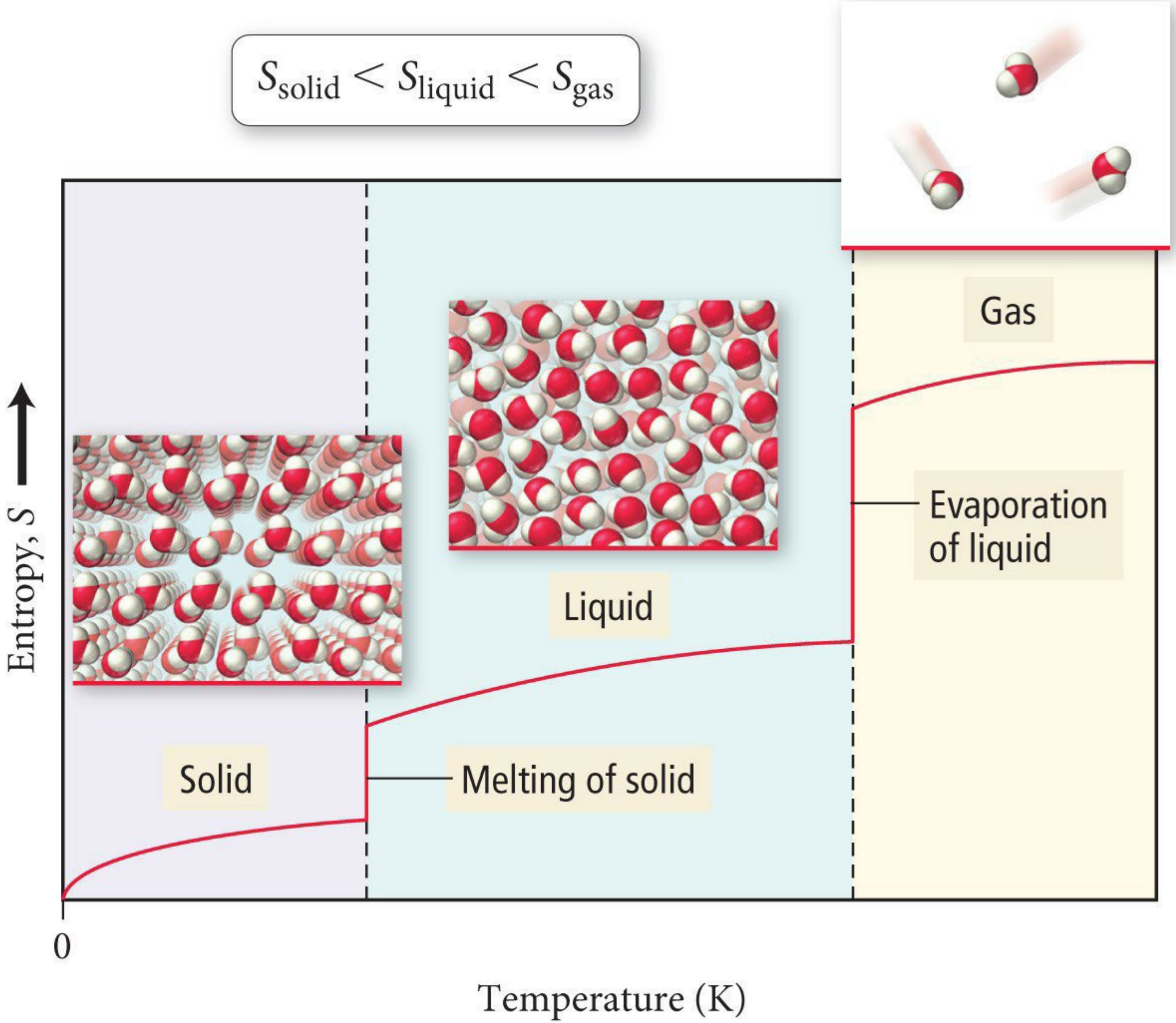
$K = 1.38 \times 10^{-23}\ \frac{J}{K}$

$-\Delta S$ decreased entropy

$\Delta S = 1.91 \times 10^{-23}\ J/K$

Entropy Change and State Change

$S_{solid} < S_{liquid} < S_{gas}$



Second Law of Thermodynamics

- **For any spontaneous process the entropy of the universe increases**

- Entropy is a state function

not specific about the path used
only need final & initial states

The Second Law of Thermodynamics

- The second law of thermodynamics says that the total entropy change of the universe must be positive for a process to be spontaneous for an irreversible process. (such as iron rusting)

$\boxed{\Delta S_{univ} > 0}$ irreversible rxn. or process

$\Delta S_{univ} = 0$ for reversible process

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

* system is the reaction

$\Delta S_{sys} = S_{final} - S_{initial}$

* $\Delta S_{rxn} = \Sigma n \Delta S^{\circ}_{products} - \Sigma n \Delta S_{reactants}$

* values in book

ΔH° or ΔS°

$\Delta S_{surr} = \frac{q_{surr}}{T}$

From thermochem

$q_{sys} + q_{surr} = 0$

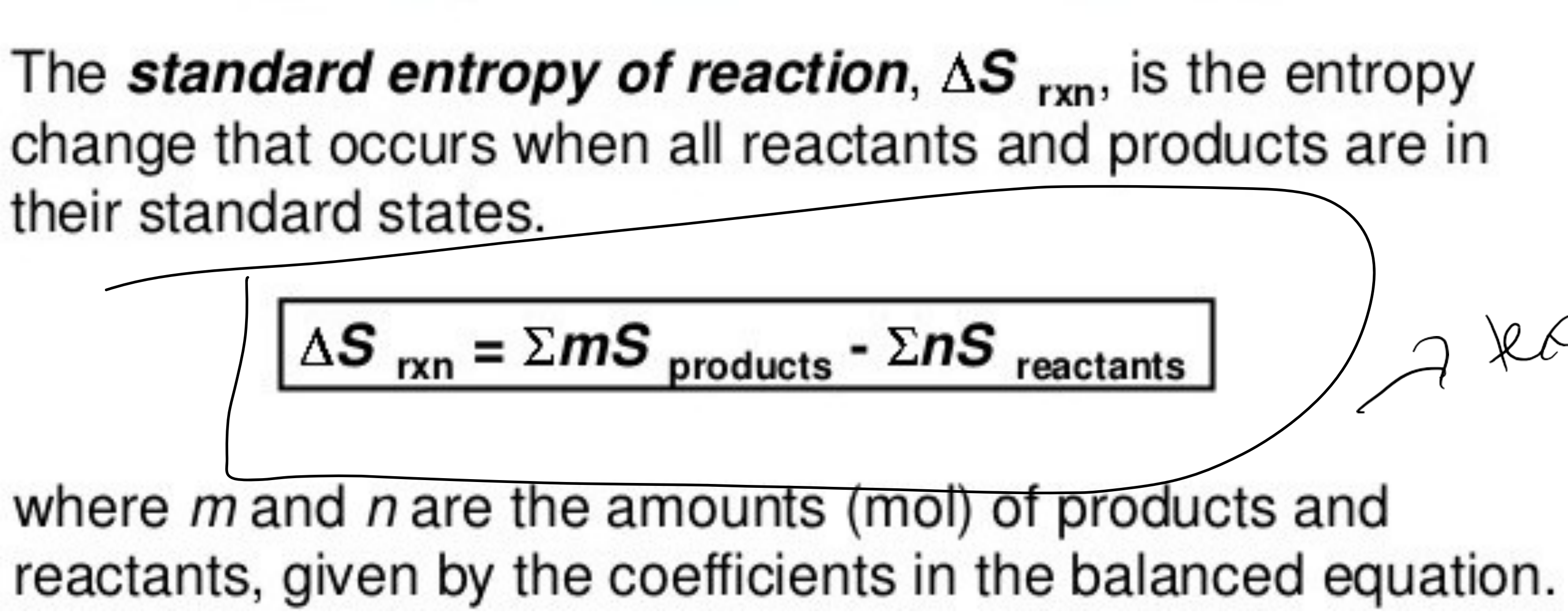
$q_{surr} = -q_{sys}$

25.0°C for gases,
1atm

The third law of thermodynamics

For a perfect crystal at absolute zero, the entropy is 0 J/mol-K

Quantifying Entropy Changes in the system



The ***standard entropy of reaction***, ΔS_{rxn}, is the entropy change that occurs when all reactants and products are in their standard states.

$$\boxed{\Delta S_{rxn} = \Sigma m S_{products} - \Sigma n S_{reactants}}$$

textbook values

where *m* and *n* are the amounts (mol) of products and reactants, given by the coefficients in the balanced equation.

Calculate ΔS_{rxn} for the balanced chemical equation:

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

Reactant or product	**$S°$ (in J/mol·K)**
$NH_3(g)$	192.8
$O_2(g)$	205.2
$NO\,(g)$	210.8
$H_2O(g)$	188.8

$\Sigma n S°_{products} - \Sigma n S°_{reactants}$

$\Delta S_{rxn}°$

$S_{rxn} = [4\,mol \cdot 210.8\,J/mol \cdot K + 6\,mol \cdot 188.8\,J/mol \cdot K$

$\Delta S_{rxn} = 175\ J/K$

System gained entropy "more" disorder after forming products

Example: calculating ΔS_{surr}

For the following reaction:

$A + B \rightarrow C$

ΔH is $-125\ kJ$

What is ΔS surroundings? @ 25.0°C

$* \Delta S_{surr} = \frac{q_{surr}}{T}$

$\Delta H_{sys} + \Delta H_{surr} = 0$

$q_{sys} + q_{surr} = 0$

$-125\ kJ = -q_{surr}$

$q_{surr} = +125\ kJ$

$$\Delta S_{surr} = \frac{+125\,kJ}{298\,K} =$$

$$0.419\,\frac{kJ}{K}$$

or

$$419\,J/K$$

Δ

$= 175 \frac{J}{K}$ $- 5\,\cancel{mol} \cdot 205 \frac{J}{\cancel{mol} \cdot K} + 4\,\cancel{mol} \cdot 192.8 \frac{J}{\cancel{mol} \cdot K}$

Gibb’s Free Energy (determines whether a reaction will happen spontaneously as written)

$\Delta G = \Delta H - T\Delta S$

* ΔG defined in terms of system

*we know $\Delta S_{univ} > 0$ for an irreversible process

How to do we go from ΔS_{univ} to ΔG_{sys}?

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$, $\Delta S_{surr} = q/T$

For irreversible process or reaction $\Delta S_{univ} > 0$

*remember first law of thermo from Ch 103

$q_{surr} + q_{sys} = 0$

$q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H_{sys}$

So… $\Delta_{surr} = q_{surr}/T$, $-\Delta H_{sys}/T$

$$\Delta_{surr} = \frac{-\Delta H_{sys}}{T}$$

$-T \cdot \Delta S_{surr} = (\Delta S_{sys} - \Delta H_{sys}/T)$, multiply both sides by -T, $\times -T$

$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$

Define $-T\Delta S_{univ}$ as ΔG "Gibb's Free energy"

$$\boxed{\mathbf{\Delta G = \Delta H - T\Delta S}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

A reaction is spontaneous when $\Delta G<0$, why?

because $\Delta G = -T\Delta S_{univ}$ & we know for irreversible process $\Delta S_{univ} > 0$, thus when ΔG is − ΔS_{univ} must have been > 0

Using Gibb's free energy example 1:

→ state function

$\Delta G = \Delta H - T\Delta S$

Consider the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

ⓐ 25.0°C and 1 atm. Calculate $\Delta G°$.

molecule	$\Delta H_f°$ kJ/mol	$S° \frac{J}{mol \cdot K}$
$SO_{2(g)}$	−297	248
$SO_{3(g)}$	−396	257
$O_{2(g)}$	0	205

Is the reaction spontaneous @ 25.0 °C?

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = \sum n\Delta H_f^\circ \text{ products} - \sum n\Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = \left[2\,\cancel{mol} \cdot -396\,\frac{kJ}{\cancel{mol}} - 2\,\cancel{mol} \cdot \left(-297\,\frac{kJ}{\cancel{mol}}\right) \cdot \emptyset\right]$$

$$\Delta H^\circ = -198\text{ kJ}$$

$$\Delta S^\circ = \sum n S^\circ \text{ products} - \sum n S^\circ \text{ reactants}$$

$$\Delta S^\circ = \left[2\,\cancel{mol} \cdot 257\,\frac{J}{\cancel{mol} \cdot K}\right] - \left[2\,mol \cdot 248\,\frac{kJ}{\cancel{mol} \cdot K}\right] + 1\,\cancel{mol} \cdot 205\,\frac{J}{\cancel{mol} \cdot K}$$

$\Delta S = -187 J/K$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -198 kJ - (298\cancel{K})(-0.187 kJ/\cancel{K})$$

$$\Delta G = -142 kJ$$

Spon

$$\Delta G = \Delta H - T\Delta S$$

what temperature is required to make this reaction non-spontaneous

$$0 = \Delta H - T\Delta S$$

$$\Delta H = T\Delta S$$

$$-198\ \text{kJ} = \boxed{T}\left(\frac{0.187125}{K}\right)$$

$$T = 1{,}058\ \text{K}$$

Using Gibb’s free energy example 2:

Ozone in the lower atmosphere is a pollutant that can form by the following reaction involving the oxidation of unburned hydrocarbons:

$$CH_4(g) + 8\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g) + 4\ O_3(g)$$

Use the standard free energies of formation to determine ΔG_{rxn} for this reaction at 25 °C.

Is the reaction spontaneous @ 25°C?

$$\Delta G^\circ = \Sigma n \Delta G_f^\circ \text{ products} - \Sigma n \Delta G_f^\circ \text{ reactants}$$

look up values in book

$$\Delta G^\circ = \left[4\,\cancel{mol}\cdot\frac{163\,kJ}{\cancel{mol}} + 2\,\cancel{mol}\cdot\frac{-228\,kJ}{\cancel{mol}} + 1\,\cancel{mol}\cdot\frac{-394\,kJ}{\cancel{mol}}\right] - \left[1\,mol\cdot\frac{-50\,kJ}{mol}\right]$$

$$\boxed{= -148\,kJ}$$

Using Gibb's Free energy example 3:

b/c State function

use Hess's Law

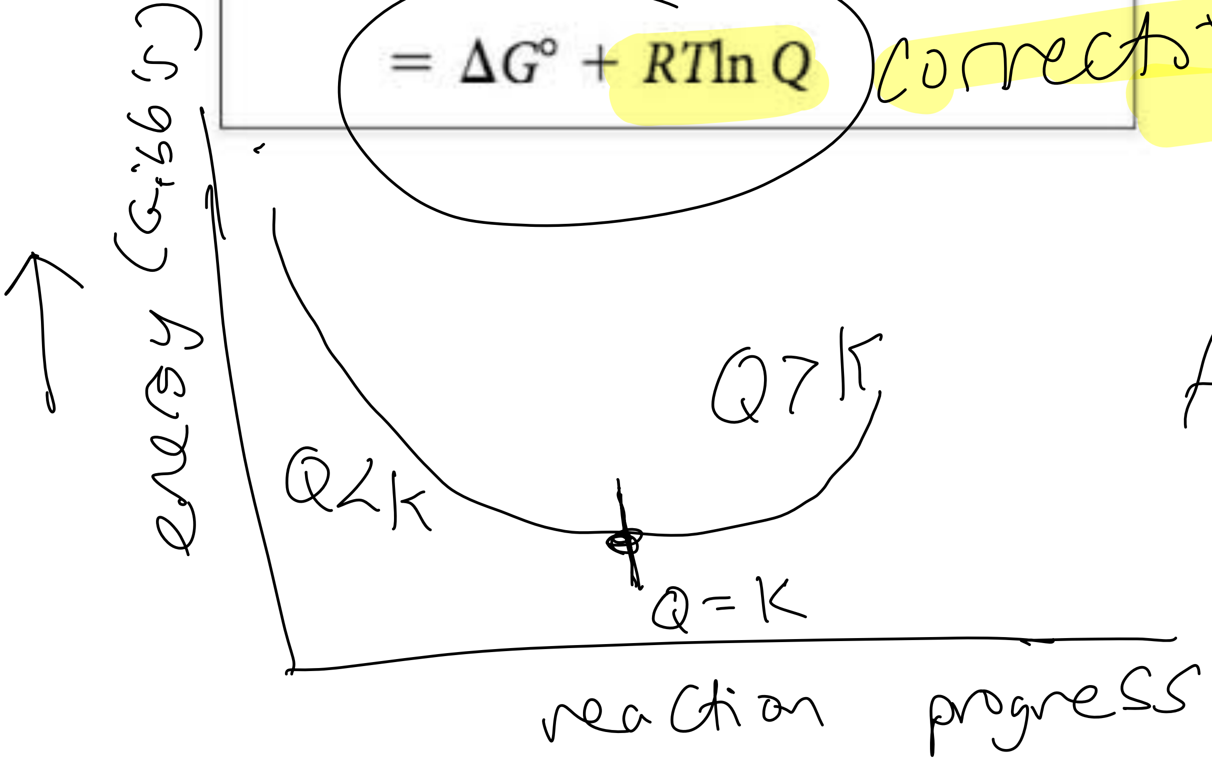
ΔG non-standard Gibb's free energy

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

$$= \Delta G^\circ + RT\ln Q$$

* any pt before eq. is established

correction factor



product favored

$A \rightleftharpoons B$

$K \sim 10^7$

@ eq. $\boxed{\underline{\Delta G} = 0}$

reach an energy minimum

$$0 = \Delta G^\circ + RT\ln K \text{ (at equilibrium)}$$

$$\boxed{\underline{\Delta G^\circ} = -RT\ln K} \text{ or } K = e^{-\frac{\Delta G^\circ}{RT}}$$

if $K = 1$

then $\Delta G^\circ = 0$

if K 10^7 product favored

$K > 1$

$\Delta G^\circ < 0$ product favored reaction @ eq.

if K 10^{-7} if $K < 1$

$\Delta G^\circ > 0$ reactant favored

Example: ΔG° and K

For $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$\Delta G^\circ = 56\ KJ/mol$ @ 25.0°C

what is the solubility product constant @ 25.0°C?

K_{sp} is solubility product constant

$$\Delta G^\circ = -RT \ln K_{sp}$$

$$\ln K_{sp} = \frac{\Delta G^\circ}{RT}$$

$R = 8.314 \frac{J}{mol \cdot K}$

$$\cancel{e \ln}\ K_{sp} = e^{(-\Delta G/RT)}$$

$$K_{sp} = e^{(-56{,}000/(8.314 \cdot 298))}$$

$$K_{sp} = 1.5 \times 10^{-10}$$

$\Delta G^\circ > 0$ $K_{sp} \ll 1$

reactant favored

$K_{sp} = 1.5\times10^{-10}$ $AgCl(s) \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$K_{new} = $ $Ag^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons \underline{AgCl(s)}$

$\frac{1}{K_{sp}}$

$= 6.7\times10^{9}$

$\Delta G^\circ = -RT\ln \underline{K}$

$\Delta G^\circ = \boxed{-}$