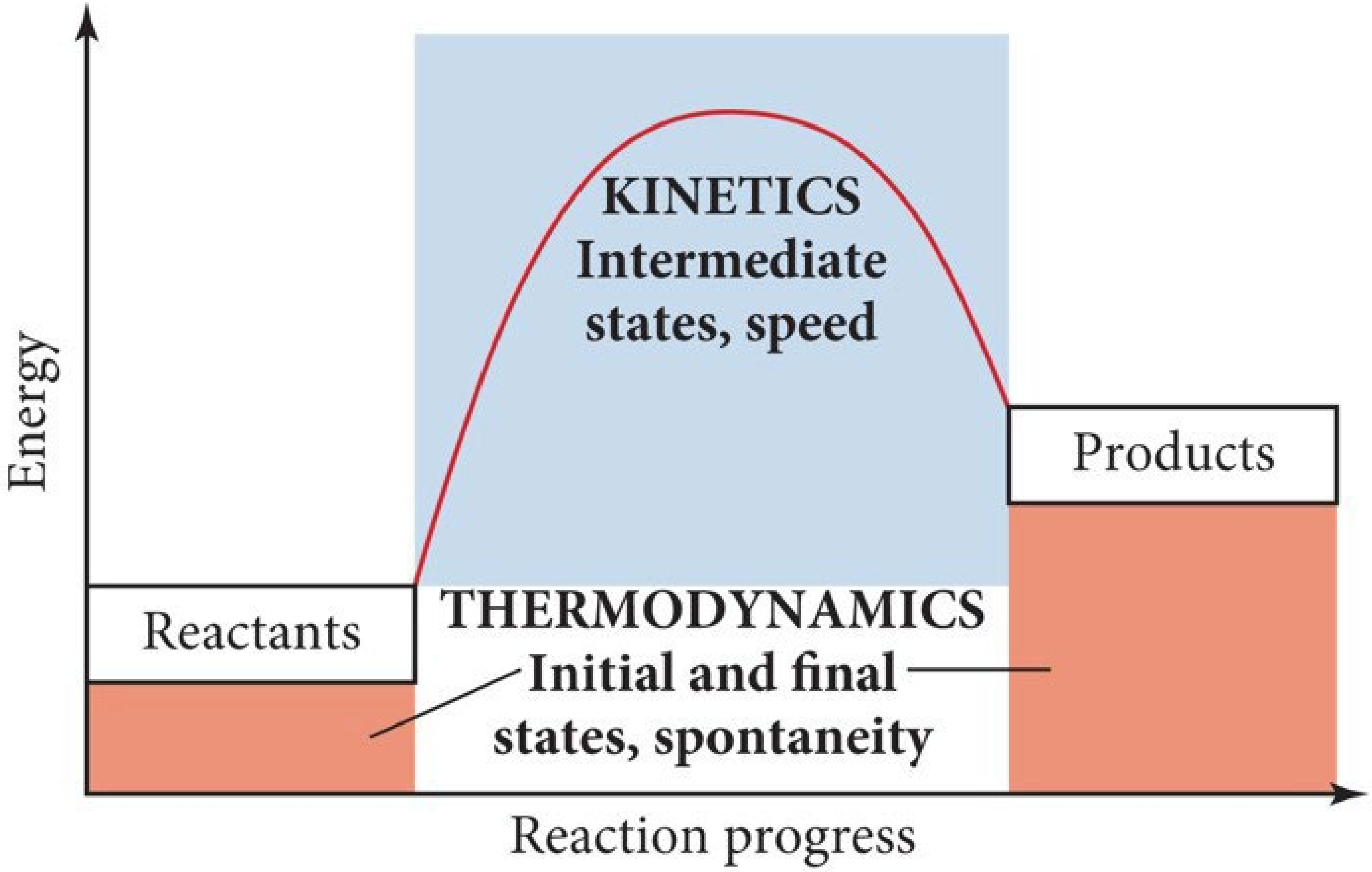
Thermodynamics versus Kinetics



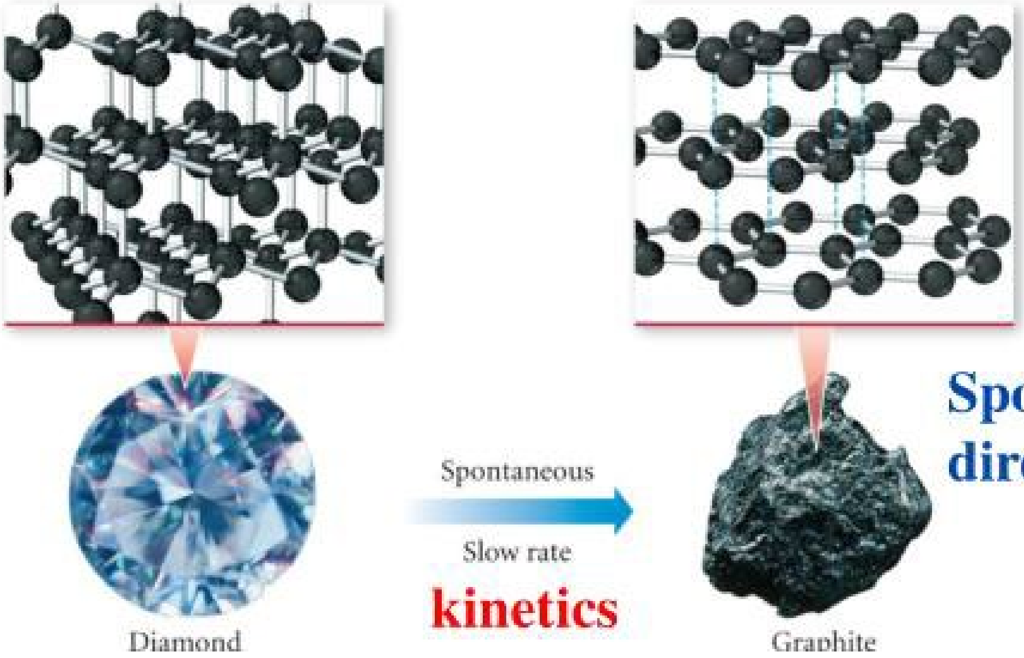
Ch 103 Enthalpy ΔH

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

Example

Diamond → Graphite

kinetics:
how fast



kinetics

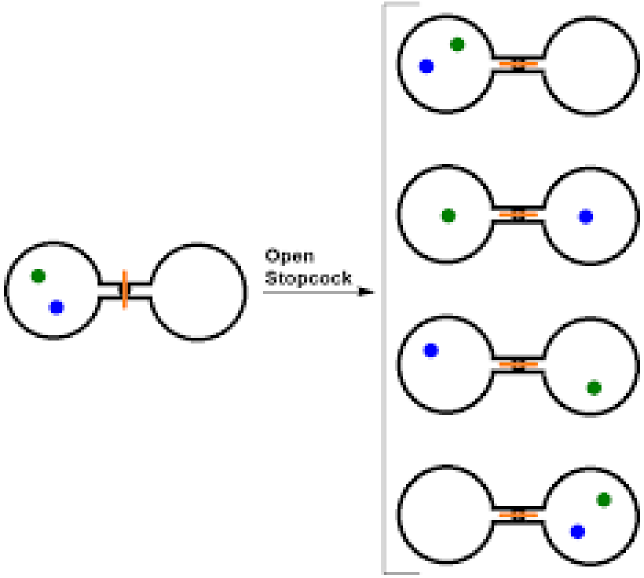
Spontaneity:
direction & extent

Entropy

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

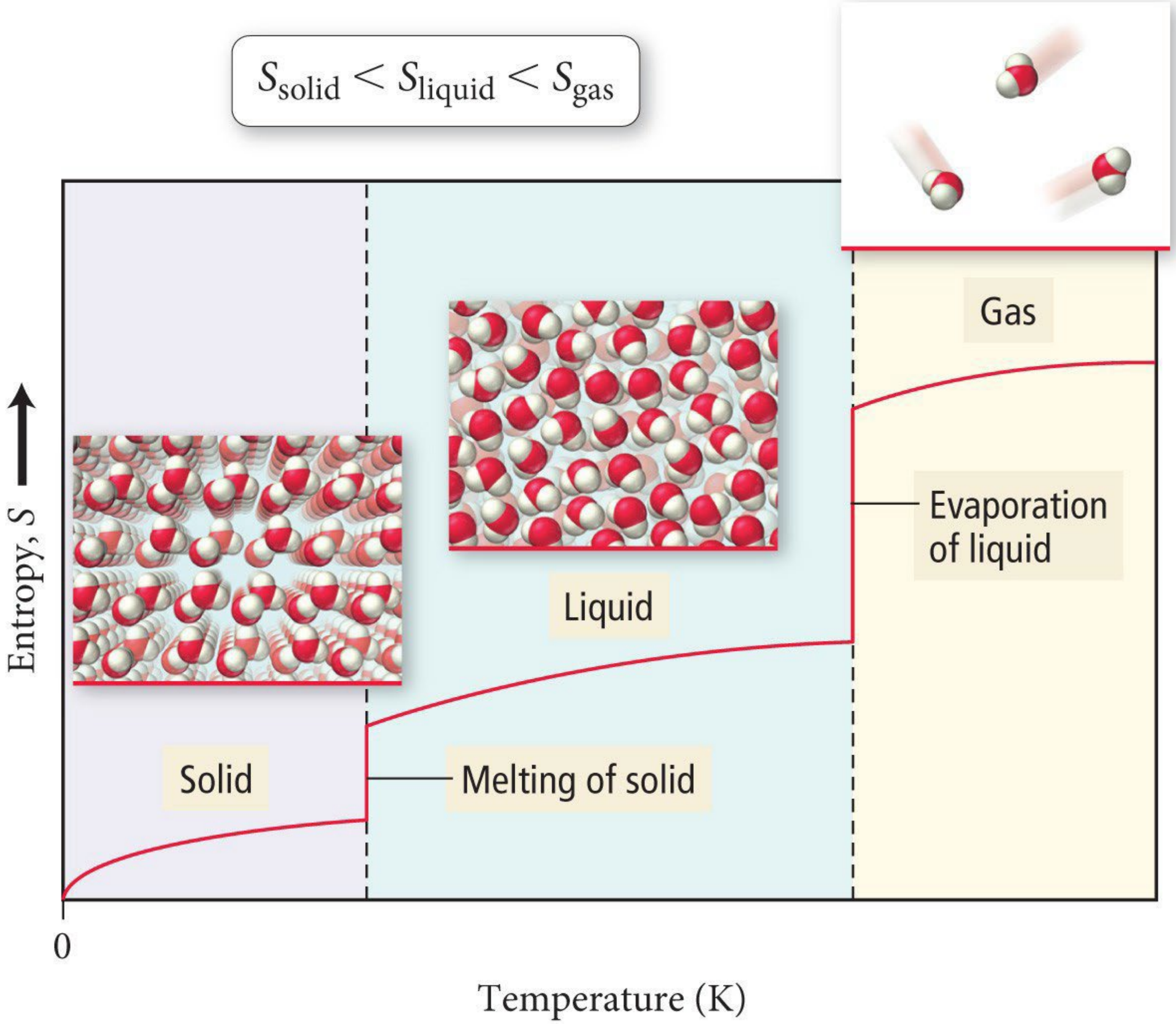
.

How many microstates?



What is the ΔS?

Entropy Change and State Change



Second Law of Thermodynamics

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

- Entropy is a state function

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)

$$\Delta S_{univ} > 0$$

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

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

ΔS_{rxn} :

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 ΔSuniv >0 for an irreversible process

How to do we go from ΔS_{univ} to ΔGsys?

ΔSuniv = ΔSsys + ΔSsurr , ΔSsurr = q/T

*remember first law of thermo from Ch 103

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

So… Δsurr = qsurr/T, -ΔHsys/T

ΔSsurr = ΔSsys –ΔHsys/T, multiply both sides by -T,

$-T\Delta S_{univ} = \Delta H - T\Delta S$

Define −TΔSuniv as ΔG

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

A reaction is spontaneous when ΔG<0, why?

Using Gibb’s free energy example 1:

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

°

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.

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

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

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