First Law of Thermodynamics

- Remember: $\Delta E_{univ} = 0$
- Total energy of the universe is constant.
- Energy can be transferred:
- $\Delta E = q + w$
- q = heat
- w = work (F*D) = ΔPV

1^{st} *Law, review*

- For constant volume process:
  - $\Delta V = 0$, $P\Delta V = 0$
  - $\Delta E_V = q_V + w = q_V + 0 = q_V = \Delta H$

Represents the Energy balance between heat in/out & work in/out.

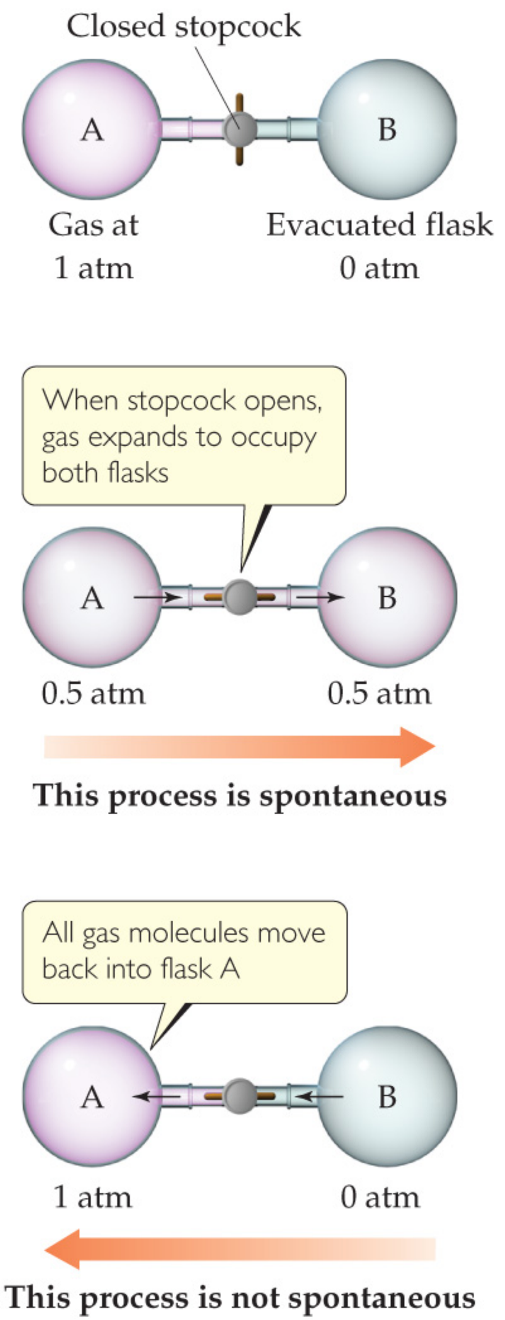
The second law of Thermodynamics

- 2nd law answers the question:
  - What can happen, what can't
  - What is the *Direction* of change.

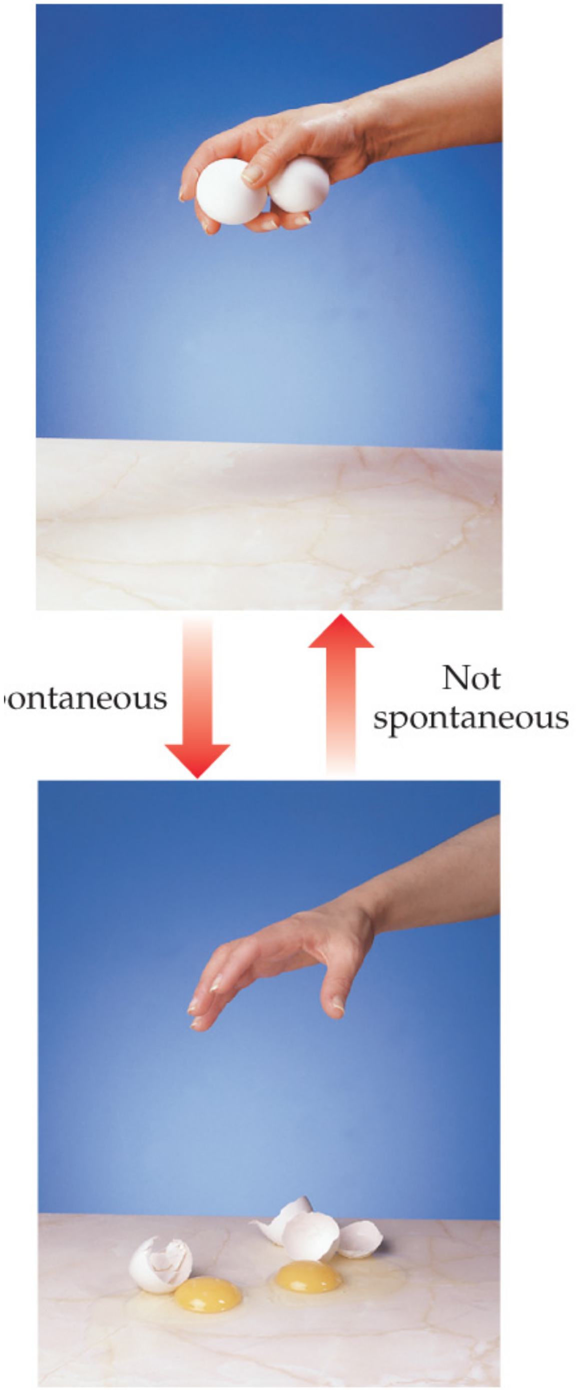
  - Why do endothermic processes happen?
  - Why don't some exothermic processes happen?
  - What determines the direction of change?

Spontaneous Process

- **Spontaneous change**
  - **Happens on its own**
  - **An irreversible process.**
- Example: The gas in vessel B will *spontaneously* effuse into vessel A,
- But ,once in both vessels, it will *not* spontaneously return to vessel B.



Spontaneous Process



Process, spontaneous in one direction

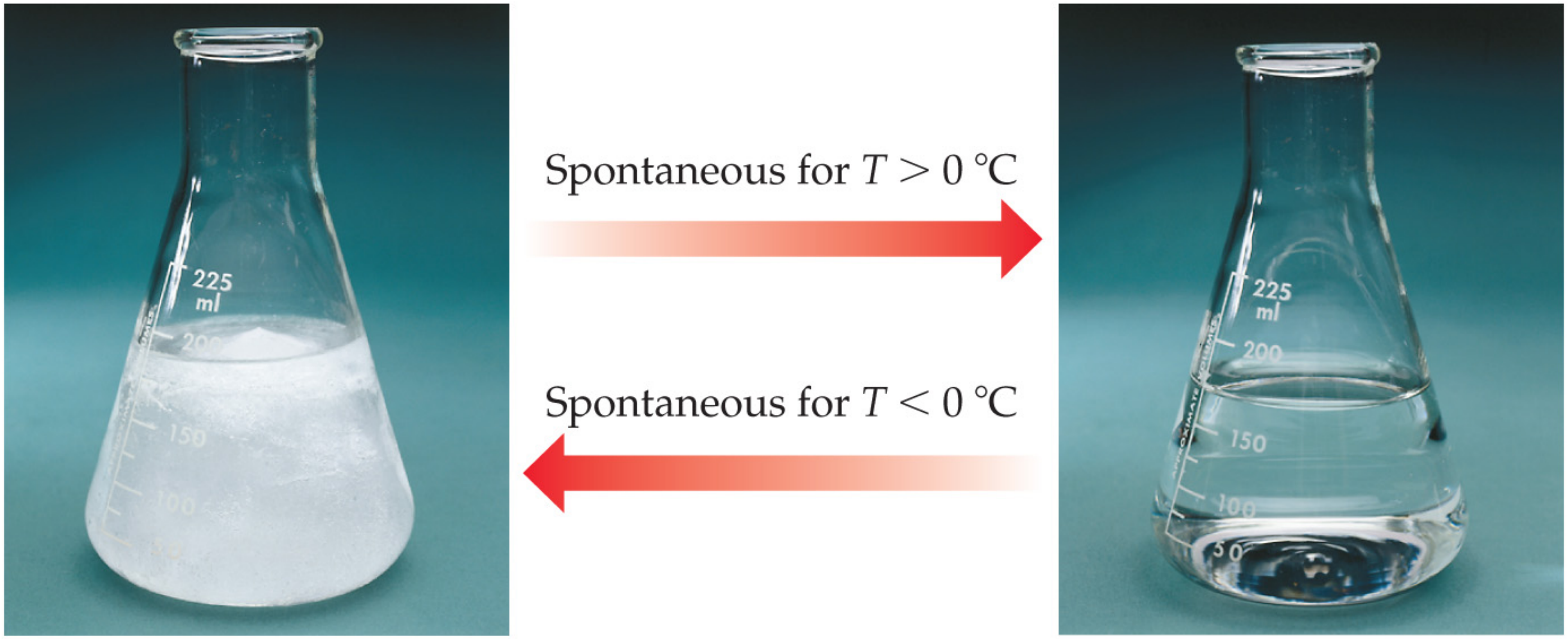
nonspontaneous in the reverse direction.

Spontaneous does NOT mean immediate.

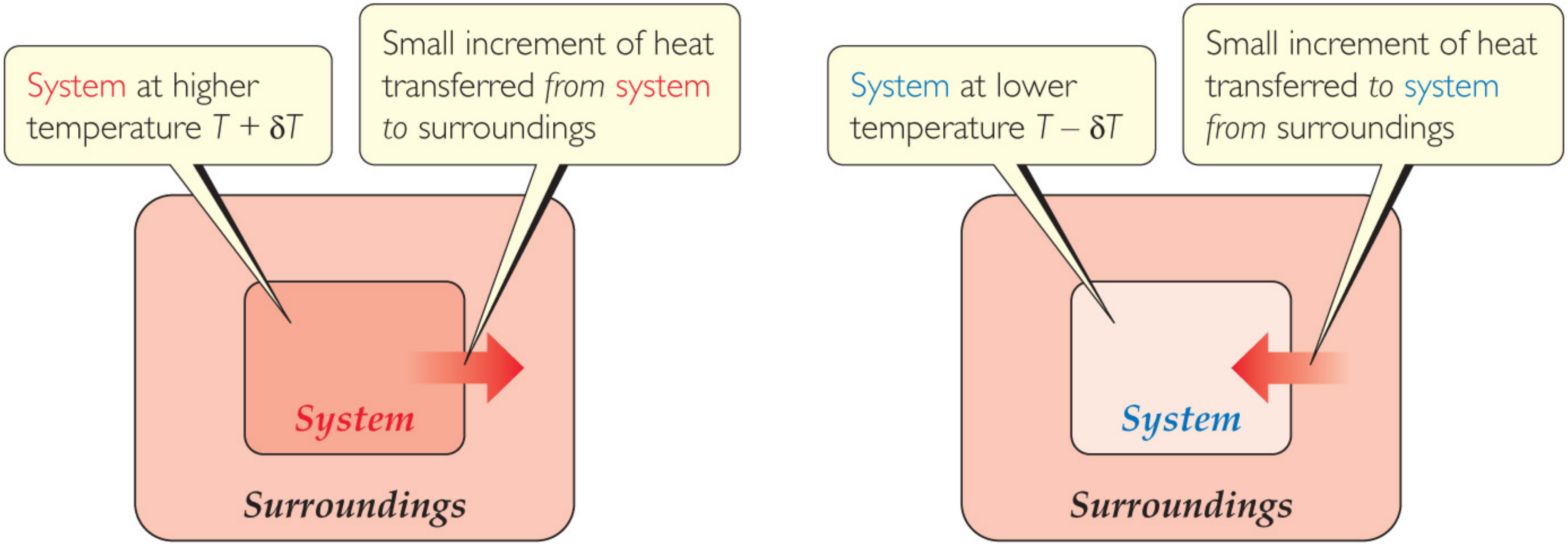
Can take a very long time.

Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0 °C, it is spontaneous for ice to melt.
- Below 0 °C, the reverse process is spontaneous.



Reversible Processes



Surroundings at temperature T

(a)

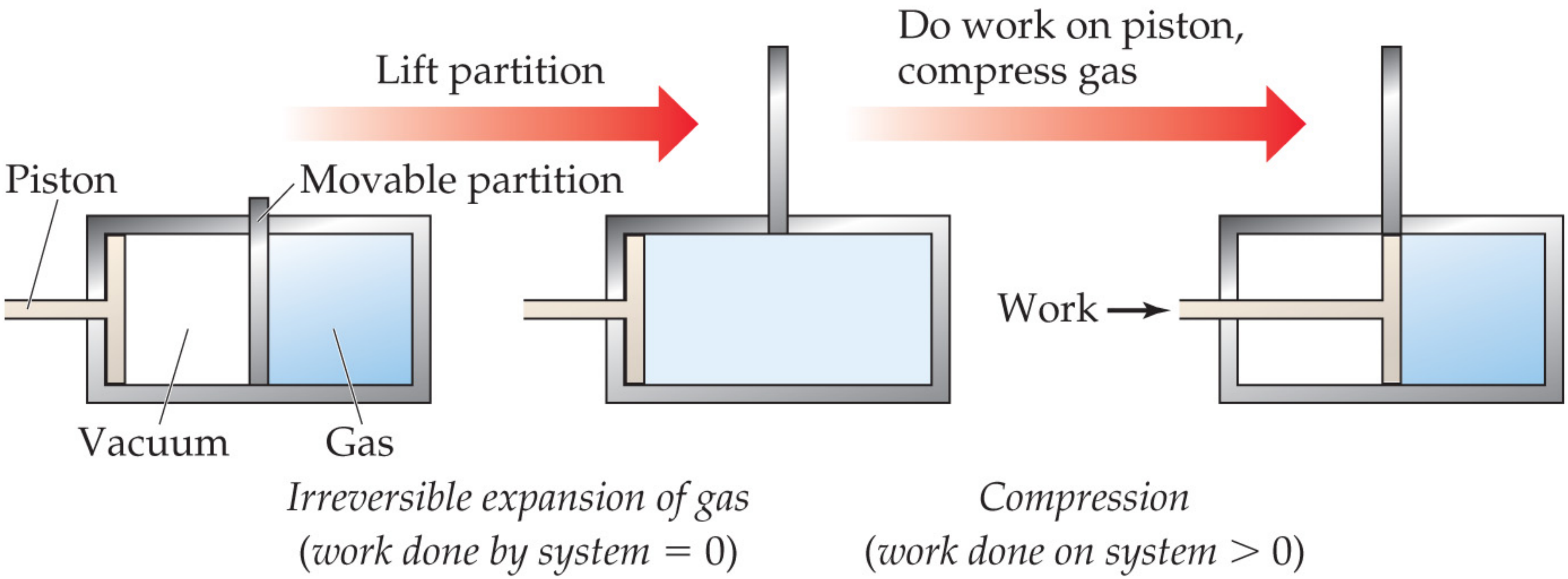
Surroundings at temperature T

(b)

reversible process:

the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

Irreversible Processes



Irreversible expansion of gas
(work done by system = 0)

Compression
(work done on system > 0)

- Irreversible processes cannot be undone by exactly reversing the change to the system.
- Spontaneous processes are irreversible.

2nd law of thermodynamics

- What determines the direction of a process?
- What determines whether a process is spontaneous or not?
- ***Entropy.***

What is Entropy (S)?

Entropy

- **Entropy:** a measure of the *randomness* of a system.
- Randomness, the possible states.

Entropy

- Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
- Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Entropy

For isothermal process:

$$\Delta S = \frac{q_{\mathrm{rev}}}{T}$$

This means that entropy change is a function of:

heat transfer

Temperature the heat transfer is happening.

Second Law of Thermodynamics

States:

entropy (randomness, disorder) of the universe:

1. increases for spontaneous processes,
2. does not change for reversible processes.

$\Delta S_{univ.} > 0$ spontaneous (irreversible) process

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

$\Delta S_{univ.} > 0$ for anything that happens (changes)

Second Law of Thermodynamics

In other words:

For reversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For irreversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Entropy Changes in Surroundings

- Heat that flows into or out of the system changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

- At constant pressure, q_{sys} is simply $\Delta H°$ for the system.

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.
- Therefore,

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

- For spontaneous processes

$$\Delta S_{\text{universe}} > 0$$

Entropy Change in the Universe

- Since

$$\Delta S_{\text{surroundings}} = \frac{-q_{\text{system}}}{T}$$

and

$$q_{\text{system}} = \Delta H_{\text{system}}$$

This becomes:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \frac{-\Delta H_{\text{system}}}{T}$$

Multiplying both sides by $-T$, we get

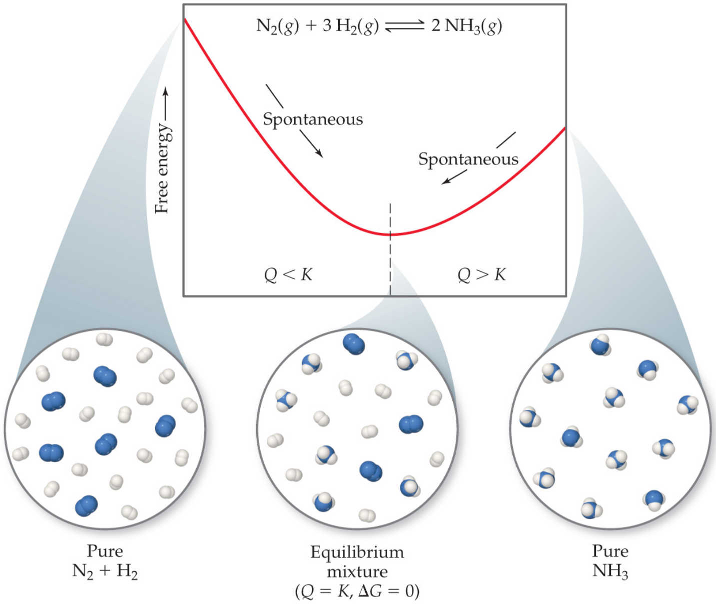
$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

Gibbs Free Energy

- $-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG.
- $\Delta S_{\text{universe}}$ positive, ΔG negative.
- ΔG negative, process spontaneous (happens).

- $\Delta G = \Delta H_{system} - T\Delta S_{\text{system}}$

Gibbs Free Energy



1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Free Energy and Temperature

- There are two parts to the free energy equation:
  - $\Delta H°$— the enthalpy term
  - $T\Delta S°$ — the entropy term
- The temperature dependence of free energy then comes from the entropy term.

Gibbs free energy examples

- ICE → WATER (T > 0°C)
- ΔH
- ΔS
- ΔG

- WATER → ICE (T < 0°C)
- ΔH
- ΔS
- ΔG

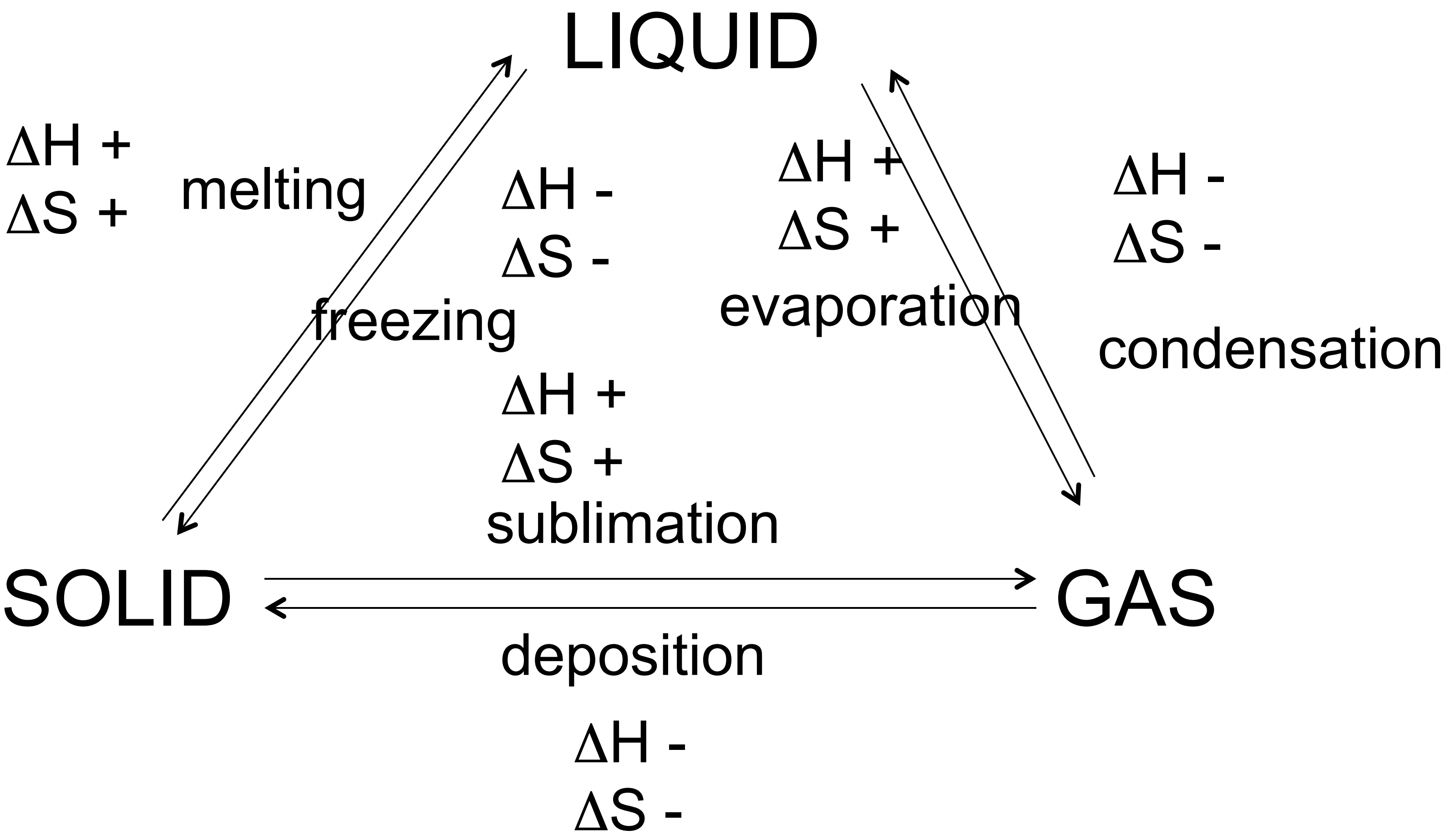
Gibbs free energy examples

- ICE → WATER (T > 0°C)
- ΔH +
- ΔS +
- ΔG -

Entropy driven

- WATER → ICE (T < 0°C)
- ΔH -
- ΔS -
- ΔG -
- *Enthalpy driven.*

Changes of state



LIQUID

ΔH +
ΔS +
melting

ΔH -
ΔS -
freezing

ΔH +
ΔS +
evaporation

ΔH -
ΔS -
condensation

ΔH +
ΔS +
sublimation

SOLID

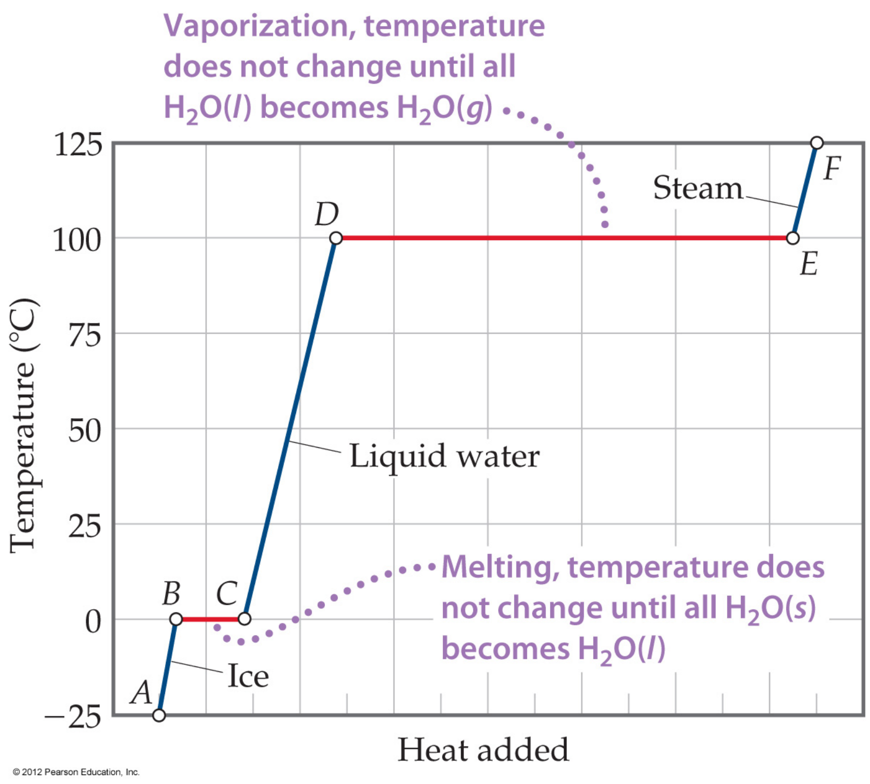
GAS

deposition

ΔH -
ΔS -

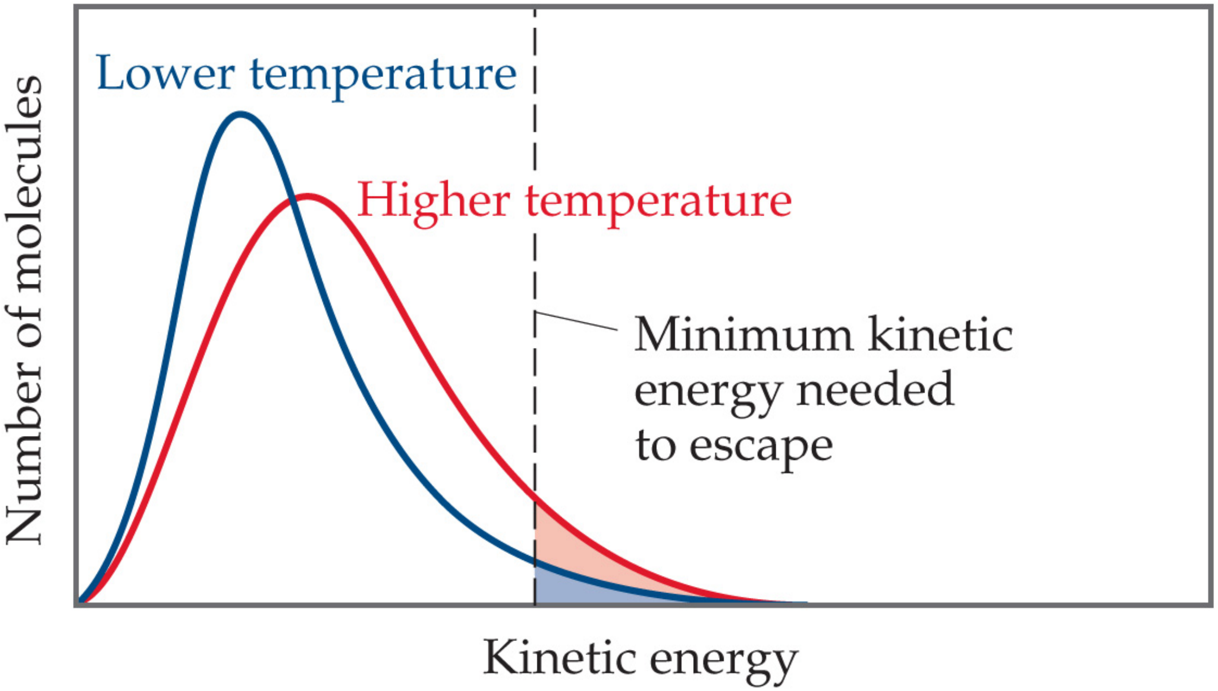
Phase transformations, changes of state

Energy Changes Associated with Changes of State



- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during a phase change.

Vapor Pressure



Blue area = number of molecules having enough energy to evaporate at lower temperature

Red + blue areas = number of molecules having enough energy to evaporate at higher temperature

- At any temperature some molecules in a liquid have enough energy to break free.

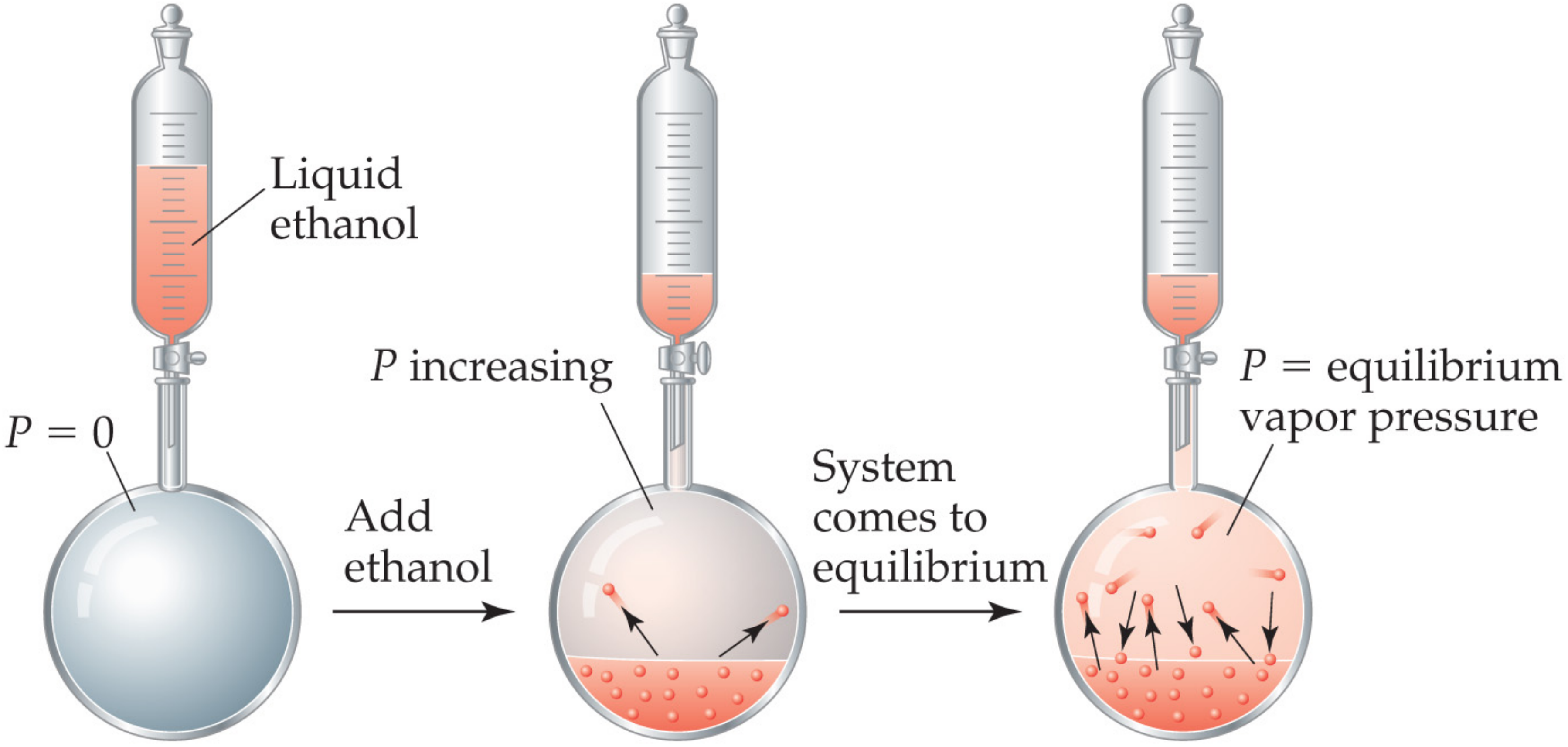
As T rises,

Higher ave. K.E.

More molecules

Break free

Vapor Pressure

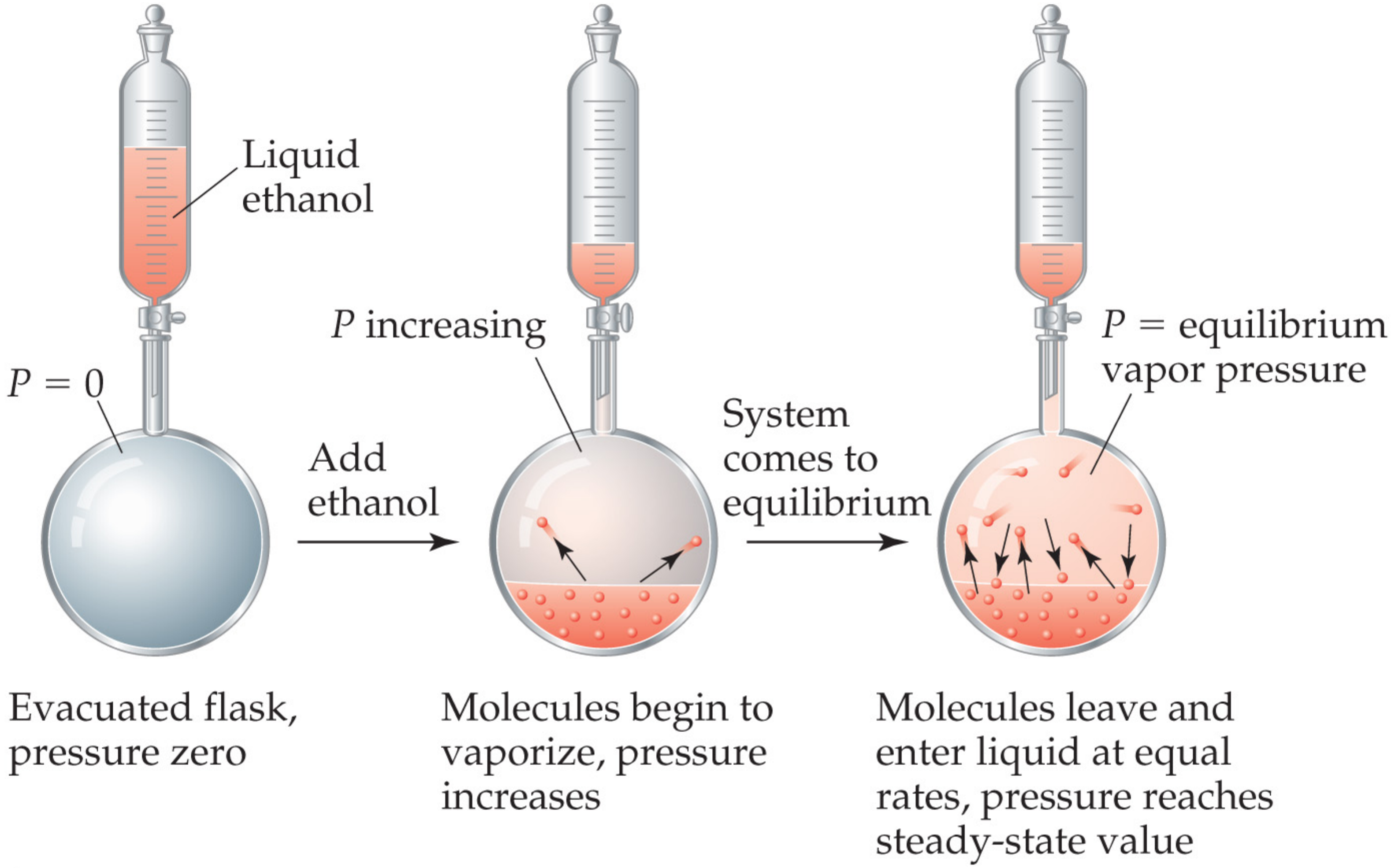


Evacuated flask, pressure zero

Molecules begin to vaporize, pressure increases

Molecules leave and enter liquid at equal rates, pressure reaches steady-state value

Vapor Pressure

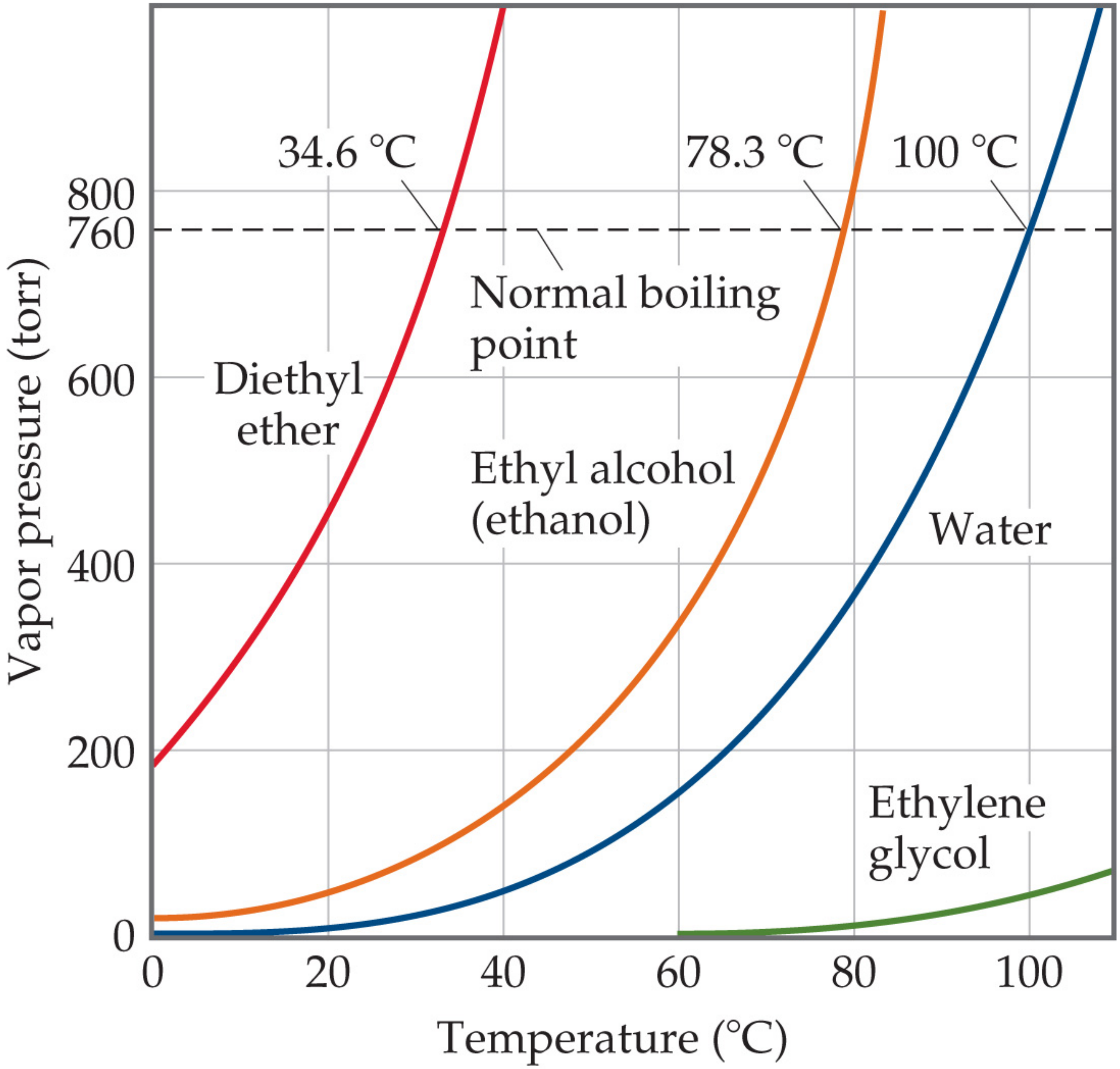


liquid molecules evaporate and vapor molecules condense *at the same rate.*

Dynamic equilibrium

Vapor Pressure

- **boiling point** temperature at which vapor pressure = atmospheric pressure.

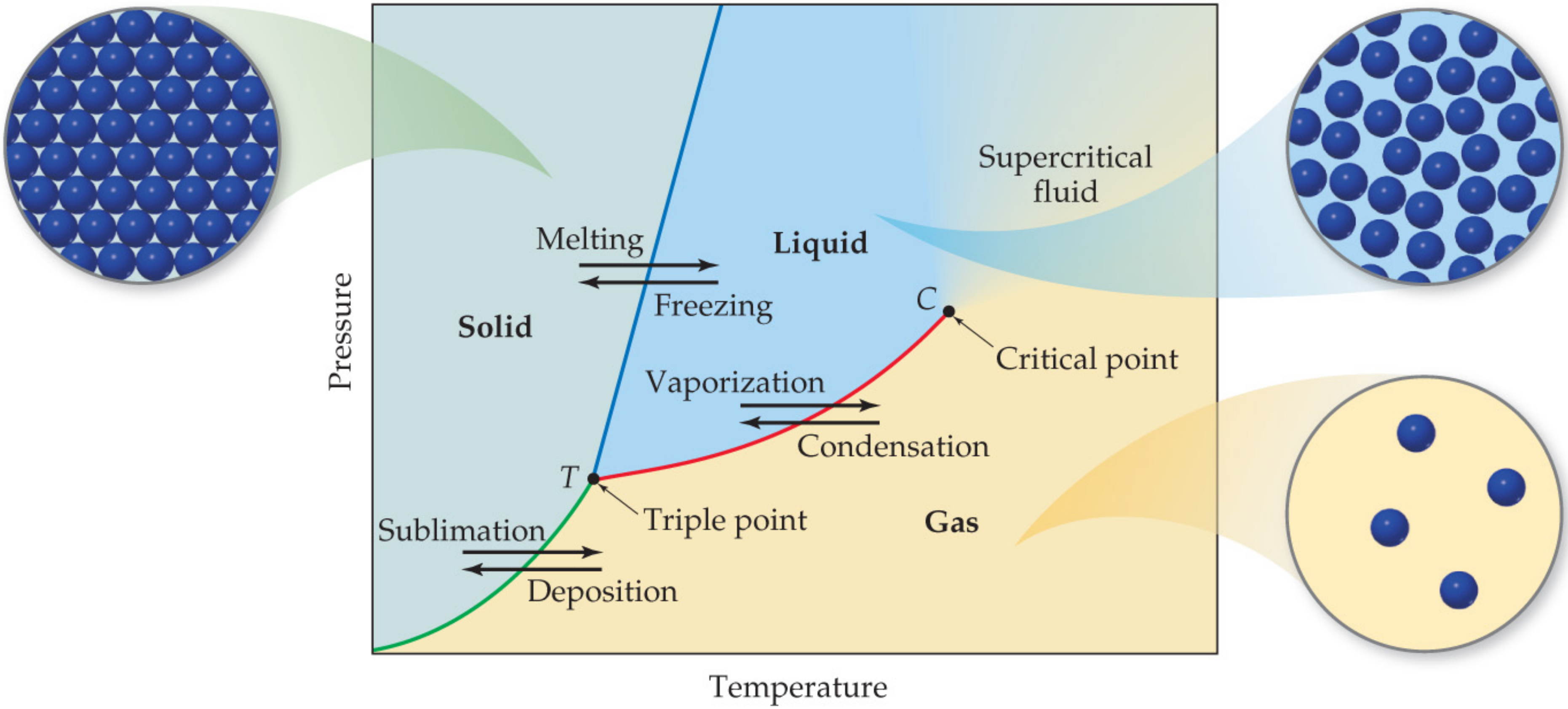


Trouton's rule

- At equilibrium:
- $\Delta G_v = 0 = \Delta H_v - T\Delta S_v$
- $\Delta S_v = \Delta H_v/T$ is approximately = 85 $JK^{-1}mol^{-1}$
- Why should entropy for vaporization be constant?

- The difference in entropy (randomness) between any gas and any liquid is similar.
- Gas: very similar (little interaction)
- Liquids, not as dependable.

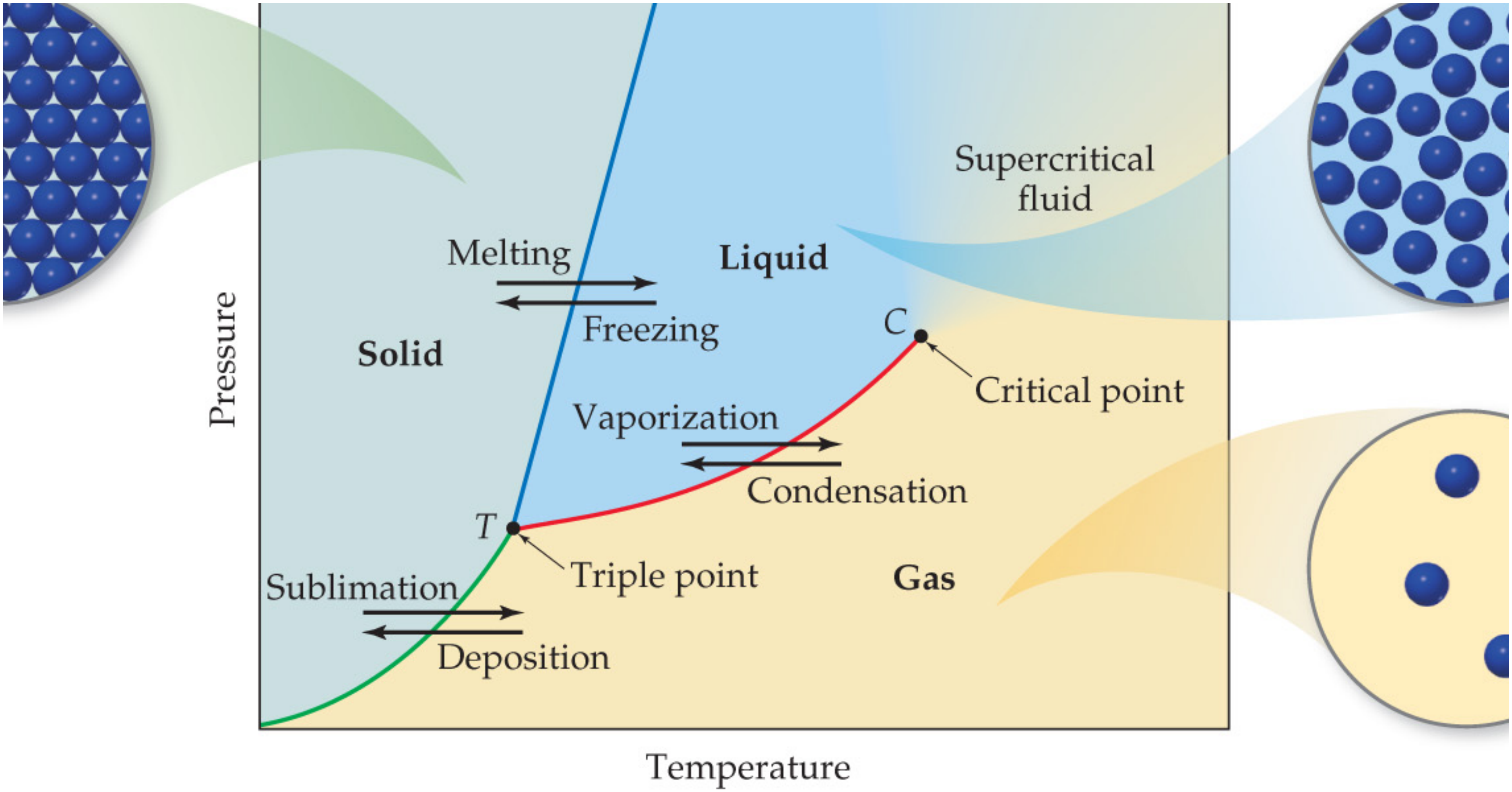
Phase Diagrams



display how the *state* of a substance (solid, liquid gas) changes versus T, and P.

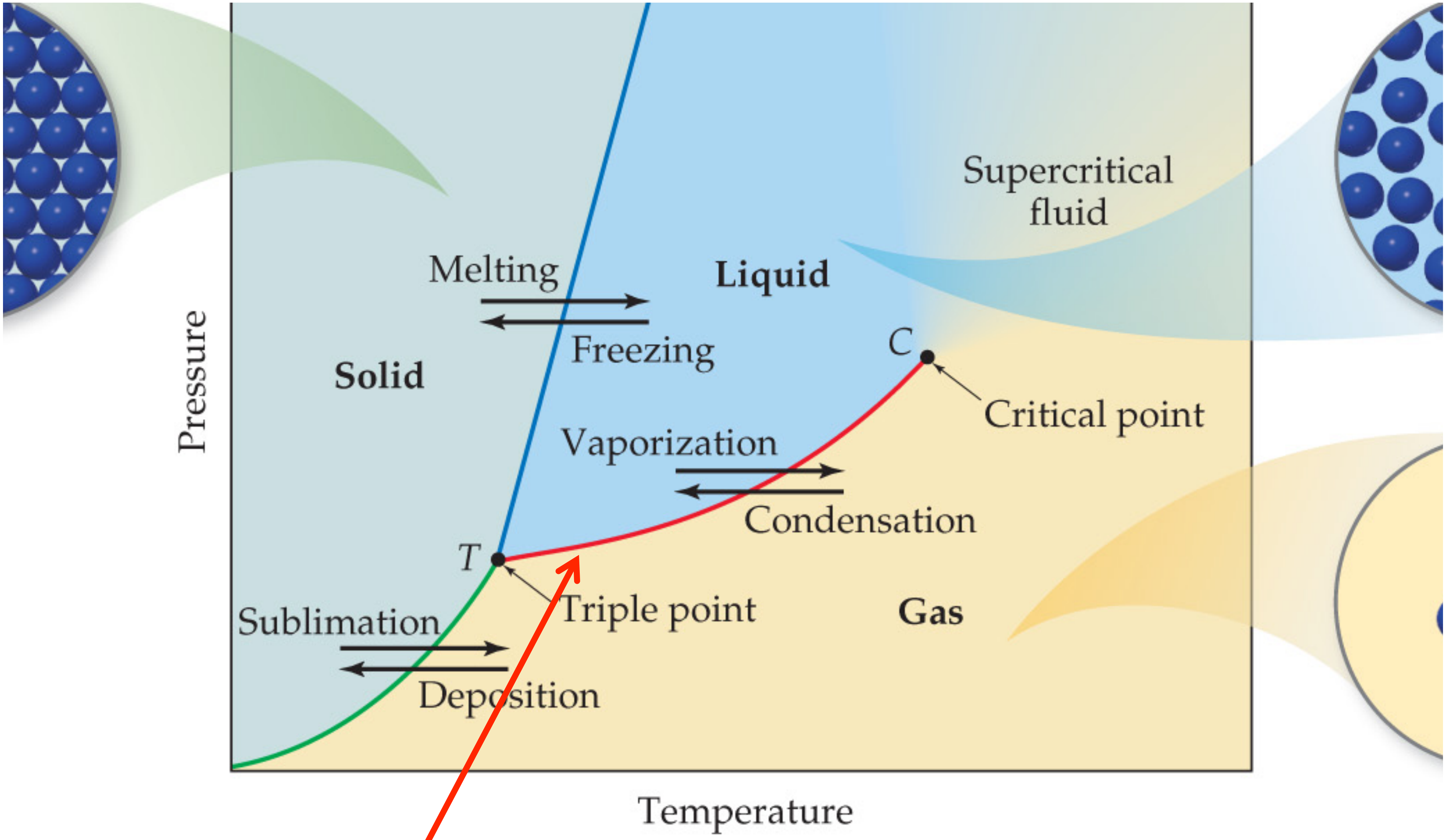
Shows where states are in *equilibrium*

By pressure, we mean *vapor pressure*.

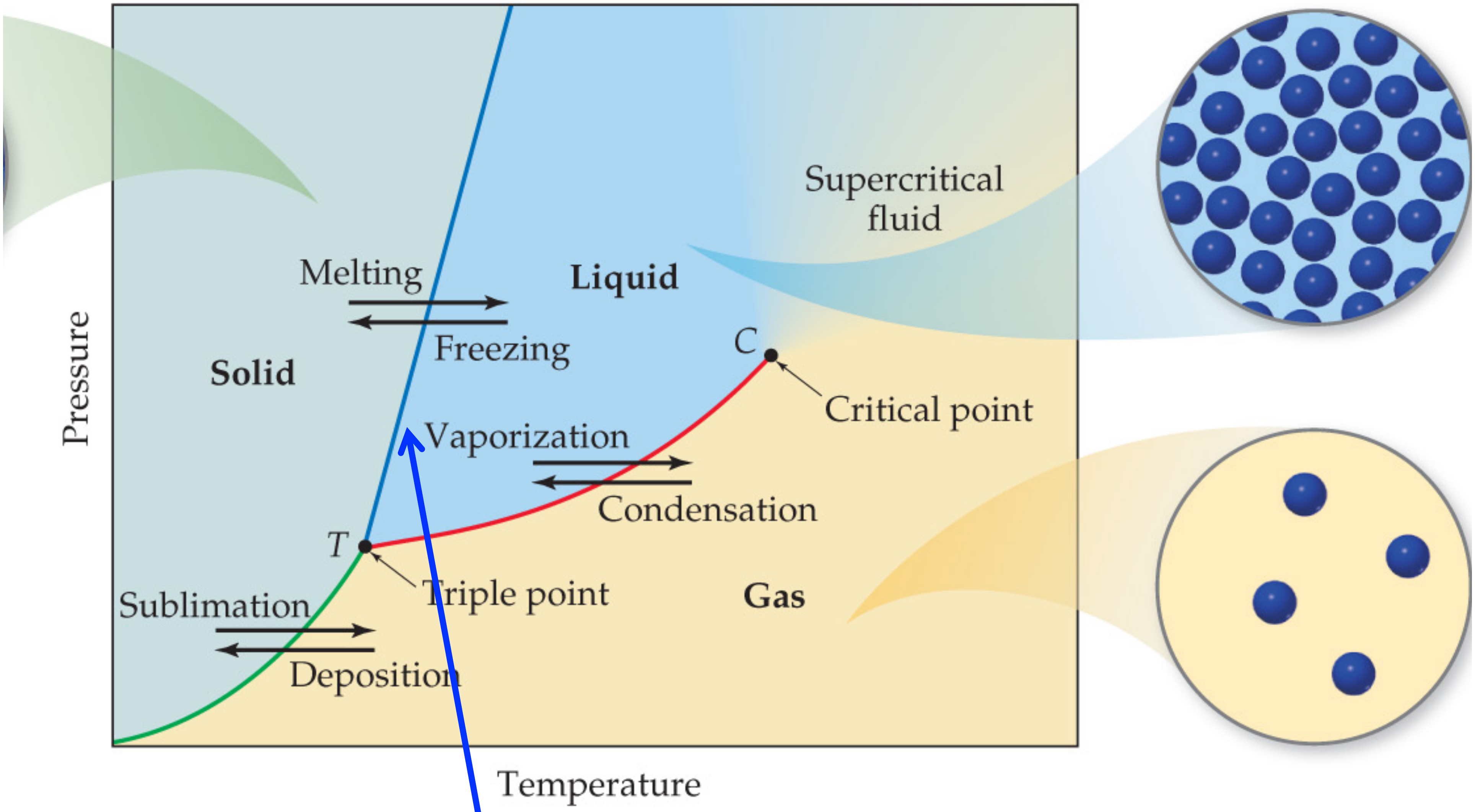


The liquid–vapor line: starts at the triple point (*T*), where all three states are in equilibrium

ends at the critical point (*C*), above which the liquid and vapor are the same.

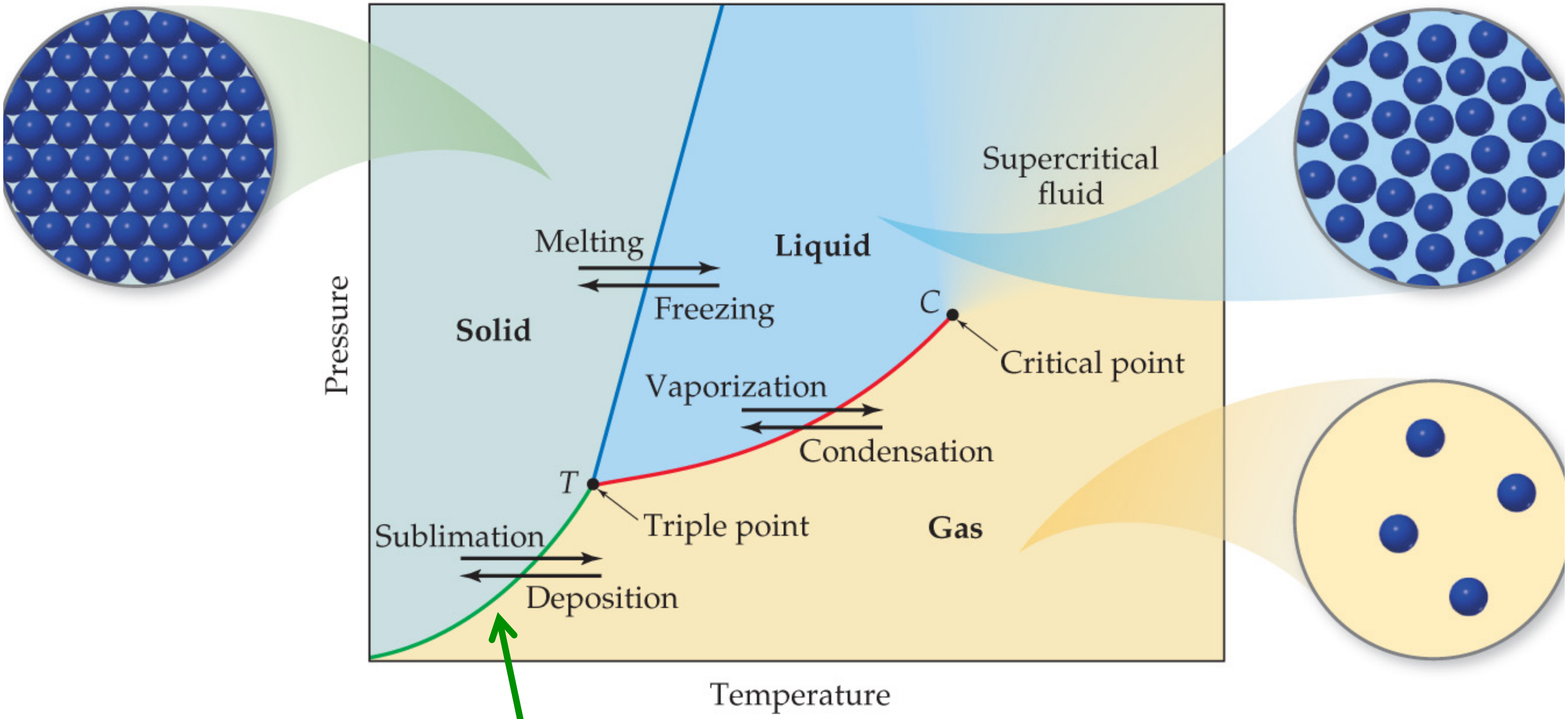


Each T along this line = boiling point of the substance at that pressure.



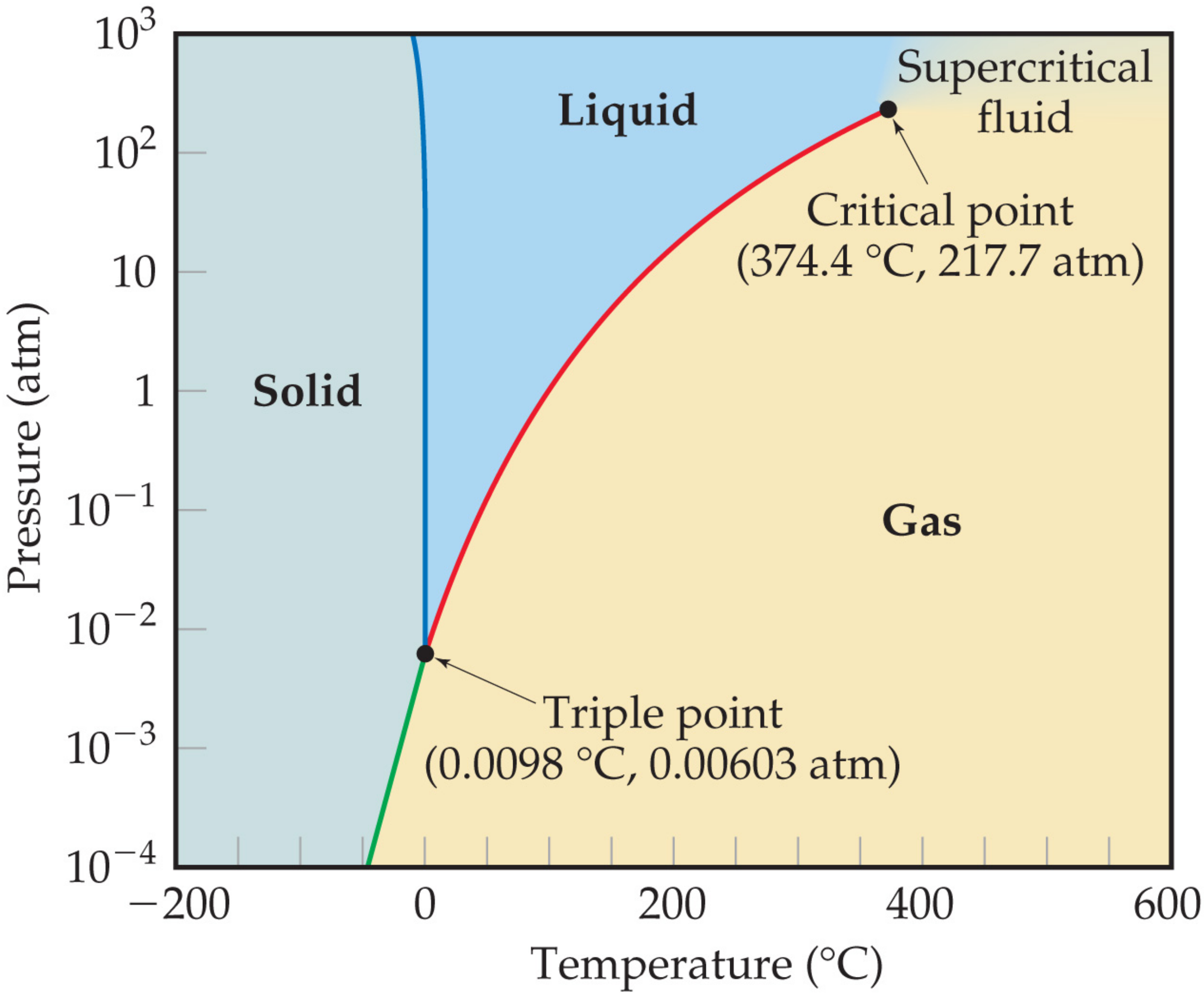
The line between liquid and solid marks the melting point of a substance at each pressure.

Phase Diagrams



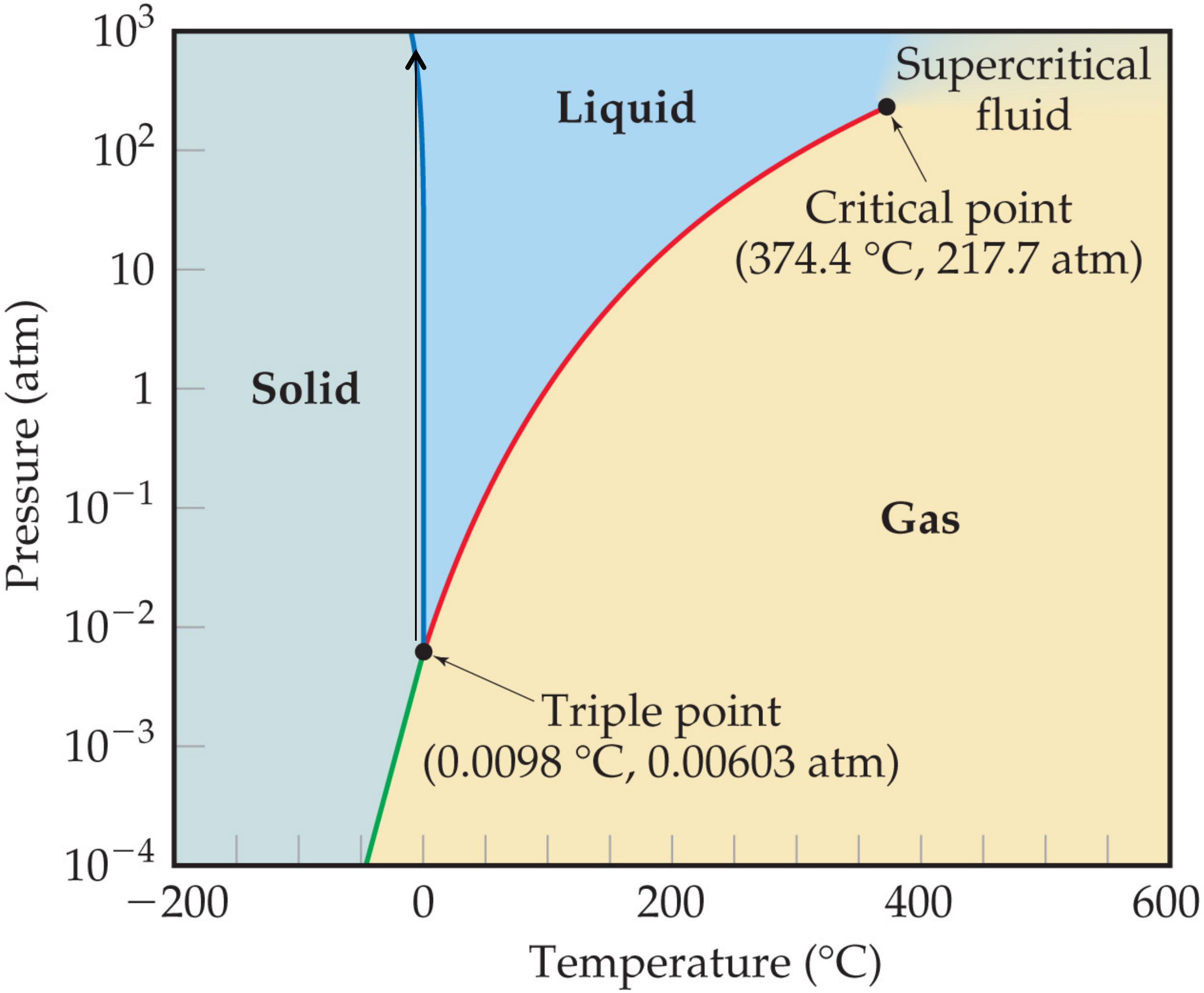
- Below *triple point* substance cannot be liquid.
- Along the *solid–gas line*, the sublimation point at each pressure is along this line. Solid/gas equilib.

Water is different



- high critical temperature and critical pressure.
  - strong van der Waals forces favors liquid/solid.

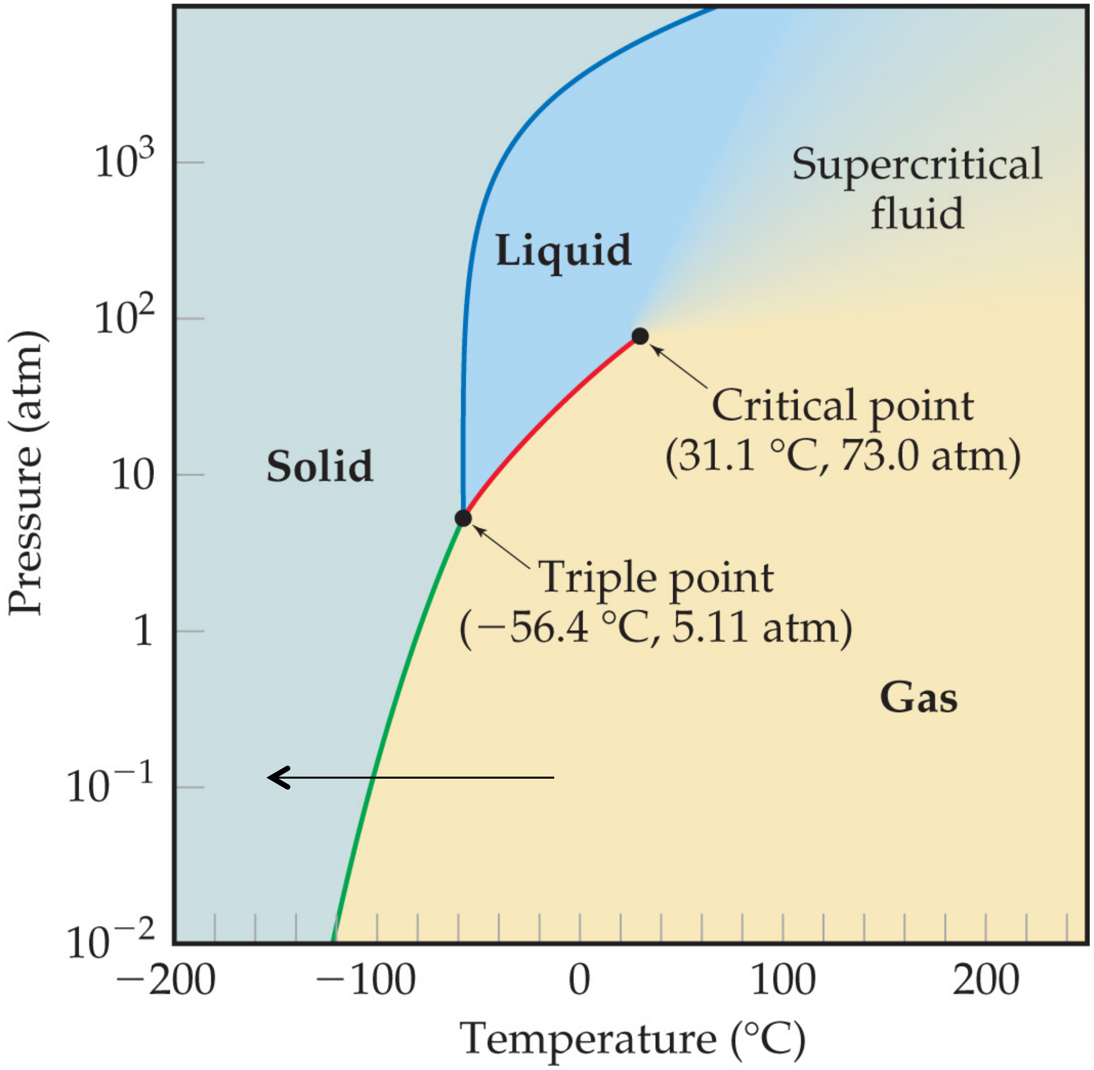
Phase Diagram of Water



slope of the solid/liquid line negative.

- As P is increases T just below the melting point, water goes from a solid to a liquid.

Phase Diagram of Carbon Dioxide



Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm; CO_2 sublimes at normal pressures.

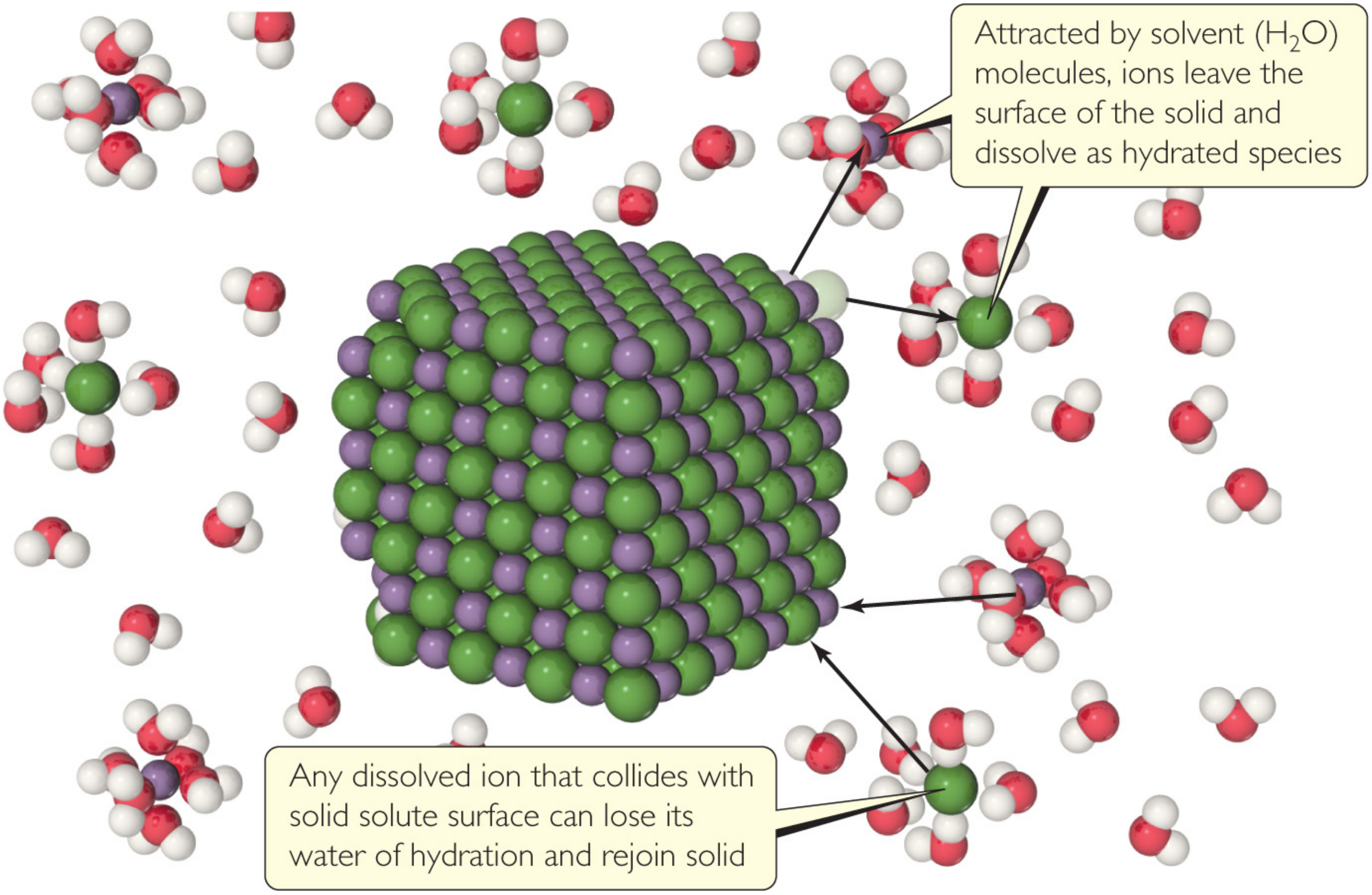
Exam prep opportunities

- LRC Mock Exam: Tuesday, November 13th, 6 - 8:30pm in room N100 BCC
- (RSVP at lrc.msu.edu)
- LRC Review: Thursday, November 15th, 6 - 8:30pm in room N100 BCC

- review session
- Sunday, November 18th 4 - 6pm in room
- 138 Chemistry. Your students are welcome to attend.

Solutions

Solutions

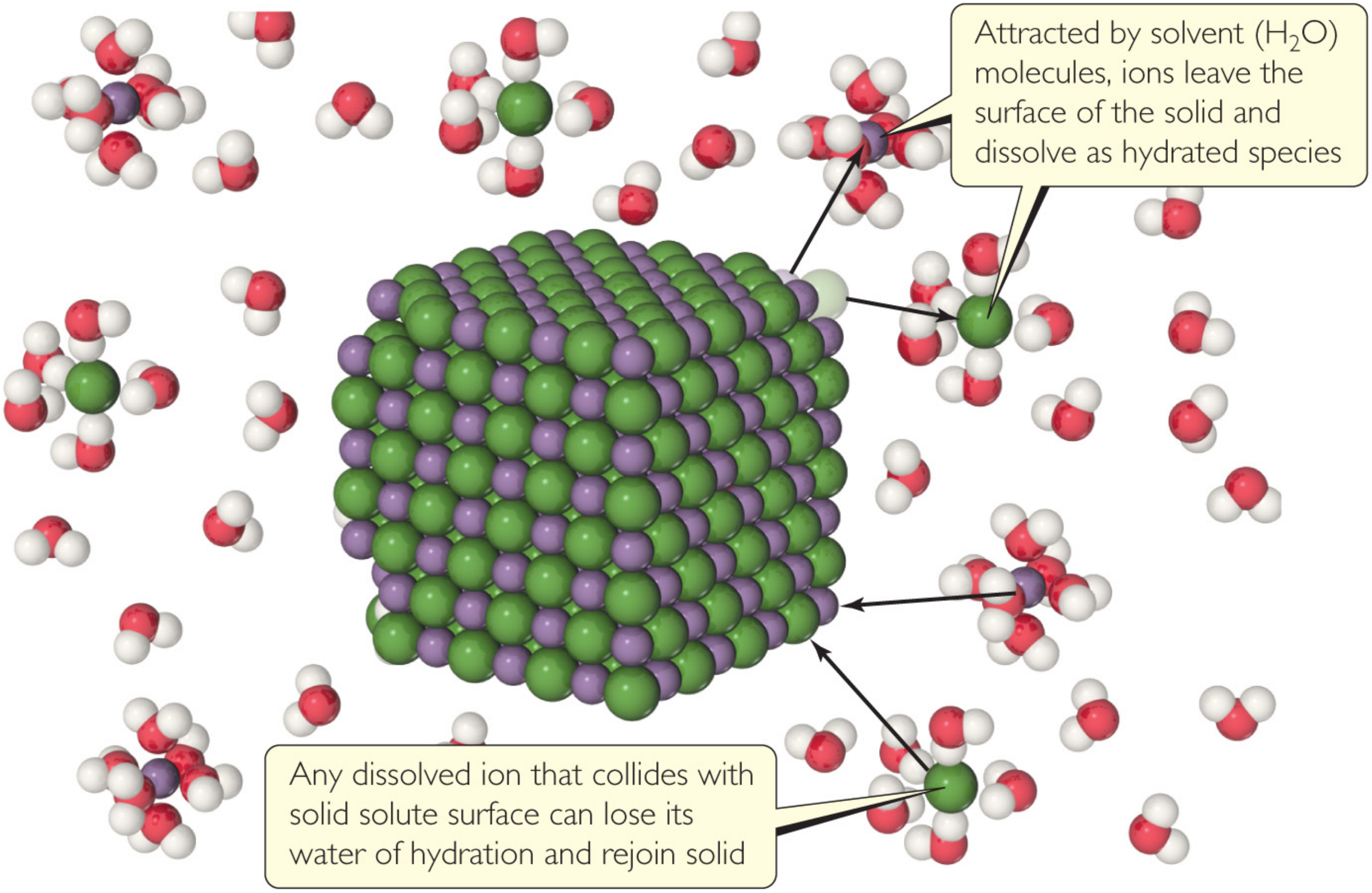


Attracted by solvent (H_2O) molecules, ions leave the surface of the solid and dissolve as hydrated species

Any dissolved ion that collides with solid solute surface can lose its water of hydration and rejoin solid

utions: homogeneous mixtures of two or more pure stances.

Solutions



Attracted by solvent (H_2O) molecules, ions leave the surface of the solid and dissolve as hydrated species

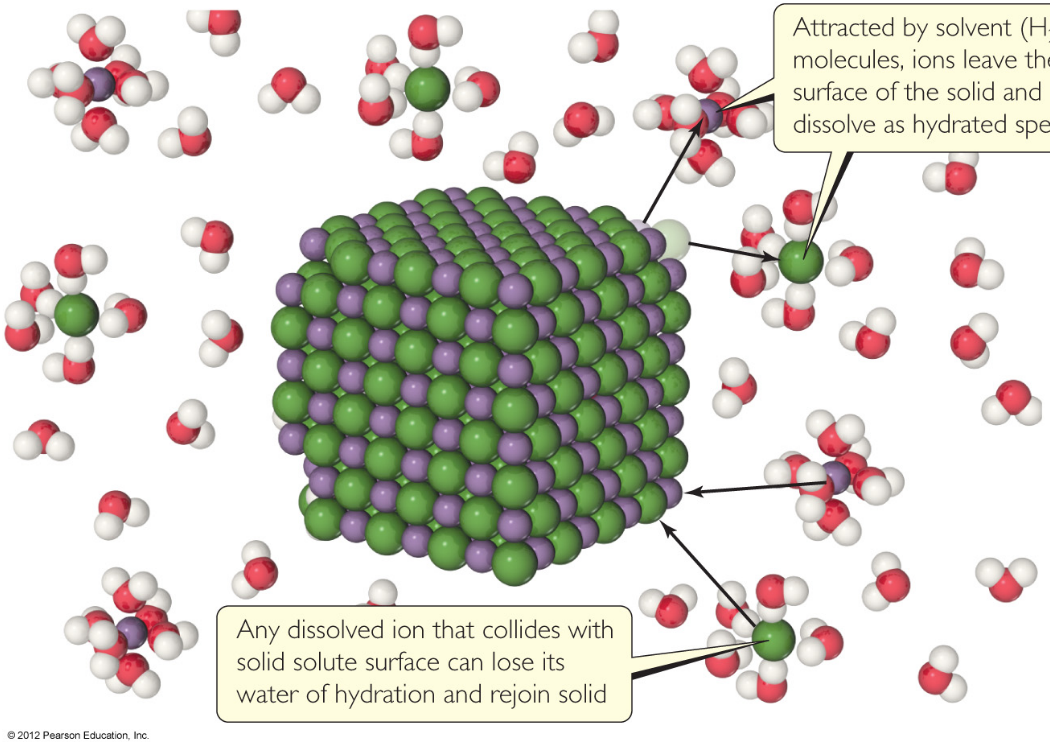
Any dissolved ion that collides with solid solute surface can lose its water of hydration and rejoin solid

vent: Determines the state (solid, liquid gas)

- » Alternatively the one in greatest amount.

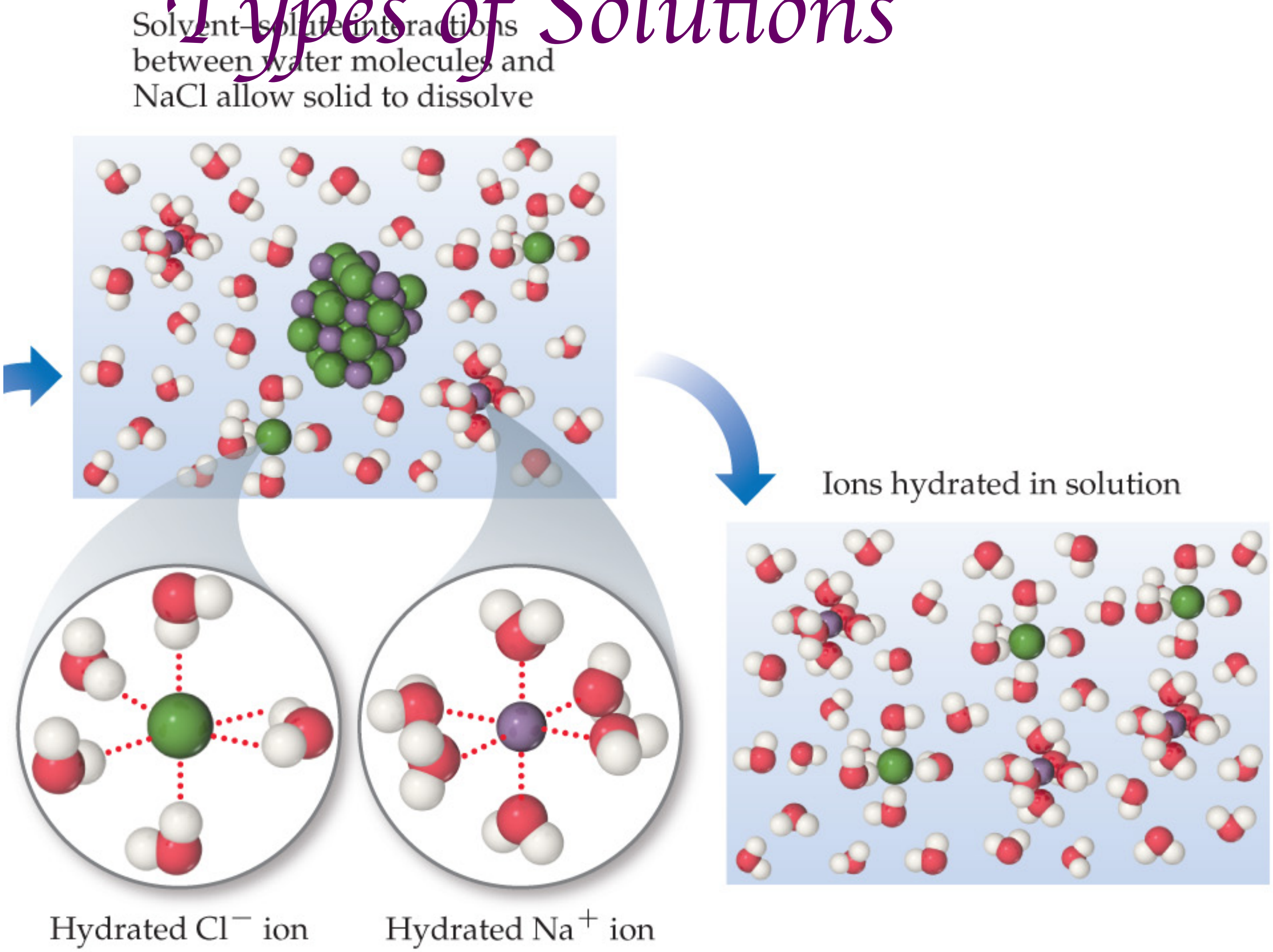
ıtes: Everything else

Types of Solutions



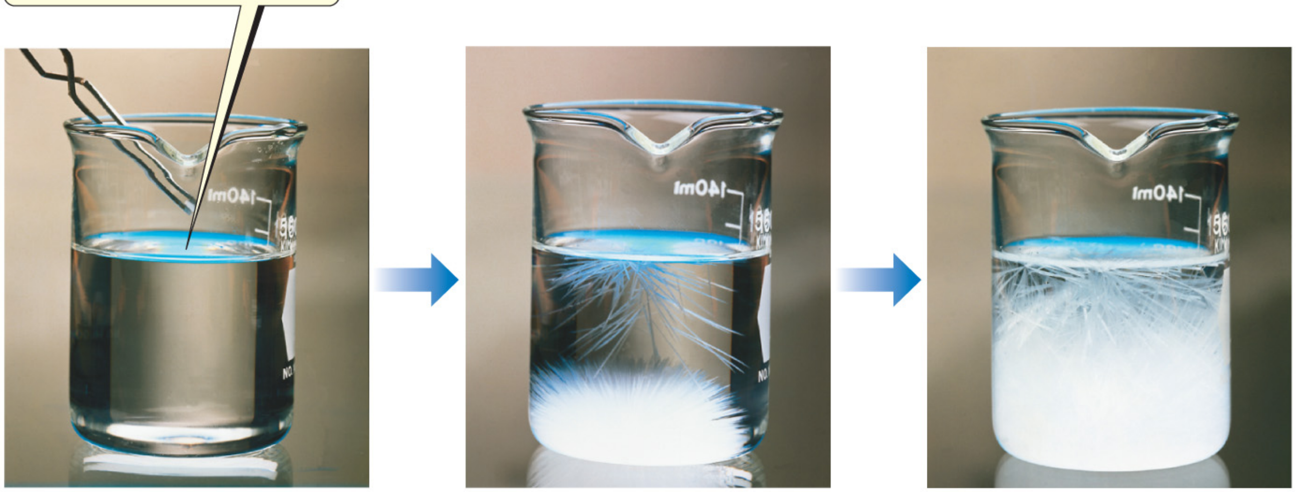
- Saturated
  - solvent holds as much solute as is possible at that temperature.
  - Dissolved solute is in dynamic equilibrium with solid solute.

Types of Solutions



- Unsaturated
  - less solute in solution than possible *at that T.*

Types of Solutions



Amount of sodium acetate dissolved is greater than its solubility at this temperature

Seed crystal of sodium acetate added to supersaturated solution

Excess sodium acetate crystallizes from solution

Solution arrives at saturation

- Supersaturated
  - – solvent holds *more* solute than is normally possible at that temperature.
  - – Solution is thermodynamically unstable; crystallization is spontaneous, but needs seed or vibration to get started.
  - – Like a spontaneous reaction that needs a match.

Ways of Expressing Concentrations of Solutions

Molarity (*M*)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

- Since volume is temperature-dependent, molarity can change with temperature.

Molality (m)

$$m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

moles & mass, amounts

temperature independent so:

molality (unlike molarity) is *not* temperature-dependent.

Mass Percentage

$$\text{Mass \% of } A = \frac{\text{mass of } A \text{ in solution}}{\text{total mass of solution}} \times 100$$

Parts per Million and Parts per Billion

Parts per million (ppm)

$$\text{ppm} = \frac{\text{mass of } A \text{ in solution}}{\text{total mass of solution}} \times 10^6$$

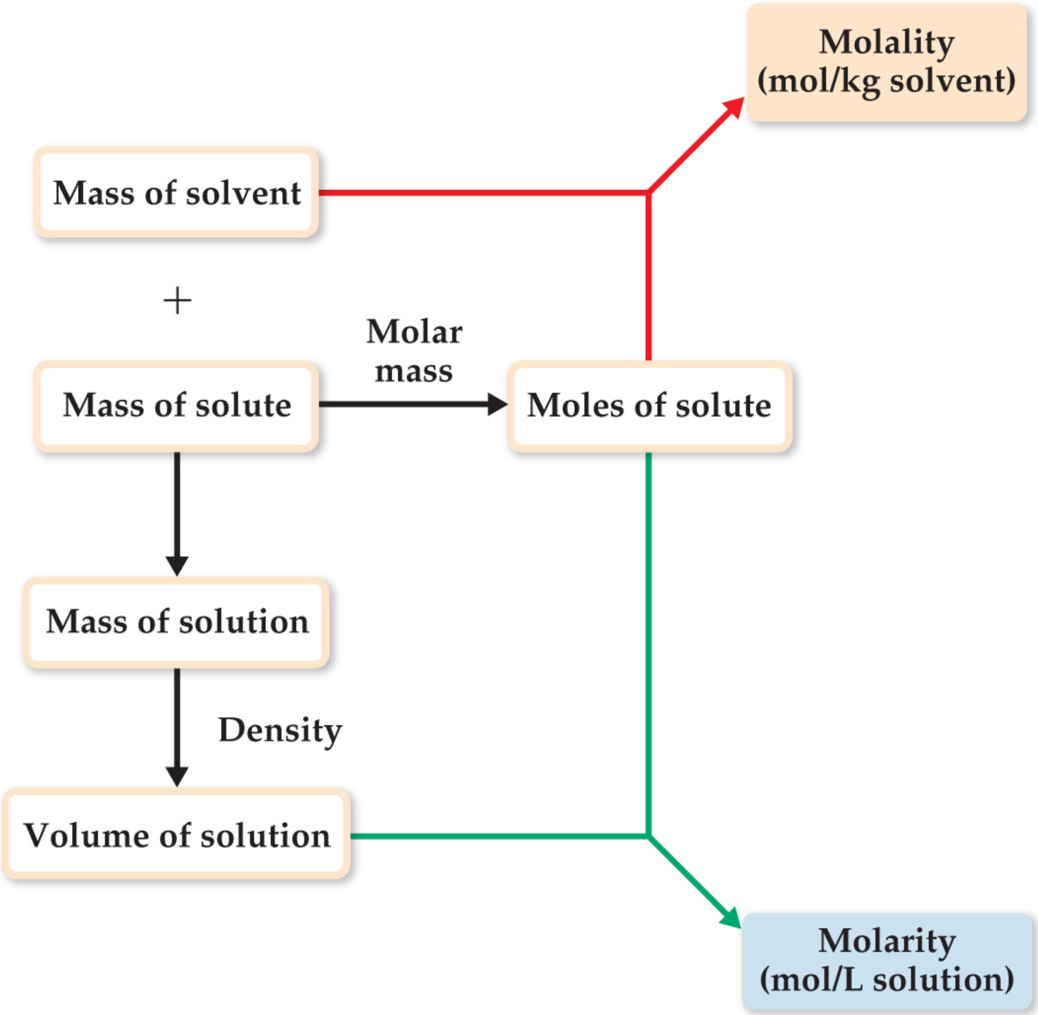
Parts per billion (ppb)

$$\text{ppb} = \frac{\text{mass of } A \text{ in solution}}{\text{total mass of solution}} \times 10^9$$

Mole Fraction (X)

$$X_A = \frac{\text{moles of } A}{\text{total moles of all components}}$$

Changing Molarity to Molality



If we know the density of the solution, we can calculate the molality from the molarity, and vice versa.

Examples

1. The density of a 19% solution of HCl is 1.0929 gmL^{-1}. What is the molarity?

19% = 190g/1000 g solution.

MW = 36.45 g/mol 190 g/36.45 $gmol^{-1}$ = 5.2 moles

Mass solution/D = V solution.

1000 g/1.0929 gmL^{-1}= 914.996 mL solution

Molarity = 5.2 moles/.914996 L = 5.7 M

Examples

1. What is the mole fraction of HCl in 19% this solution?

Moles HCl in 1000g: 190 g/36.45 $\mathrm{gmol^{-1}}$ = 5.2 moles

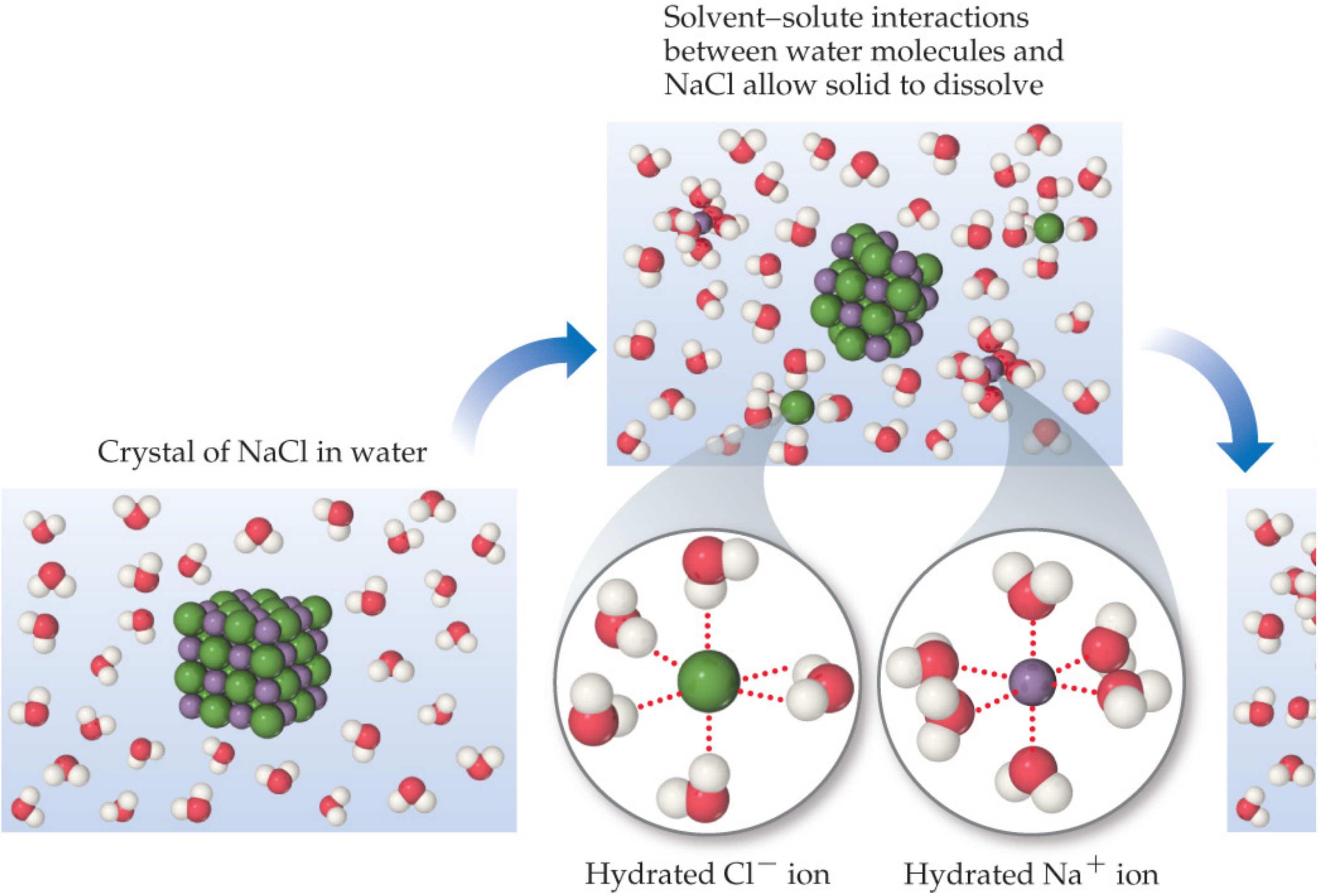
Moles water in 1000g: 1000-190=810 g water.

810 g/18 $\mathrm{gmol^{-1}}$ = 4.5 moles water.

Mole fraction = moles HCl/tot. moles = 5.2/(4.5 + 5.2)

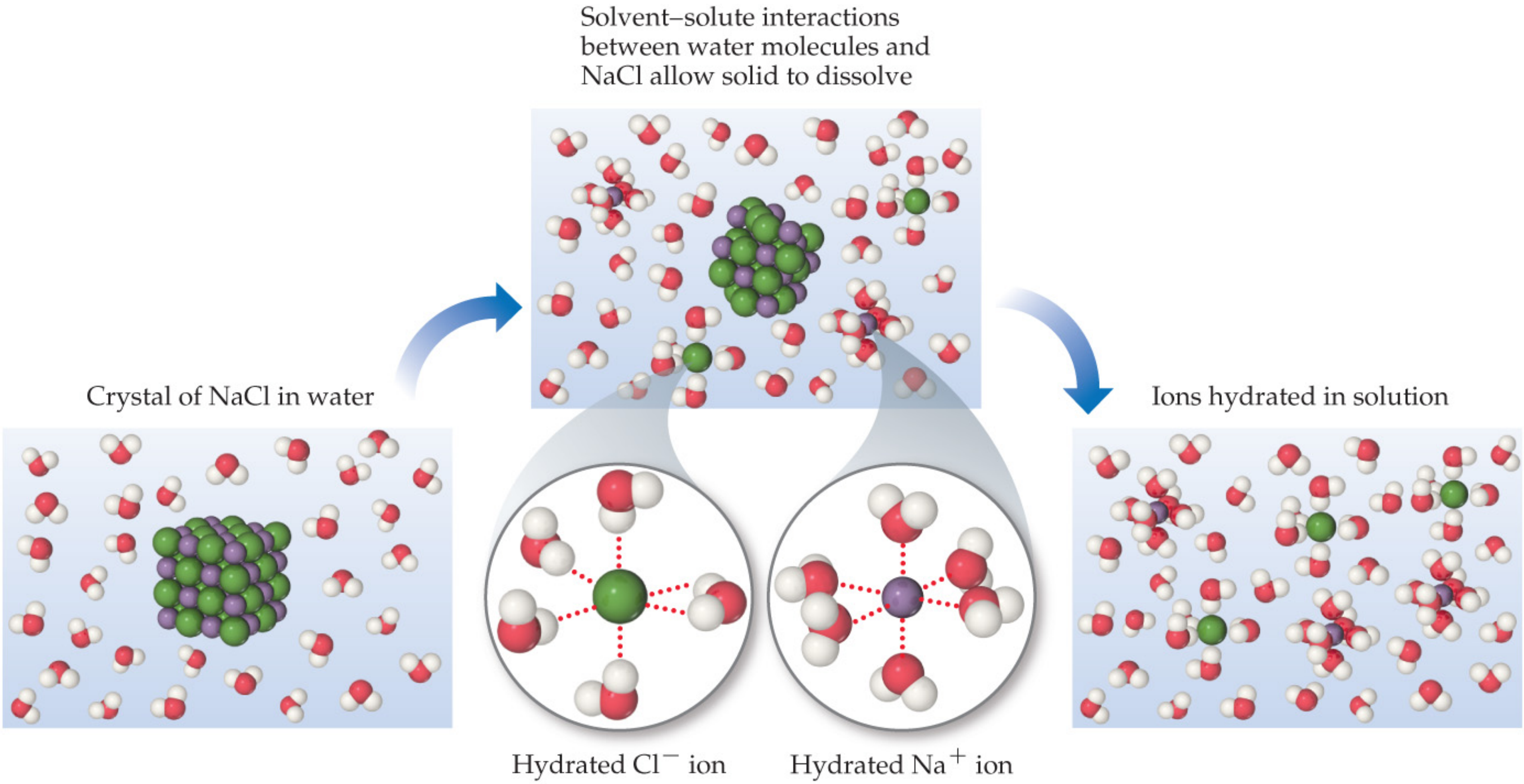
5.2/9.7 = 0.54

The Solution Process



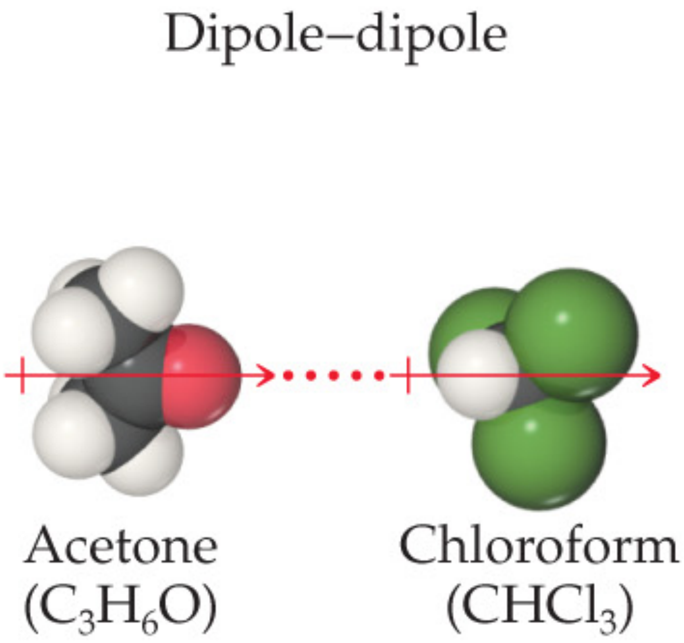
Dissolution (dissolving): A “war breaks out” between: solute-solute interactions and Solute-solvent interactions.

How Does a Solution Form?



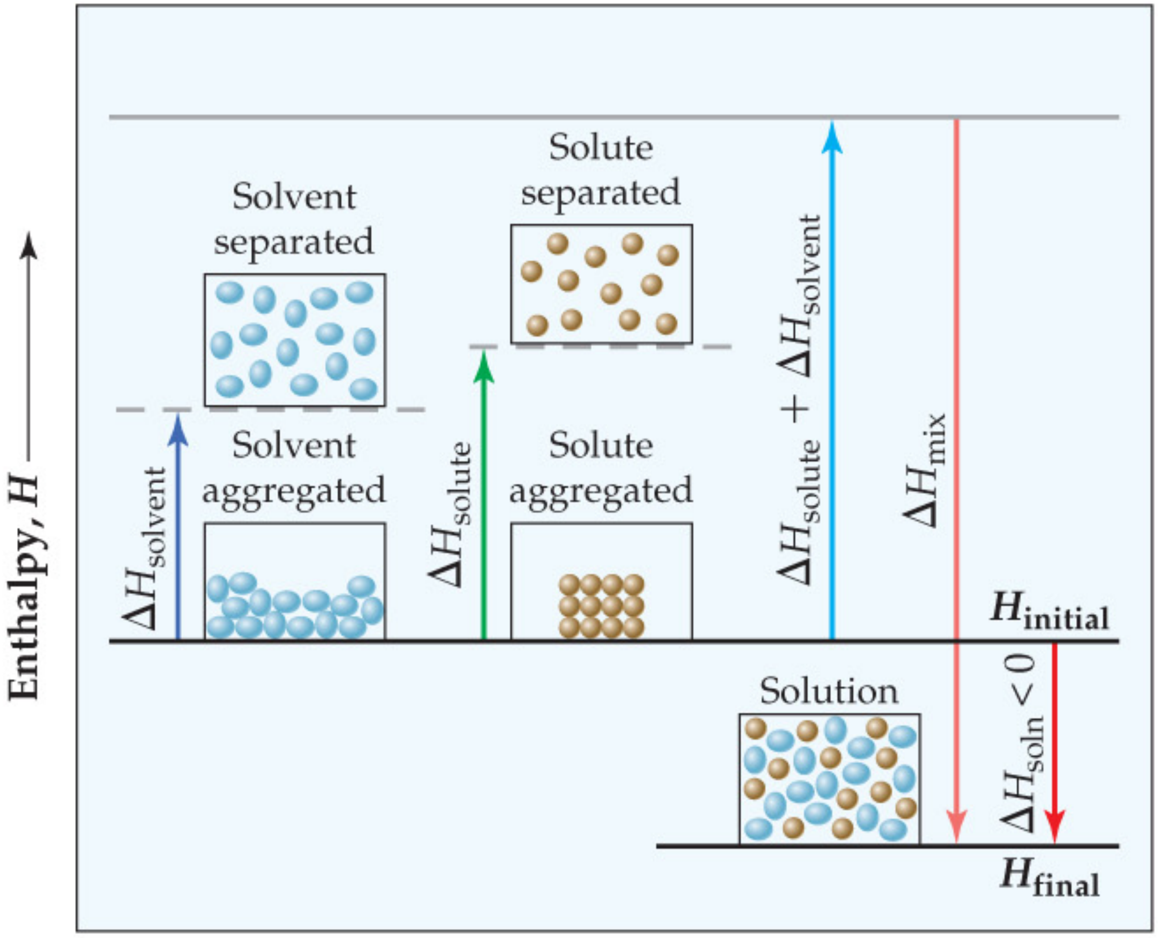
As a solution forms, the solvent pulls solute particles apart and surrounds, or **solvates**, them.

How Does a Solution Form?



If an ionic salt is soluble in water, it is because the ion–dipole interactions are strong enough to overcome the lattice energy of the salt crystal.

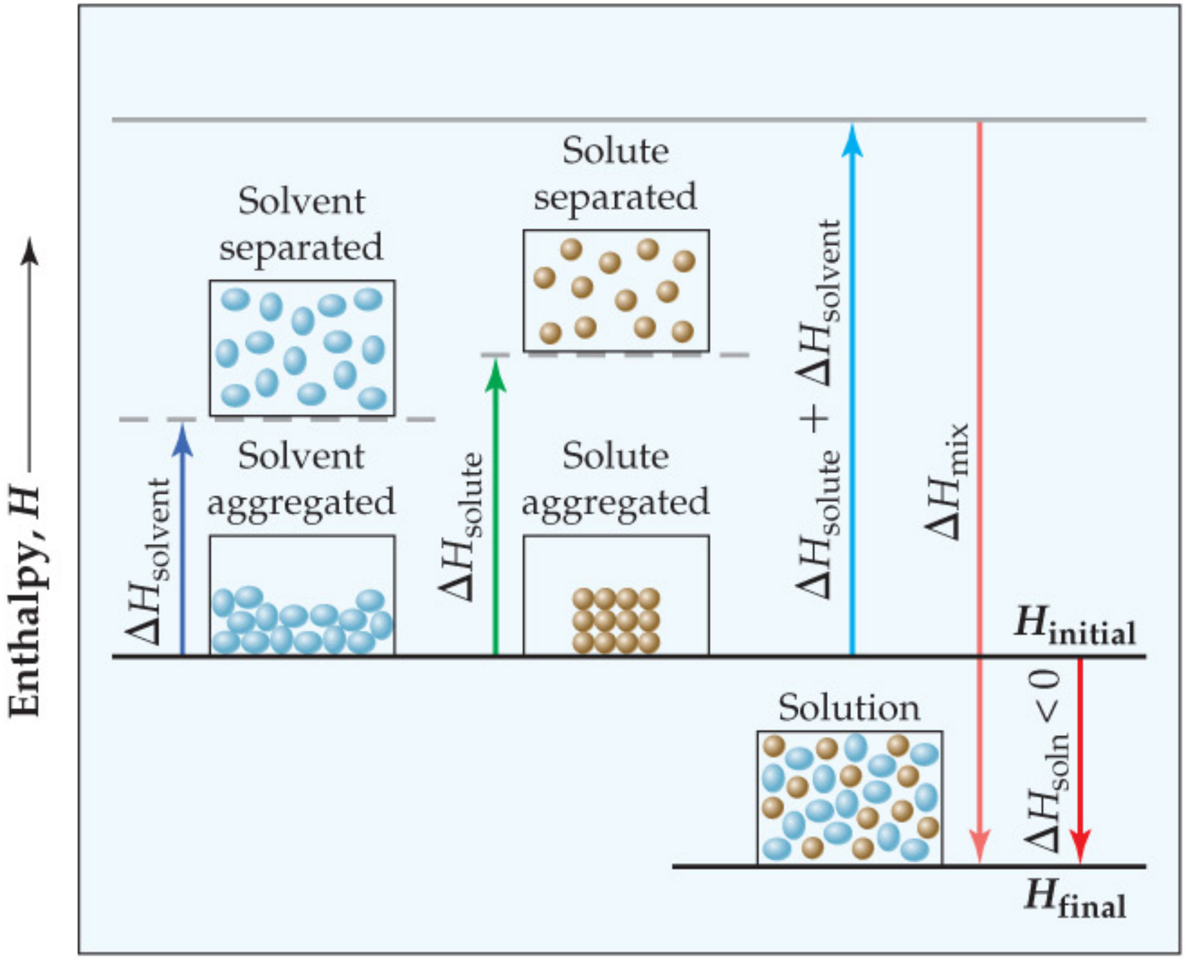
Energy Changes in Solution



Exothermic solution process

- Separation of solute particles,
- Separation of solvent particles,
- New interactions between solute and solvent.

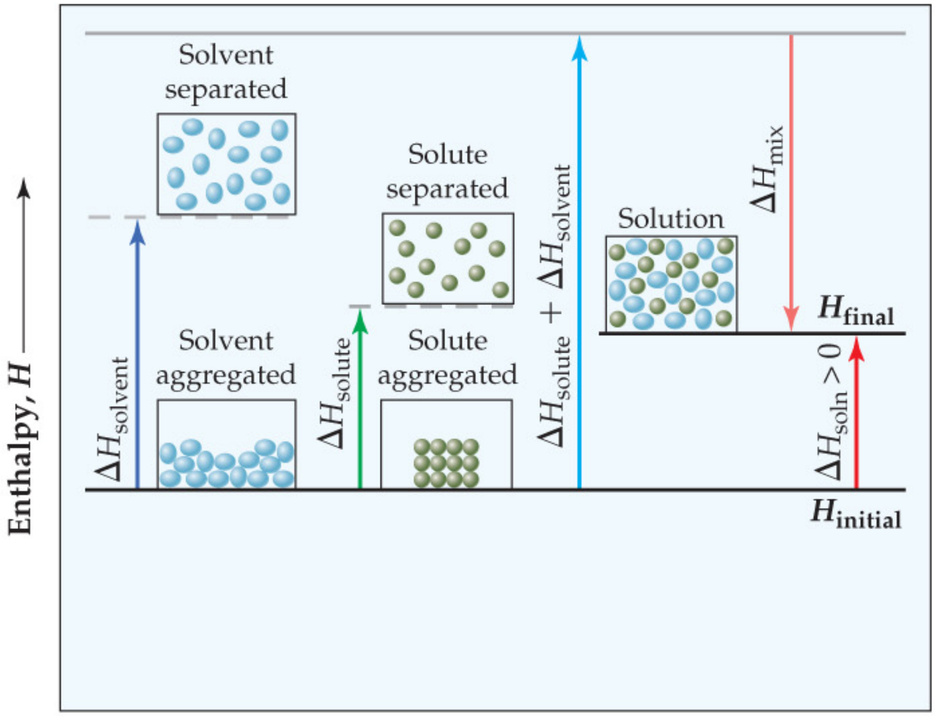
Energy Changes in Solution



Exothermic solution process

The enthalpy change of the overall process depends on Δ*H* for each of these steps.

Why Do Endothermic Processes Occur?



Endothermic solution process

Can a solute dissolve if the lattice energy is greater than the energy of solvation?

Various possibilities

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

	ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
Always spontaneous	-	+	always -
Often for gas solutes	-	-	depends
Often for ionic solutes	+	+	depends
Never spontaneous	-	-	always +

Exam topics:

Exam 3: Covers lecture 20 - 32.

Lewis structures

VSEPR, shape, geometry

Hybridization

Valence bond theory.

Gases, $PV = nRT$

Bonding in the solid state

crystalline structure.

Inter-atomic forces

Exam topics:

Exam 3: Covers lecture 20 - 32.

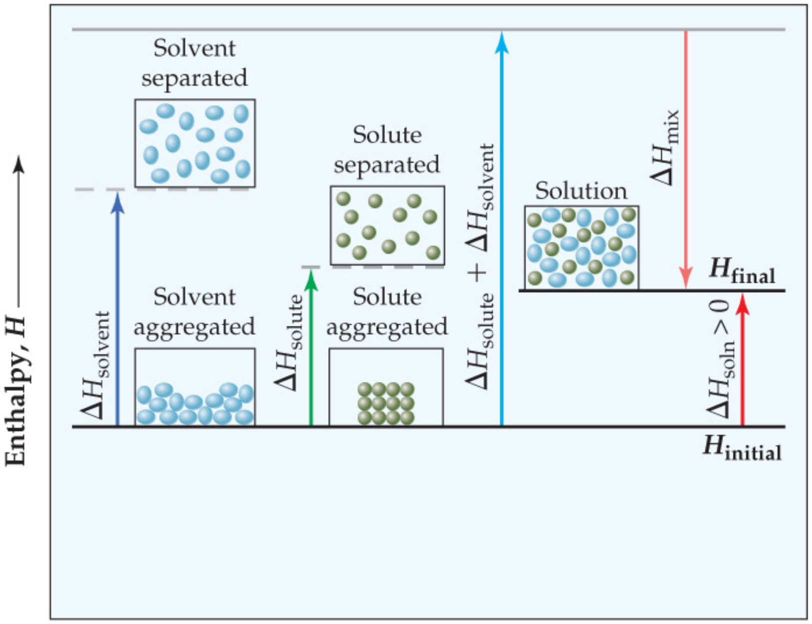
Entropy and Gibbs free energy.

2nd law of thermodynamics

Changes of state

- vapor pressure
- phase diagrams
- Solutions
  - types (saturated, supersaturated, unsaturated)
  - Thermo of solutions
  - concentration of solutions.

Why Do Endothermic Processes Occur?



Endothermic solution process

Yes! Dissolving NH_4NO_3 is endothermic (brings in heat)

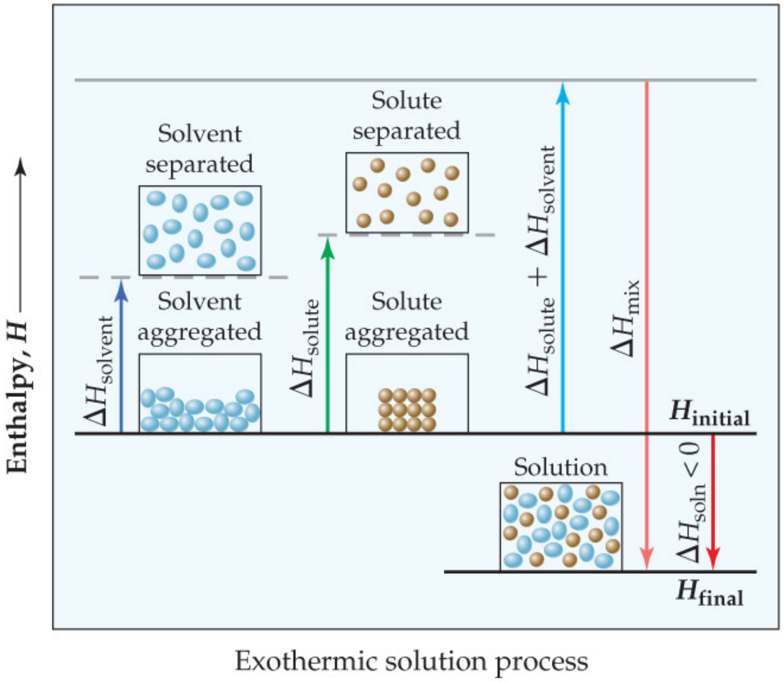
So: lattice Energy was greater than heat of solvation. (interactions between solute and solvent)

Enthalpy Is Only Part of the Picture

Must be *Entropy driven.* Randomness of system must get bigger.

Solid→ liquid ΔS +

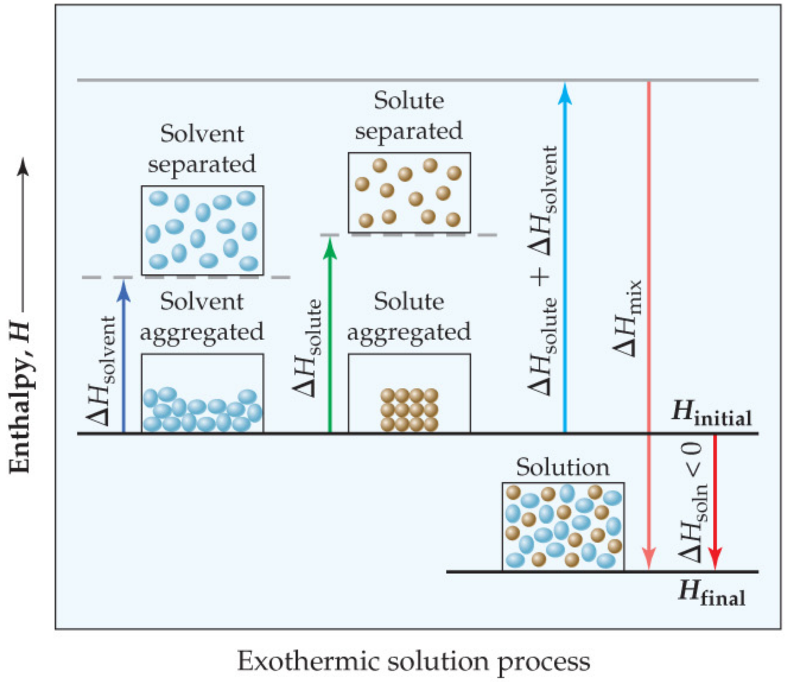
Dissolving solid in liquid should always be +.



Exothermic solution process

Enthalpy Is Only Part of the Picture

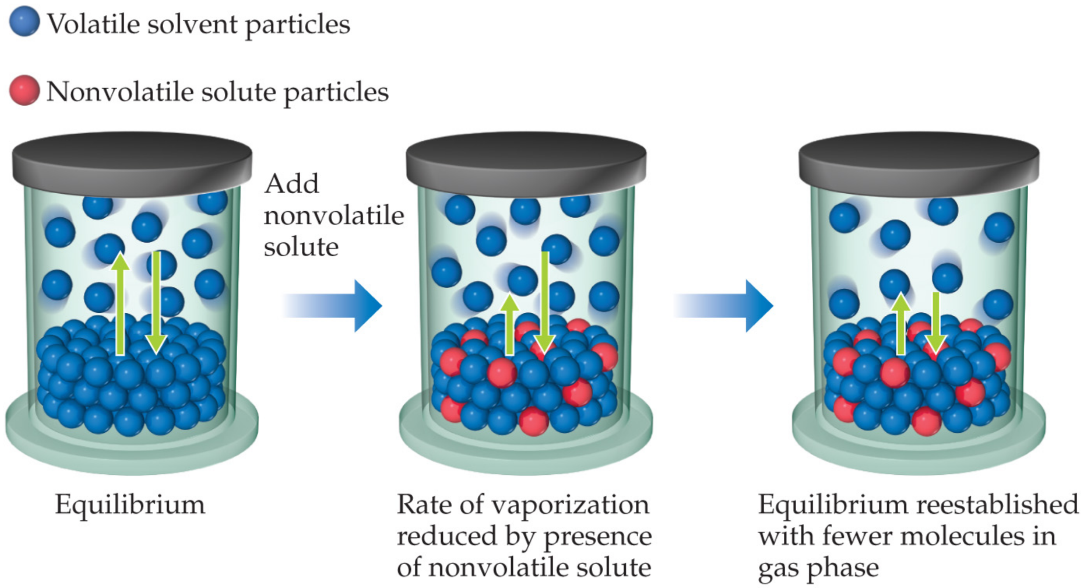
So even though enthalpy may increase, the overall energy of the system can still decrease if the system becomes more disordered.



Colligative Properties

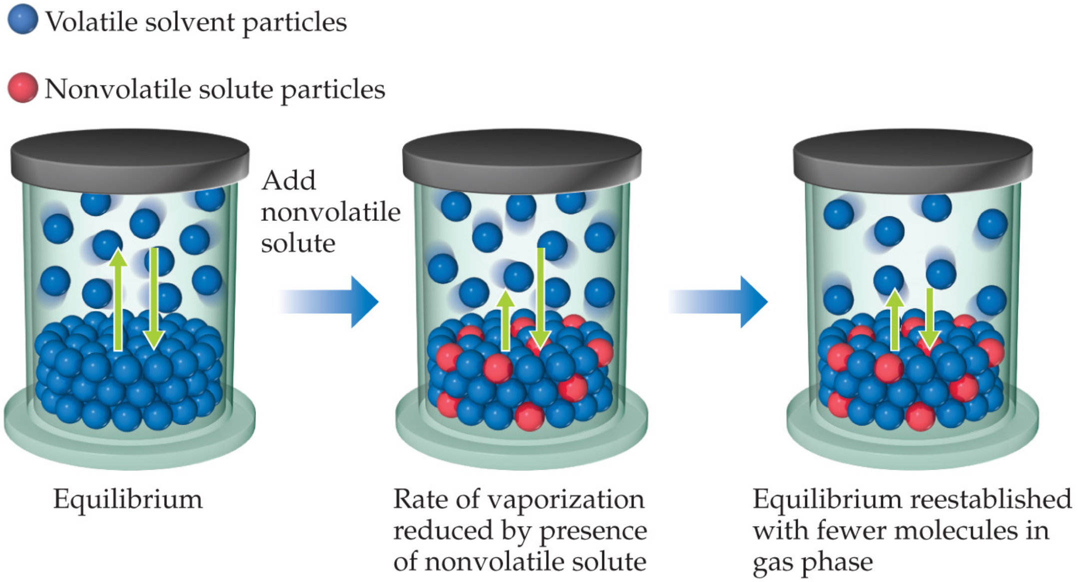
- Changes in **colligative properties** depend only on the *number* of solute particles present, not on the *identity* of the solute particles.
- Among colligative properties are
  - Vapor-pressure lowering
  - Boiling-point elevation
  - Melting-point depression
  - Osmotic pressure

Vapor Pressure



Because of solute–solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapor phase.

Vapor Pressure



Therefore, the vapor pressure of a solution is lower than that of the pure solvent.

Raoult' s Law

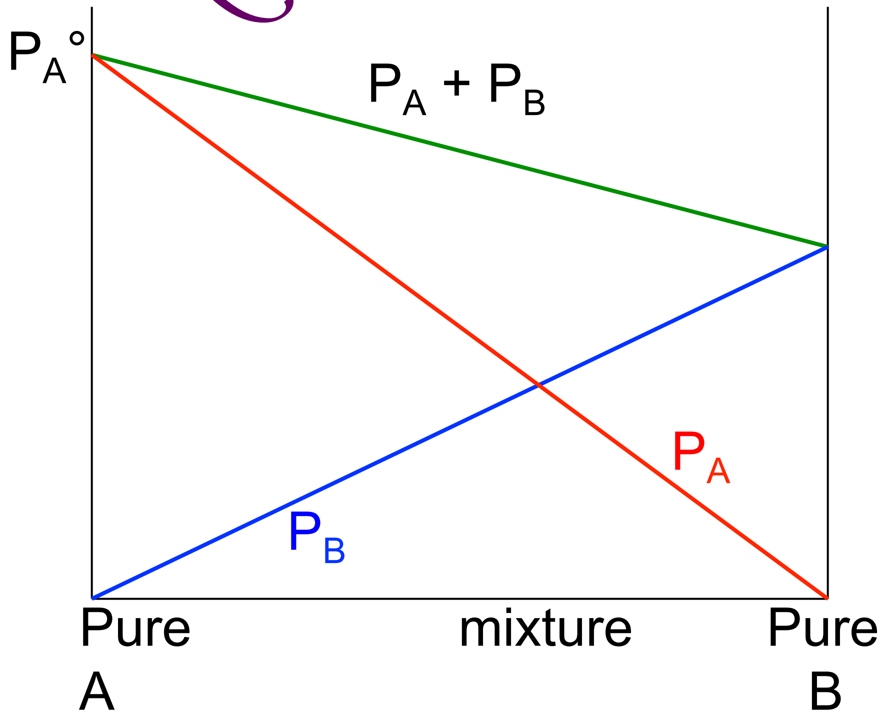
$$P_A = X_A P°_A$$

where

- X_A is the mole fraction of compound *A*, and
- $P°_A$ is the normal vapor pressure of *A* at that temperature.

Note: This is one of those times when you want to make sure you have the vapor pressure of the *solvent*.

Raoult’ s Law



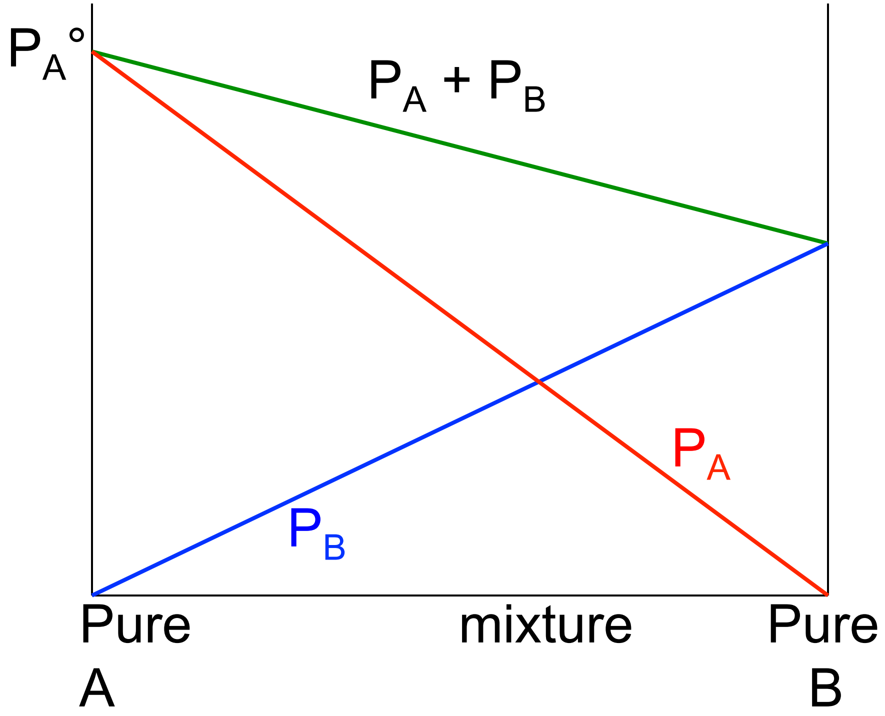
Vapor pressure above solution = the sum of all the partial vapor pressures of all components

Partial V.P. depends on 2 things:

1. How much (mole fraction)?
2. How volatile (V.P. of pure A)

Raoult' s Law

$$P_A = X_A P^\circ_A$$

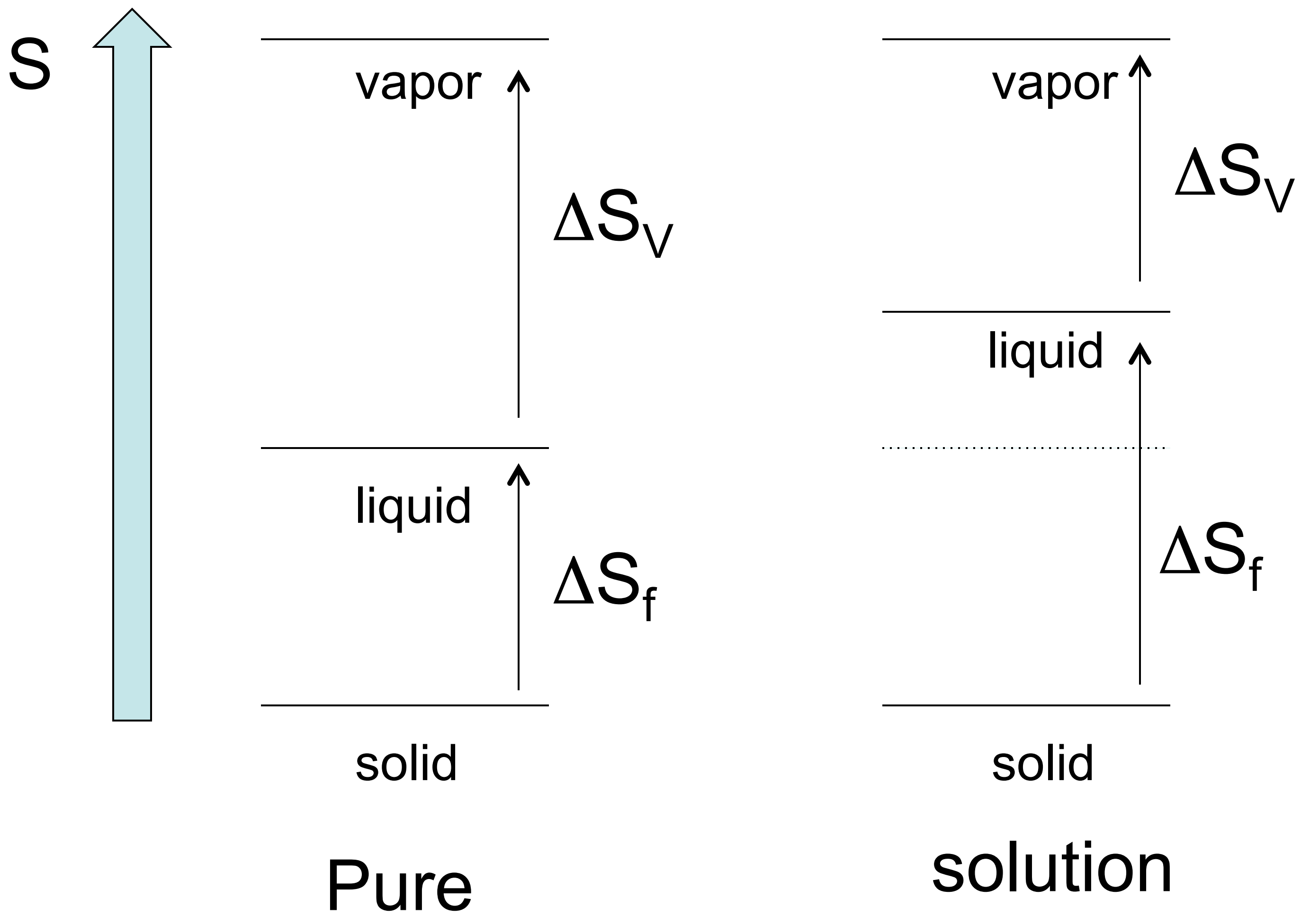


- X_A is the mole fraction of compound *A*, and
- P°_A is the normal vapor pressure of *A* at that temperature.
- $P_{tot} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$

Colligative properties & non volatile solvents

- *If solute is nonvolatile:* $P°_{solute} = 0$.
- So: $P_{tot} = P_A + P_B = X_A P_A° = X_{solvent} P_{solvent}°$
- Addition of nonvolatile solute will decrease $X_{solvent}$
- And so decrease vapor pressure.
- But why?

Colligative properties & non volatile solvents



S

vapor

ΔS_V

liquid

ΔS_f

solid

Pure

vapor

ΔS_V

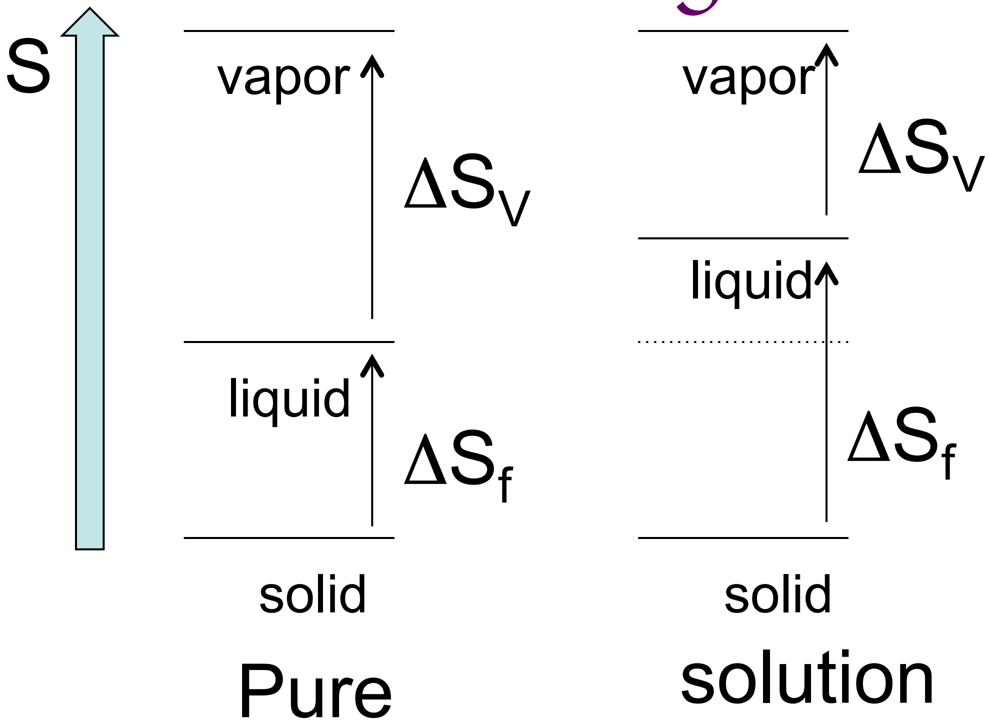
liquid

ΔS_f

solid

solution

Colligative properties & non volatile solvents



S

vapor

ΔS_V

liquid

ΔS_f

solid

Pure

vapor

ΔS_V

liquid

ΔS_f

solid

solution

Only the S of the liquid changes

Vapor and solid, pure.

Entropy of solution increases vs. pure liquid

ΔG_V = 0 (equilibrium)

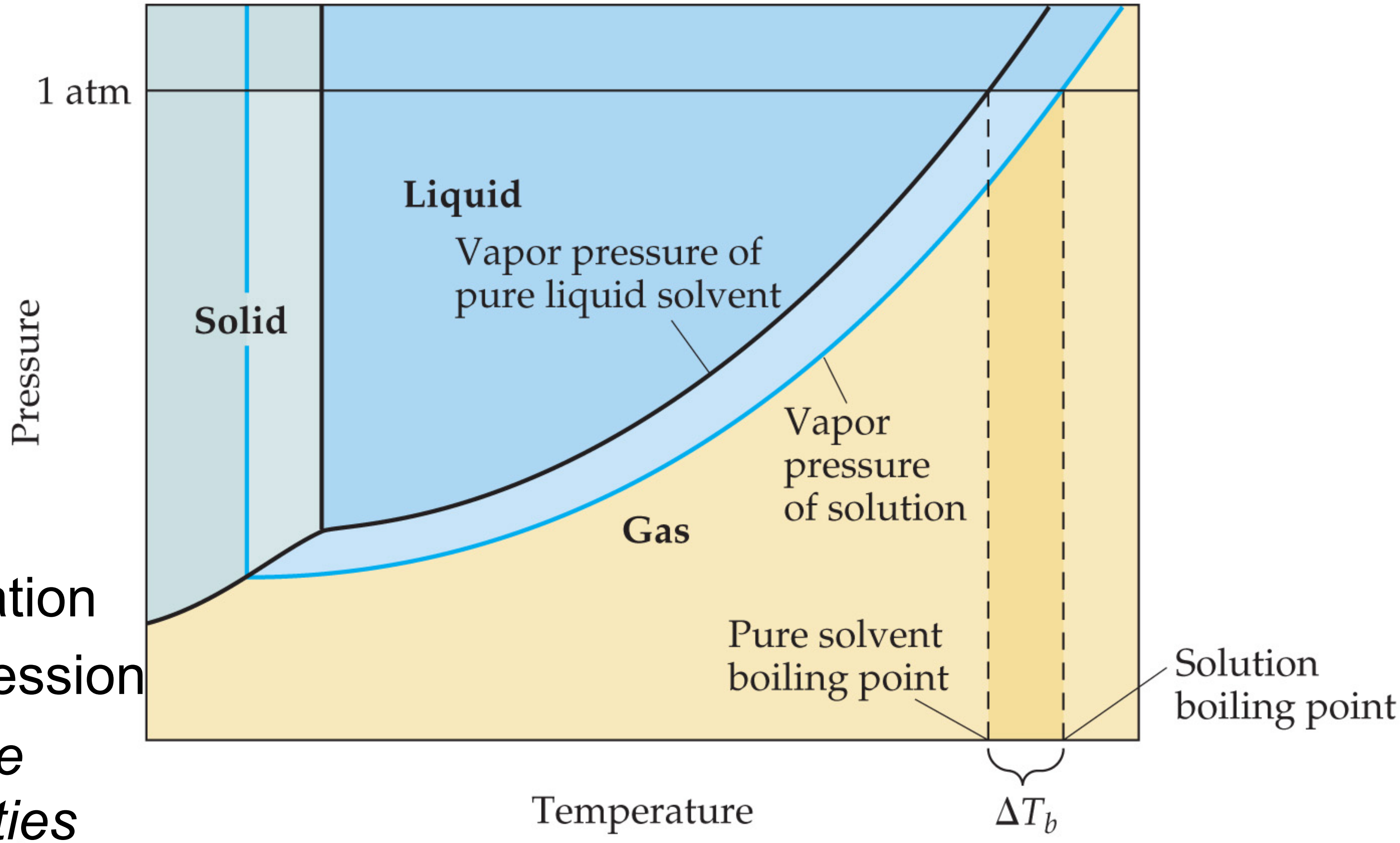
ΔH_V = constant (solvent)

$\Delta G_V = \Delta H_V - T\Delta S_V$ so $-T\Delta S_V$ = constant (solvent)

ΔS_V smaller, T larger (boiling pt. elevation)

ΔS_V larger, T smaller (freezing pt depression)

B.P. Elevation and F.P Depression



b.p. elevation

f. p. depression

Colligative properties

-depend on *number of particles*

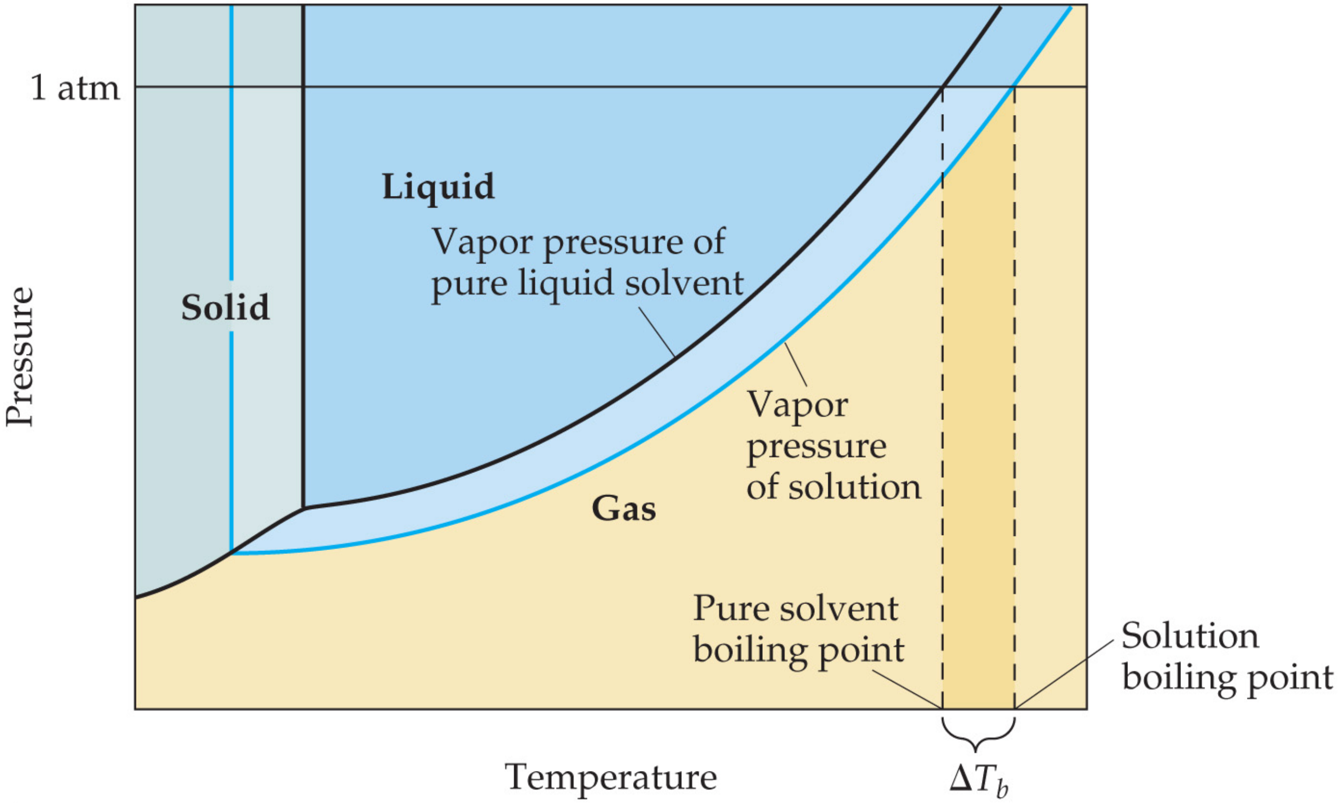
B.P. Elevation and F.P Depression

b.p. elevation

f. p. depression

Colligative properties

-depend on *number of particles*



Example 1 mole NaCl versus 1 mole sugar:

NaCl → $Na^+ + Cl^-$ 2 moles particles Van’t Hoff factor (i): 2
Sugar → Sugar (1 mole particles) Van’t Hoff factor (i): 1

Examples

Substance	i
NaCl	
KNO_3	
$Mg(NO_3)_2$	
$Ca_3(PO_4)_2$	
HCl	
CH_3CO_2H	

Examples

Substance	i
NaCl	2
KNO_3	2
$Mg(NO_3)_2$	3
$Ca_3(PO_4)_2$	5
HCl	2
CH_3CO_2H	1 (not all dissociated)

$$\Delta T = Kmi$$

K = constant (depends on solvent

m = molality (moles solute/Kg solvent)

i = Van't Hoff factor

Examples

Which substance has the lowest freezing pt.?

1.5 m NaCl

1.2 m Na_2SO_4

3.0 m sugar

1.6 m KNO_3

ΔT = Kmi
K = constant (depends on solvent
m = molality (moles solute/Kg solvent)
i = Van't Hoff factor

Examples

Which substance has the lowest freezing pt.?

1.5 m NaCl	3 m part
1.2 m Na_2SO_4	3.6 m part.
3.0 m sugar	3 m part.
1.6 m KNO_3	3.2 m part.

$\Delta T = Kmi$

K constant, depends on m*i

Examples

When 1.0 mole of magnesium acetate was dissolved in water, the b.pt. increased by 6 °C to 106 °C. How much water was used to make the solution?

Examples

When 1.0 mole of magnesium acetate was dissolved in water, the b.pt. increased by 6 °C to 106 °C. How much water was used to make the solution? ($K_B(H_2O) = 0.5$?

$m = n_{solute}/Kg_{solvent}$

$Mg(Ac)_2$ i = 2

$\Delta T = Kmi$

$6 = 0.5(1.0/Kg)2$

$6 = 1/Kg$

Kg = 0.2 Kg (0.16666 Kg)

‘Unit 34.
Introduction to chemical equilibrium

Why do reactions happen?

Reaction

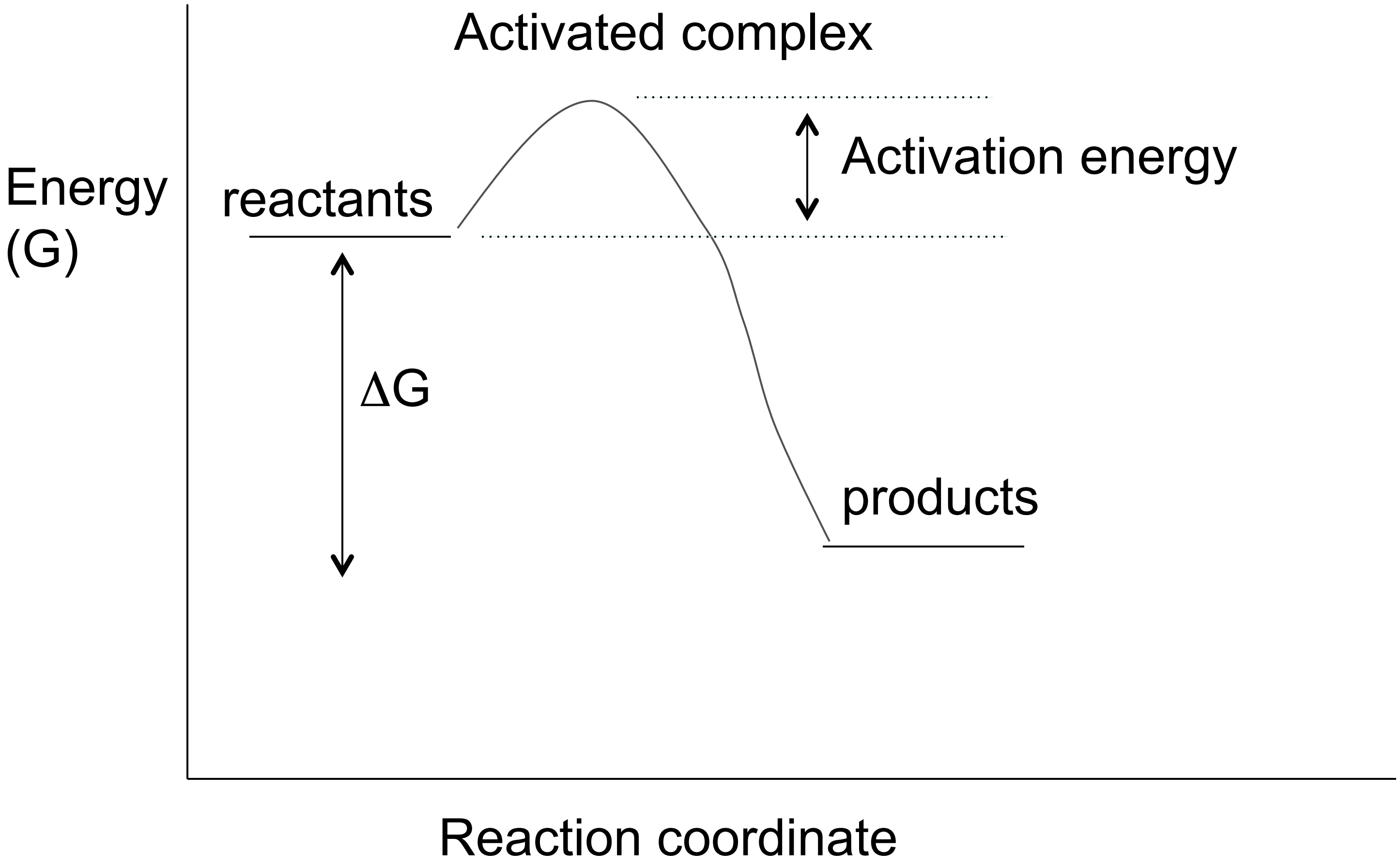
Thermodynamics

1. will it go (ΔG -)
2. How far will it go? ($\Delta G=0$)

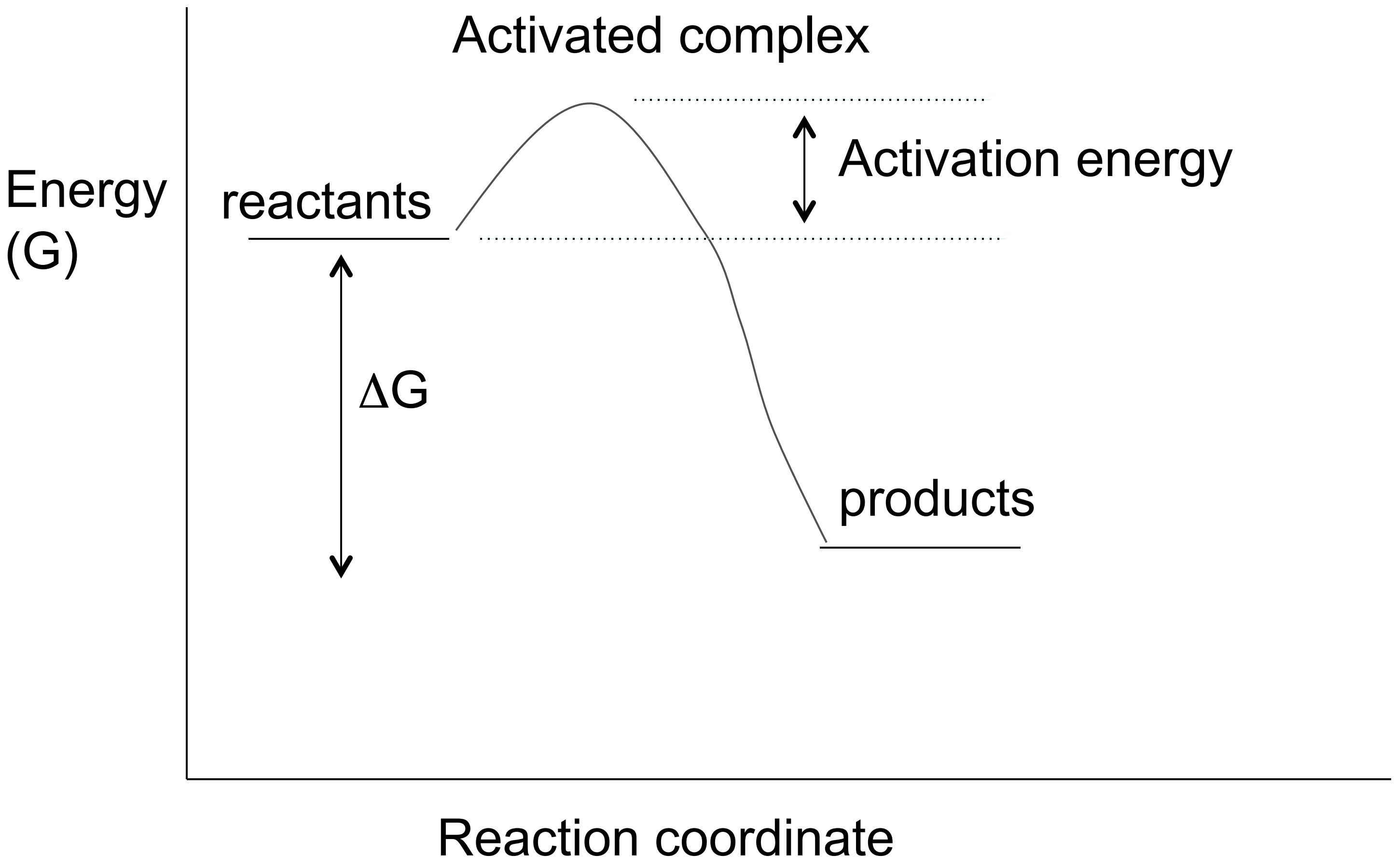
Kinetics

1. By what route (mechanism)
2. How fast will it go (rate)

Charting the path of a reaction,
One molecule at a time.



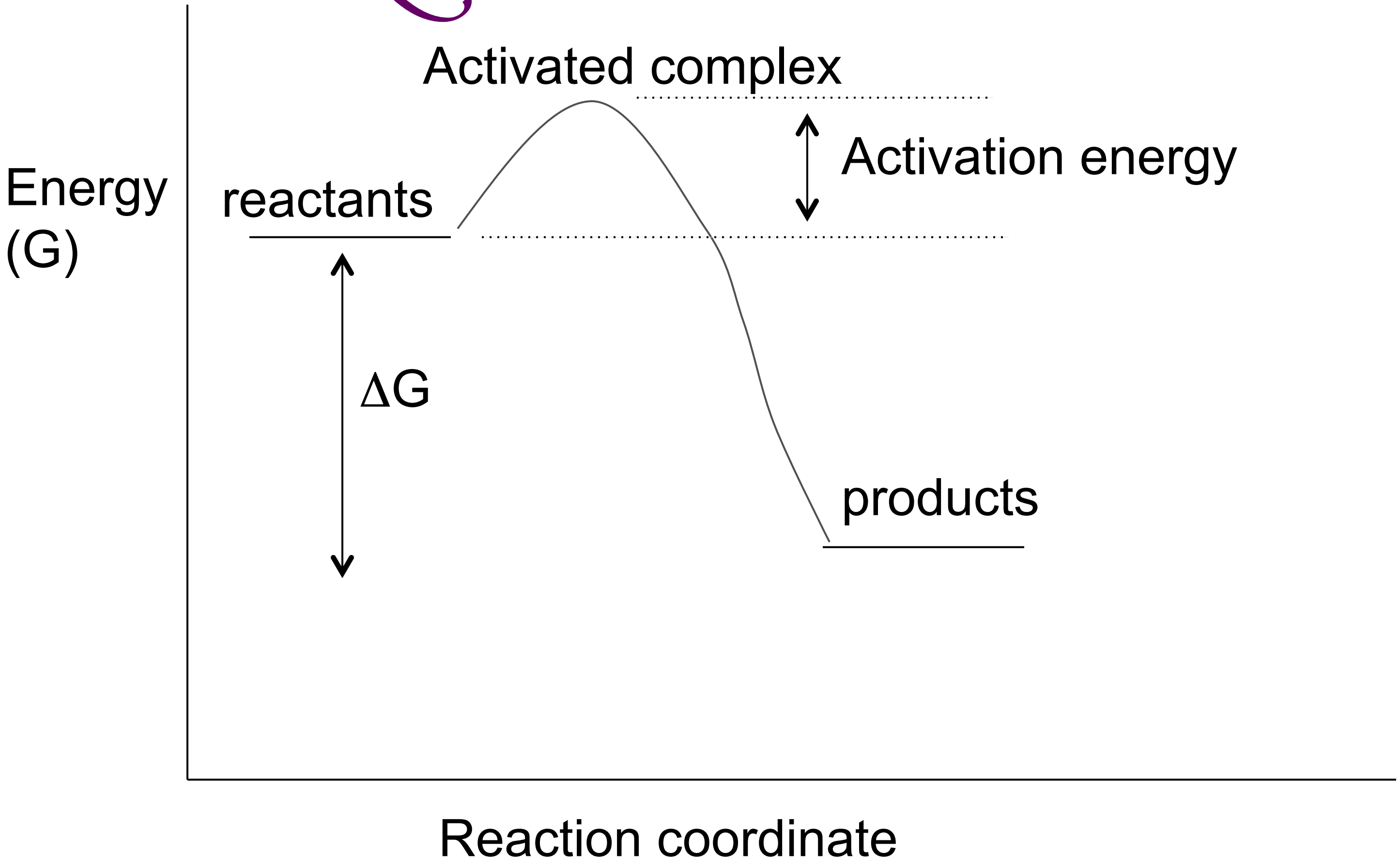
Reaction coordinate.



NO_2 CO O—N---O----C—O NO CO_2

Reactants activated complex products

Reaction coordinate.



Activated complex

Activation energy

Energy (G)

reactants

ΔG

products

Reaction coordinate

NO_2 CO O—N---O----C—O NO CO_2

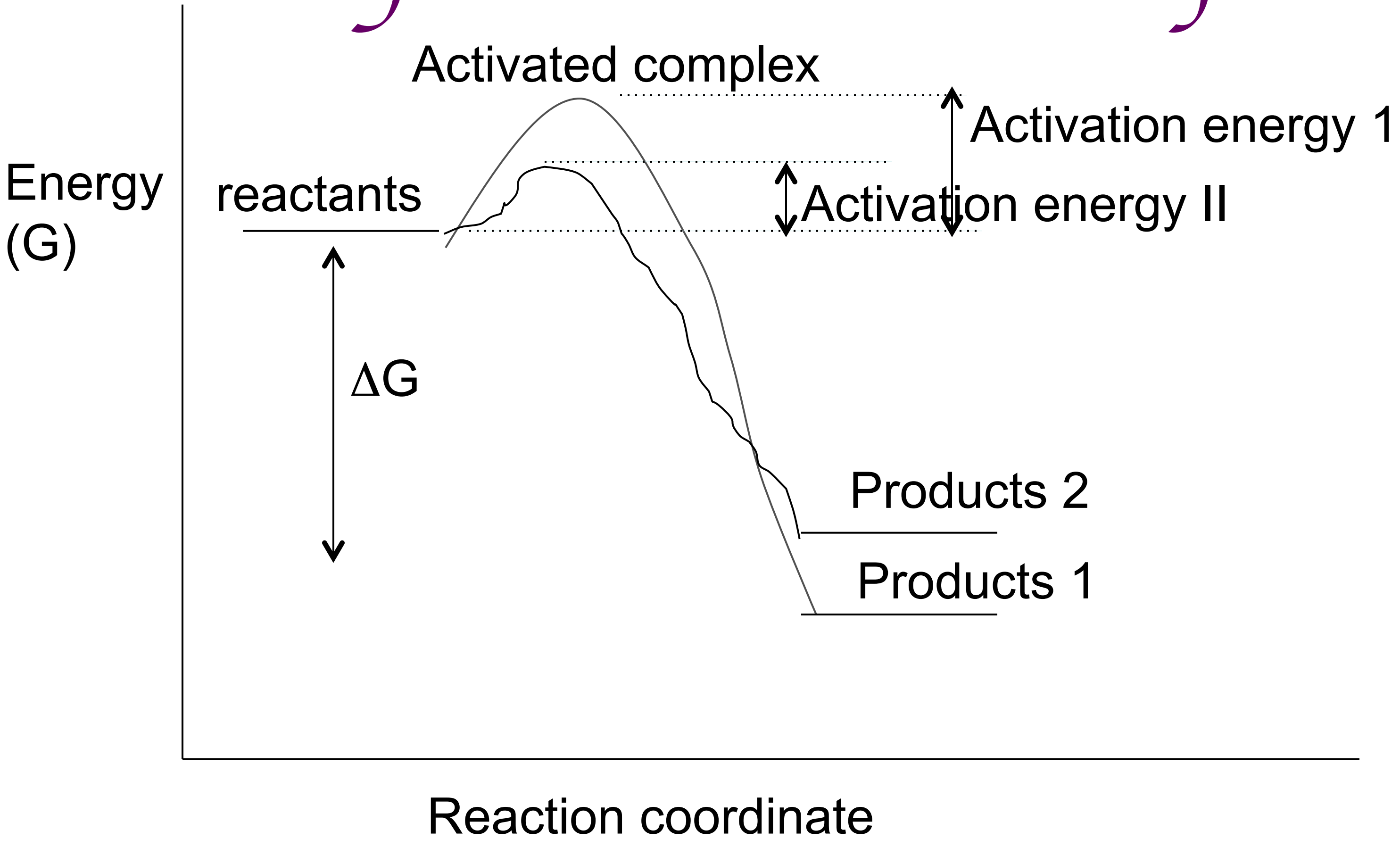
Reactants activated complex products

For a reaction to happen: 1. species much collide

2. Must collide with enough E

3. Must be oriented right.

Thermodynamic vs. kinetic product.



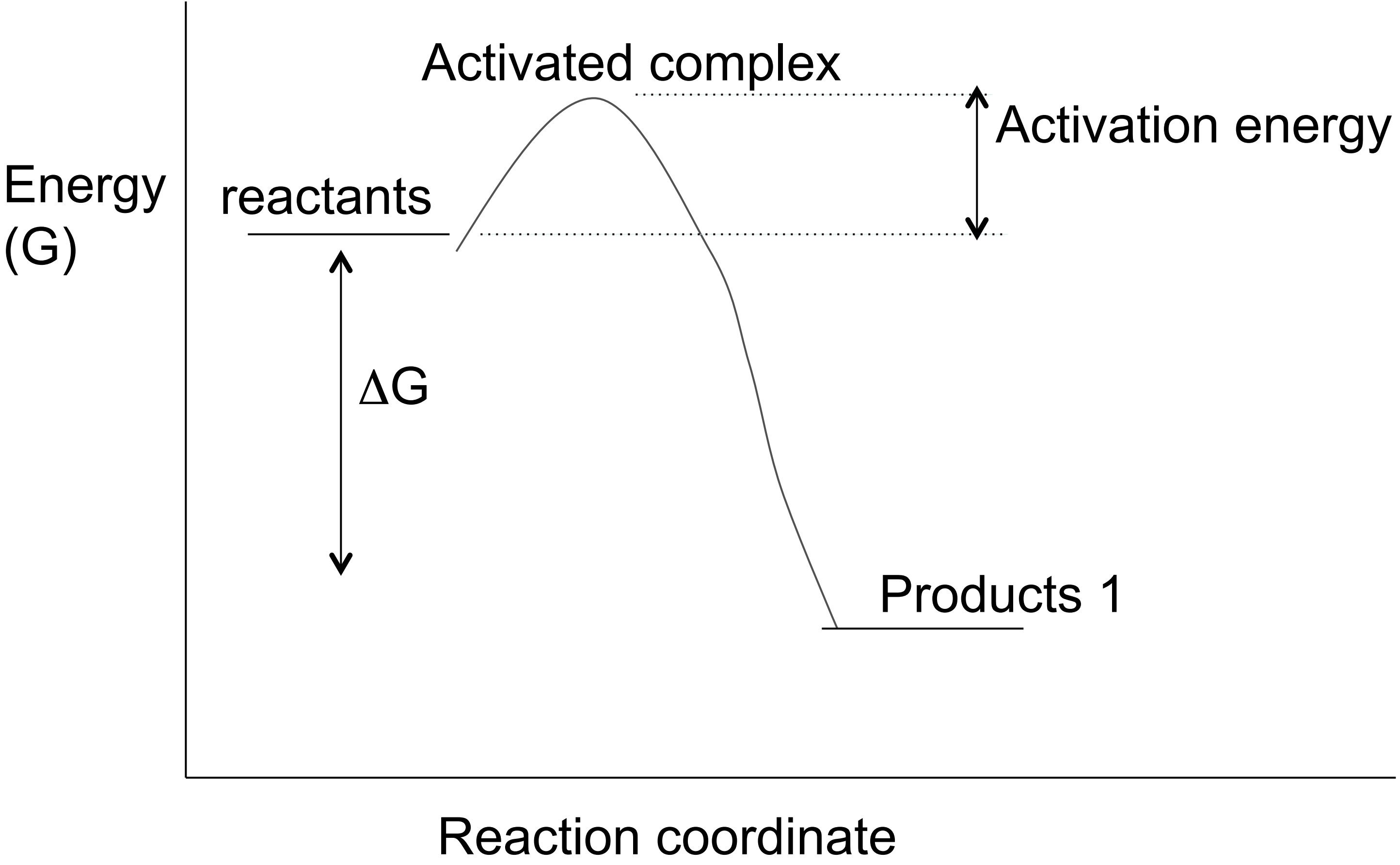
Kinetic product: smaller hill to climb, higher E product
- not enough E, Kinetic product.

Thermodynamic product: Higher hill to climb, lower E product.
Plenty of E, thermodynamic product.

Chemical kinetics How fast will it go?

The more activated complexes formed, the faster the reaction.

1. Increase collision frequency (higher concentration
2. Increase collision energy (higher T).



Chemical kinetics: Concentration

The more activated complexes formed, the faster the reaction.

1. Increase collision frequency (higher concentration
2. Increase collision energy (higher T).