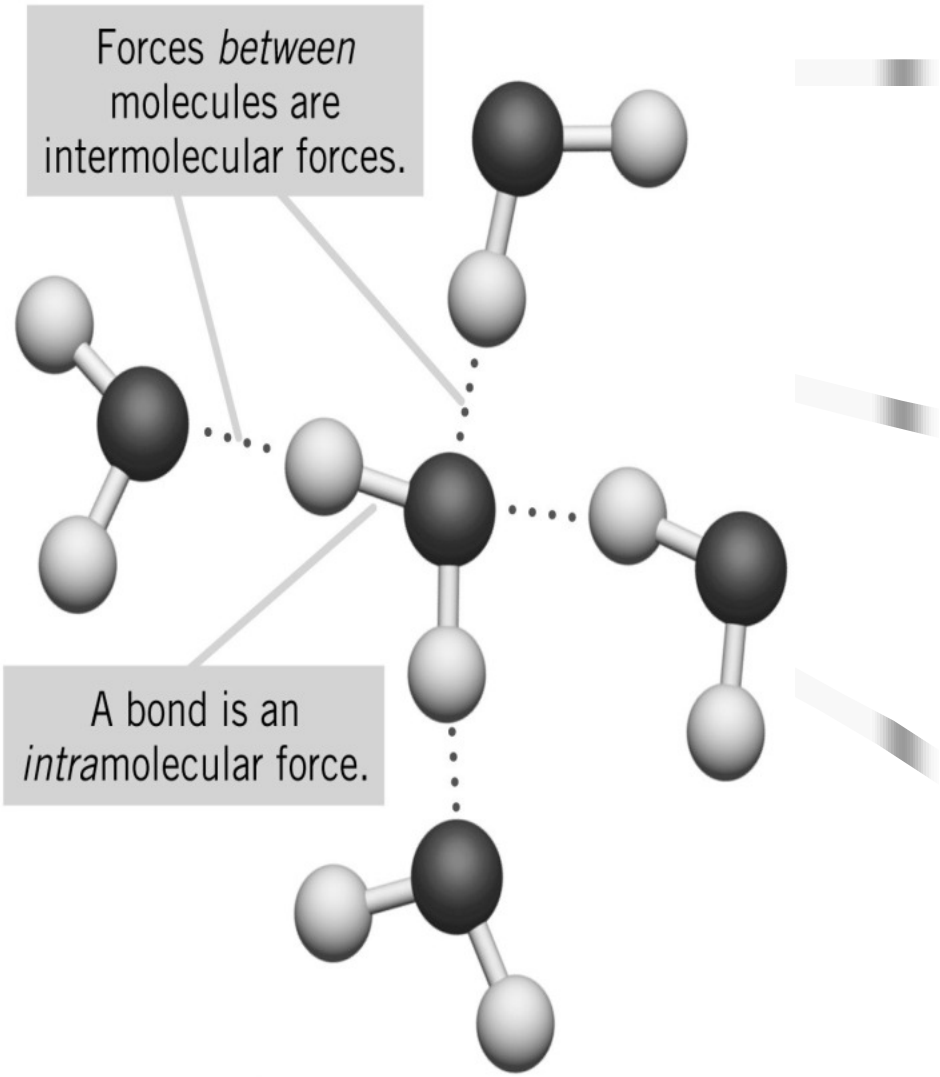
Chemistry Olympiad - Kolack

Module 4

Intermolecular forces, solutions, reaction rate, equilibria, acids/bases, thermodynamics

Inter vs. intra

- We've studied chemical bonds which are INTRAmolecular forces...
- We now explore the forces between molecules, or INTERmolecular forces which you might rightly assume to be weaker since they are over longer distances



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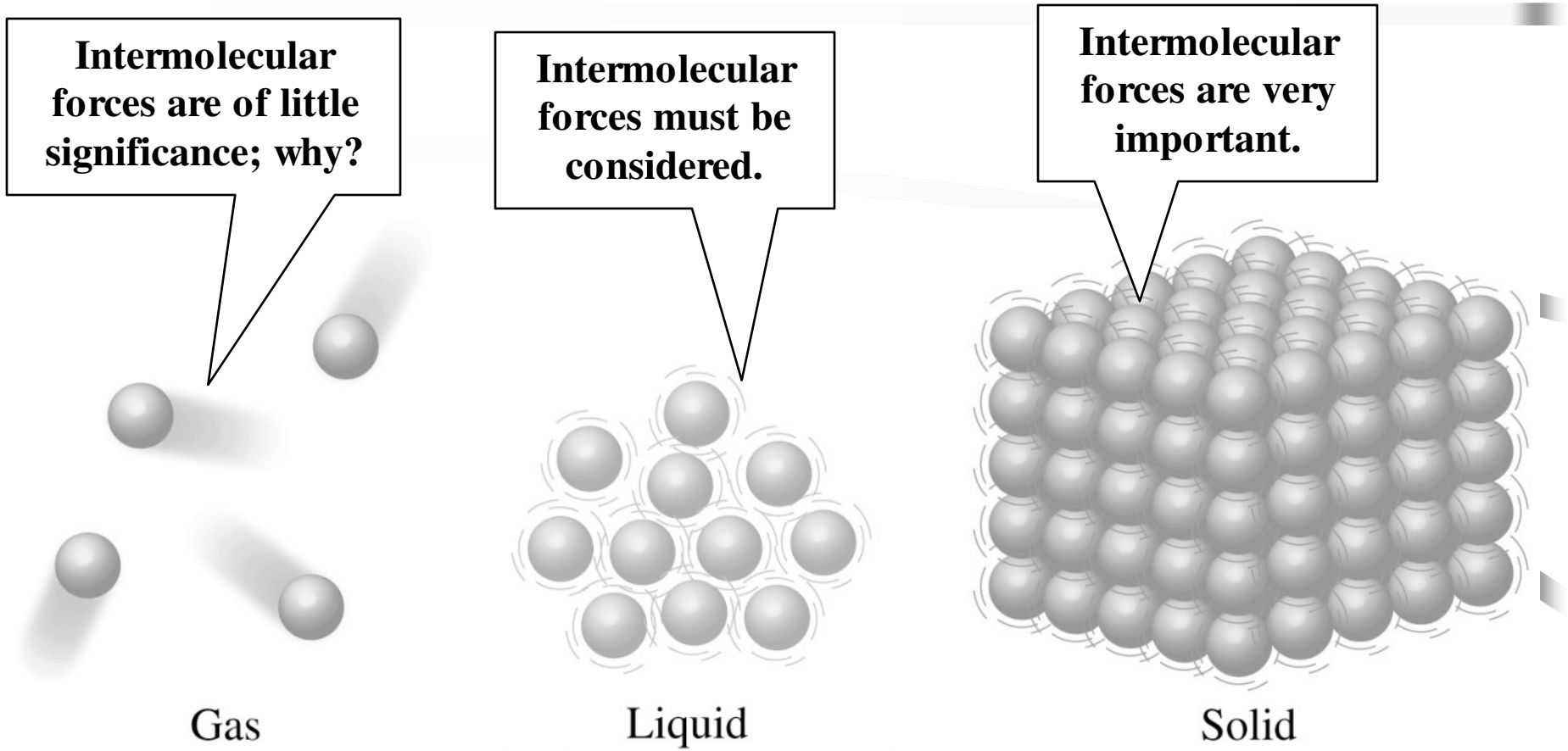
Inter vs. intra (cont'd)

- We did discuss the ideal gas law earlier, but what MAKES something a gas?
- Space between molecules determines state, but what determines the spacing?
- Intramolecular forces (bonds) govern molecular properties such as molecular geometries and dipole moments.
- Intermolecular forces determine the macroscopic physical properties of liquids and solids such as melting points, freezing points, and other physical properties.

States of matter compared



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Vaporization

- Going from a liquid to a gas
- Requires energy (endothermic- ΔH_{vap} is a POSITIVE number since energy is being supplied to the system FROM the surroundings)
- Reverse is condensation, which gives off energy (exothermic- ΔH_{cond} is a NEGATIVE number since energy is coming OUT of the system into the surroundings)
- Enthalpy is a function of state: therefore, if a liquid is vaporized and the vapor condensed at constant temperature, the total ΔH must be zero:

$$\Delta H_{vap} + \Delta H_{cond} = 0$$

$$\Delta H_{cond} = -\Delta H_{vap}$$

- The vaporization-condensation cycle is the basis of refrigeration and air conditioning
- The study of energy changes involved in this phenomenon is called calorimetry

Table 11.1 Some Enthalpies (Heats) of Vaporization at 298 K[a]

Liquid	ΔH_{vapn}, kJ/mol
Carbon disulfide, CS_2	27.4
Carbon tetrachloride, CCl_4	37.0
Methanol, CH_3OH	38.0
Octane, C_8H_{18}	41.5
Ethanol, CH_3CH_2OH	43.3
Water, H_2O	44.0
Aniline, $C_6H_5NH_2$	52.3

[a] ΔH_{vapn} values are somewhat temperature-dependent.

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Example

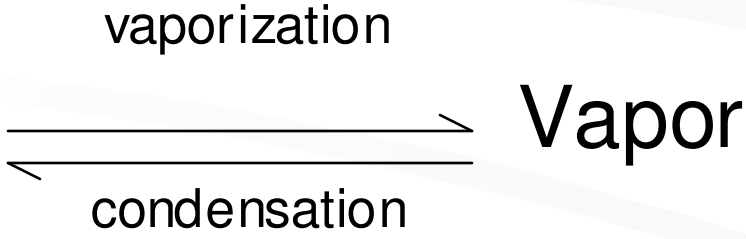
How much heat, in kilojoules, is required to vaporize 175 g methanol, CH_3OH, at 25 °C?

Example An Estimation Example

Without doing detailed calculations, determine which liquid in Table 11.1 requires the greatest quantity of heat for the vaporization of 1 kg of liquid.

Vaporization (cont'd)

- Vapor pressure- the partial pressure exerted by the vapor when it is in DYNAMIC EQUILIBRIUM with a liquid at constant temperature



- BOILING point- occurs when vapor pressure = atmospheric pressure

Liquid–vapor equilibrium

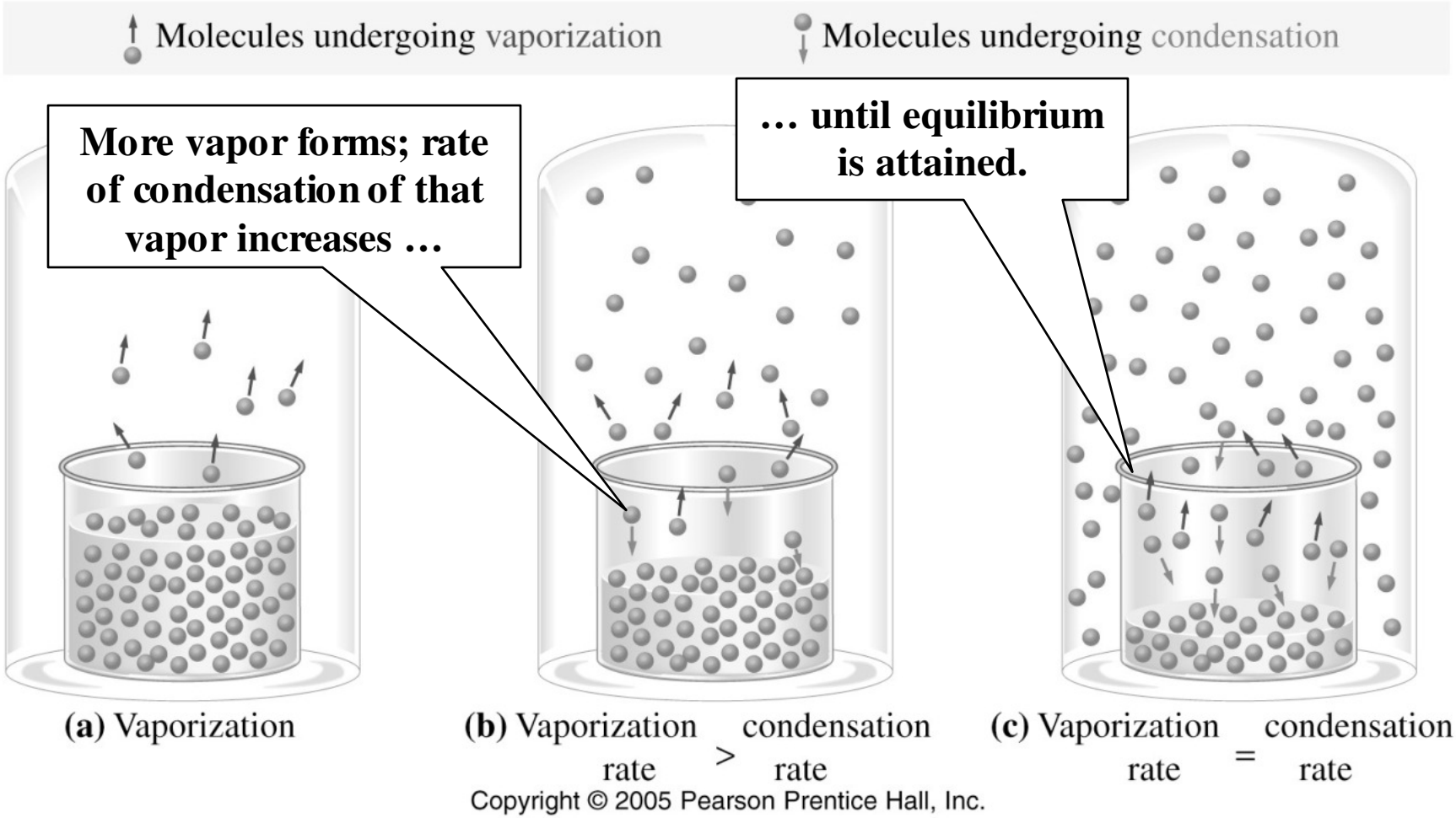


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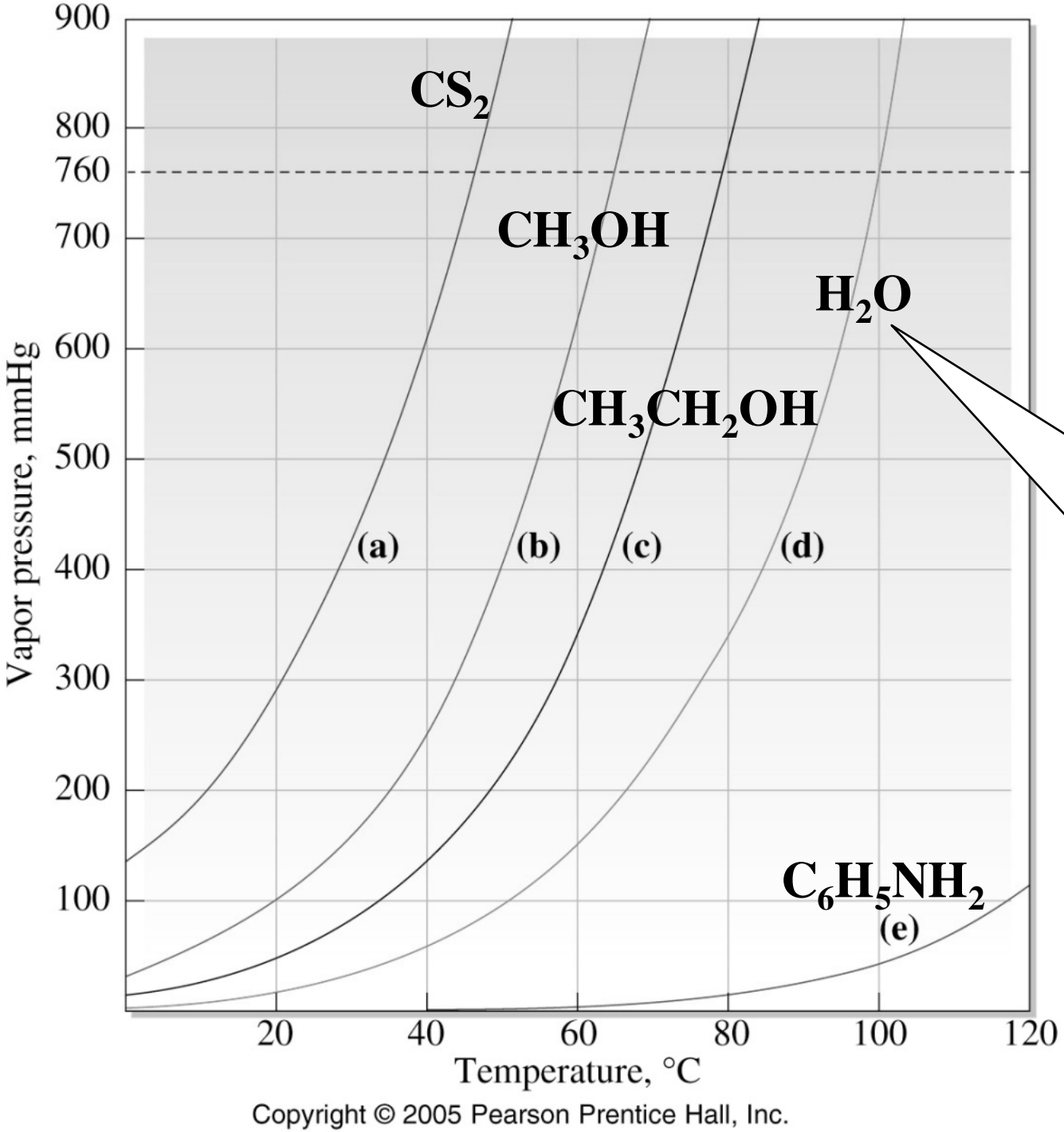
Table 11.2 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg
0.0	4.6	29.0	30.0	93.0	588.6
10.0	9.2	30.0	31.8	94.0	610.9
20.0	17.5	40.0	55.3	95.0	633.9
21.0	18.7	50.0	92.5	96.0	657.6
22.0	19.8	60.0	149.4	97.0	682.1
23.0	21.1	70.0	233.7	98.0	707.3
24.0	22.4	80.0	355.1	99.0	733.2
25.0	23.8	90.0	525.8	100.0	760.0
26.0	25.2	91.0	546.0	110.0	1074.6
27.0	26.7	92.0	567.0	120.0	1489.1
28.0	28.3				

Vapor pressure increases with temperature; why?

Vapor pressure curves



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What is the vapor pressure of H_2O at 100 °C, according to this graph? What is the significance of that numeric value of vapor pressure?

Which of the five compounds has the *strongest* intermolecular forces? How can you tell?

Boiling point and critical point

- ***Boiling point:*** the temperature at which the vapor pressure of the liquid equals the external (atmospheric) pressure.
- ***Normal boiling point:*** boiling point at 1 atm.
- ***Critical temperature*** (T_c): the highest temperature at which a liquid can exist.
- The ***critical pressure***, P_c, is the vapor pressure at the critical temperature.
- The condition corresponding to a temperature of T_c and a pressure of P_c is called the ***critical point***.

The critical point

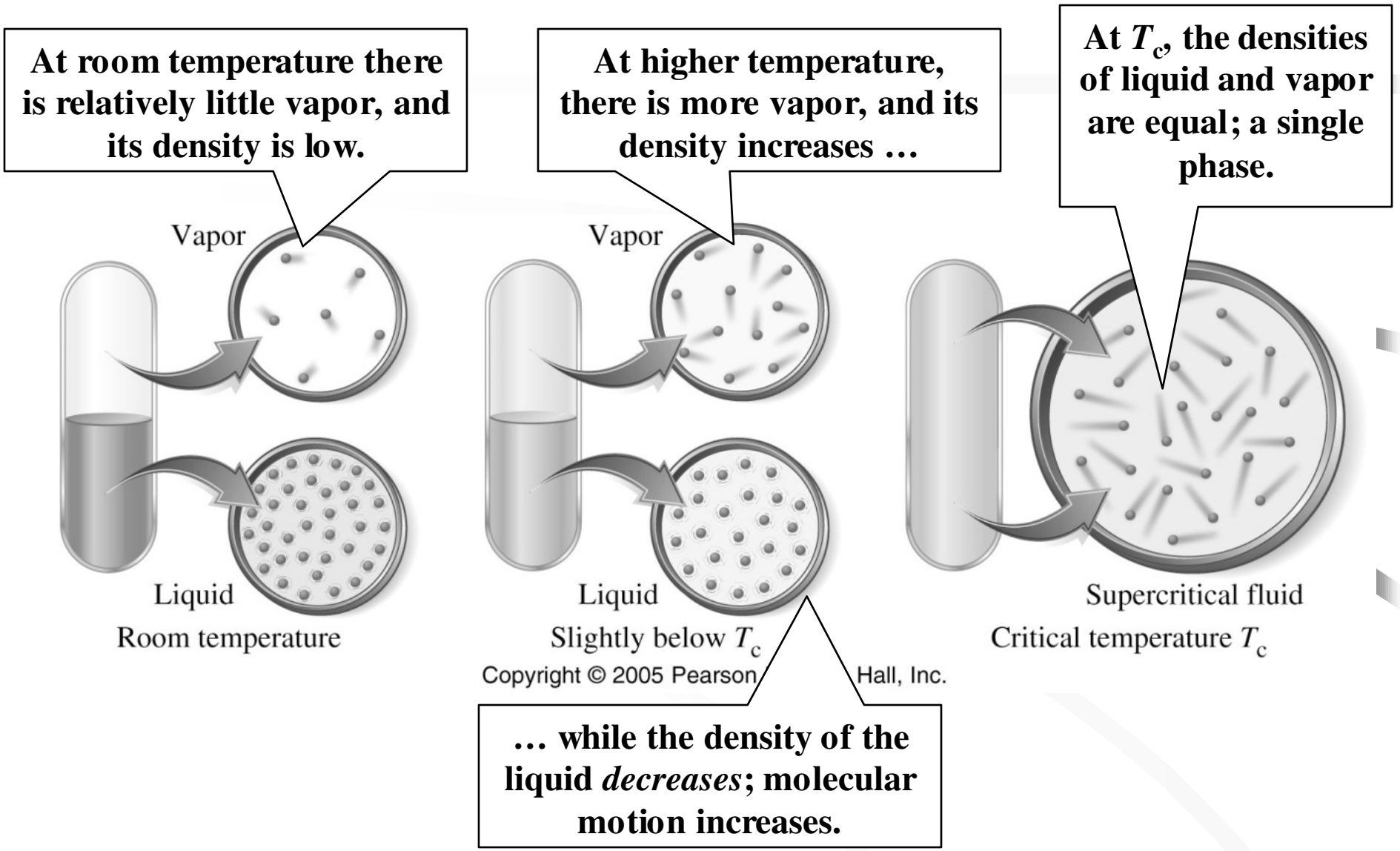

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Table 11.3 Critical Temperature and Pressure of Various Substances

	T_c, K	P_c, atm
H_2	33.0	12.8
N_2	126.3	33.5
O_2	154.8	50.1
CH_4	190.6	45.4
CO_2	304.2	72.9
C_2H_6	305.4	48.2
HCl	324.6	81.5
C_3H_8	369.8	41.9
NH_3	405.6	111.3
SO_2	430.6	77.9
H_2O	647.3	218.3

These four gases can't be liquefied at room temperature, no matter what pressure is applied; why not?

Phase changes

- **FUSION** is the reverse of **MELTING** which is the transition of a solid to a liquid, as you know
- *Melting point* and *freezing point* are the same temperature, just different direction (warming or cooling)
- ***Enthalpy of fusion***, ΔH_{fus}, is the quantity of heat required to melt a set amount (one gram, one mole) of solid.
- *Sublimation*- going directly from solid to gas
- Example?
- Remember the Jack Black/Ben Stiller movie *Envy*?
- ***Enthalpy of sublimation***, ΔH_{sub}, is the sum of the enthalpies of fusion and vaporization.
- **TRIPLE POINT**: all three phases—solid, liquid, vapor—are in equilibrium.

Some enthalpies of fusion

Table 11.4 Some Enthalpies (Heats) of Fusion

Substance	Melting Point, °C	ΔH_{fusion}, kJ/mol
Mercury, Hg	−38.9	2.30
Ethanol, CH_3CH_2OH	−114	5.01
Water, H_2O	0.0	6.01
Benzene, C_6H_6	5.5	9.87
Silver, Ag	960.2	11.95
Iron, Fe	1537	15.19

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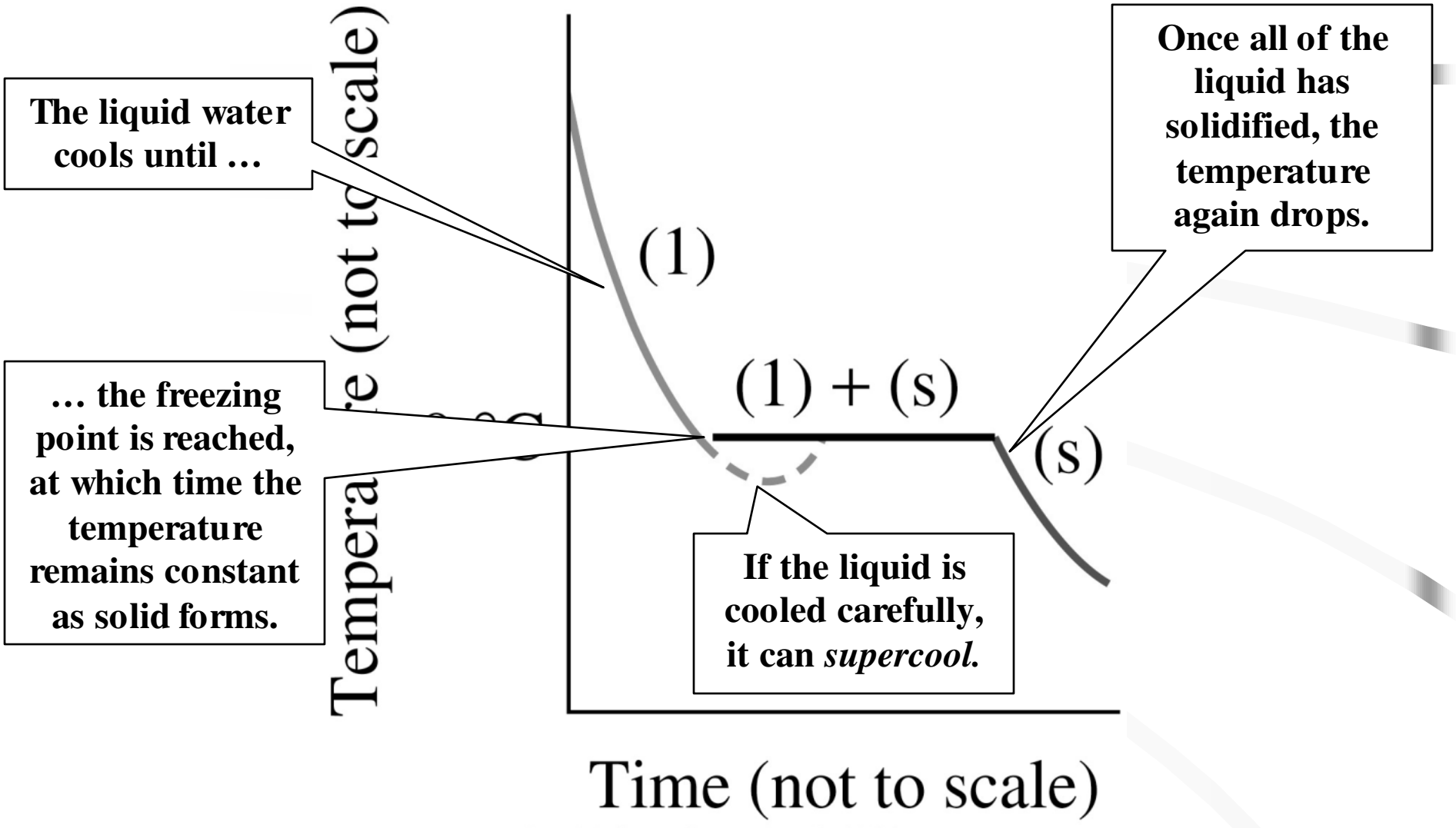
Cooling curve for water



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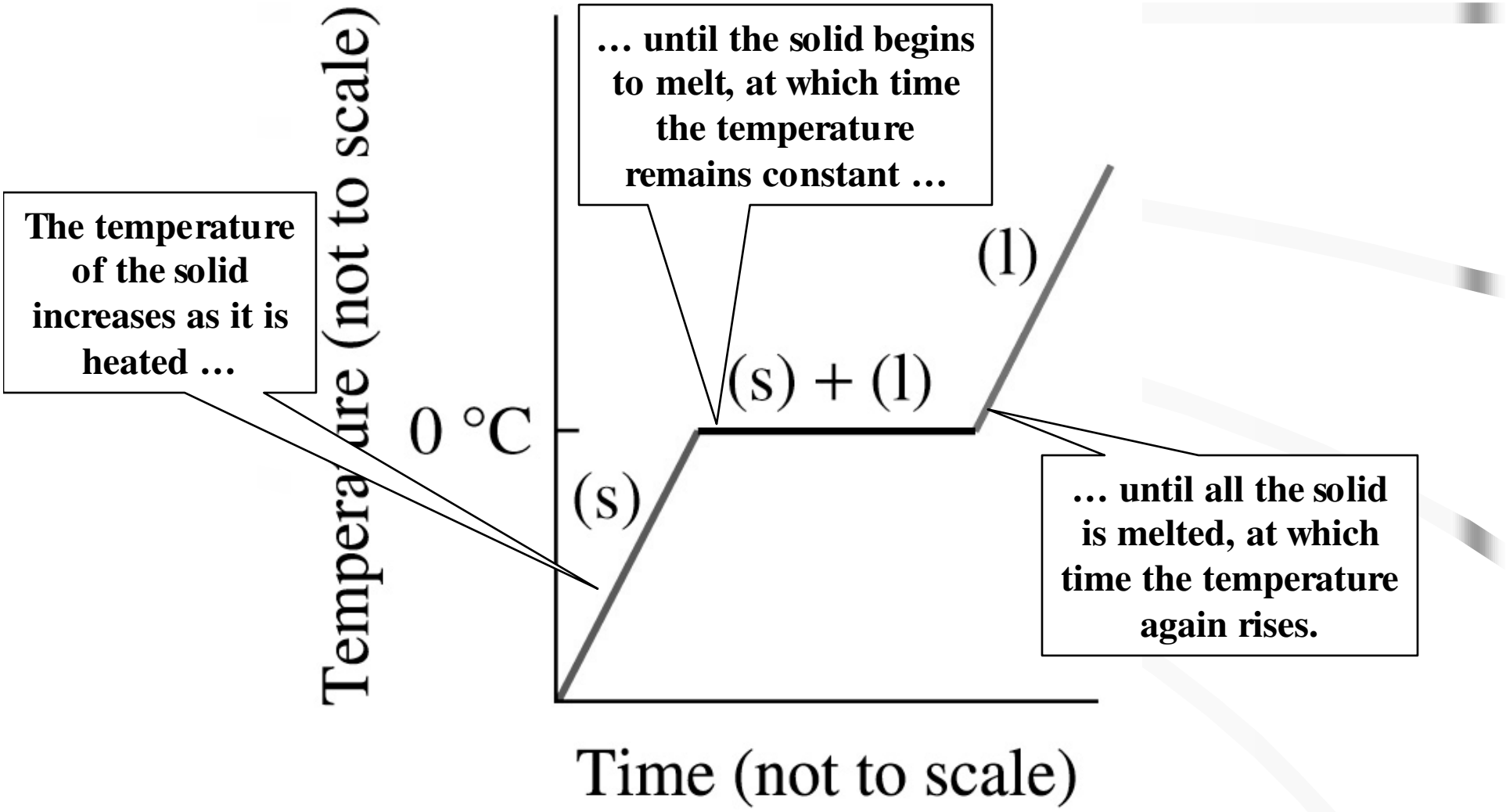
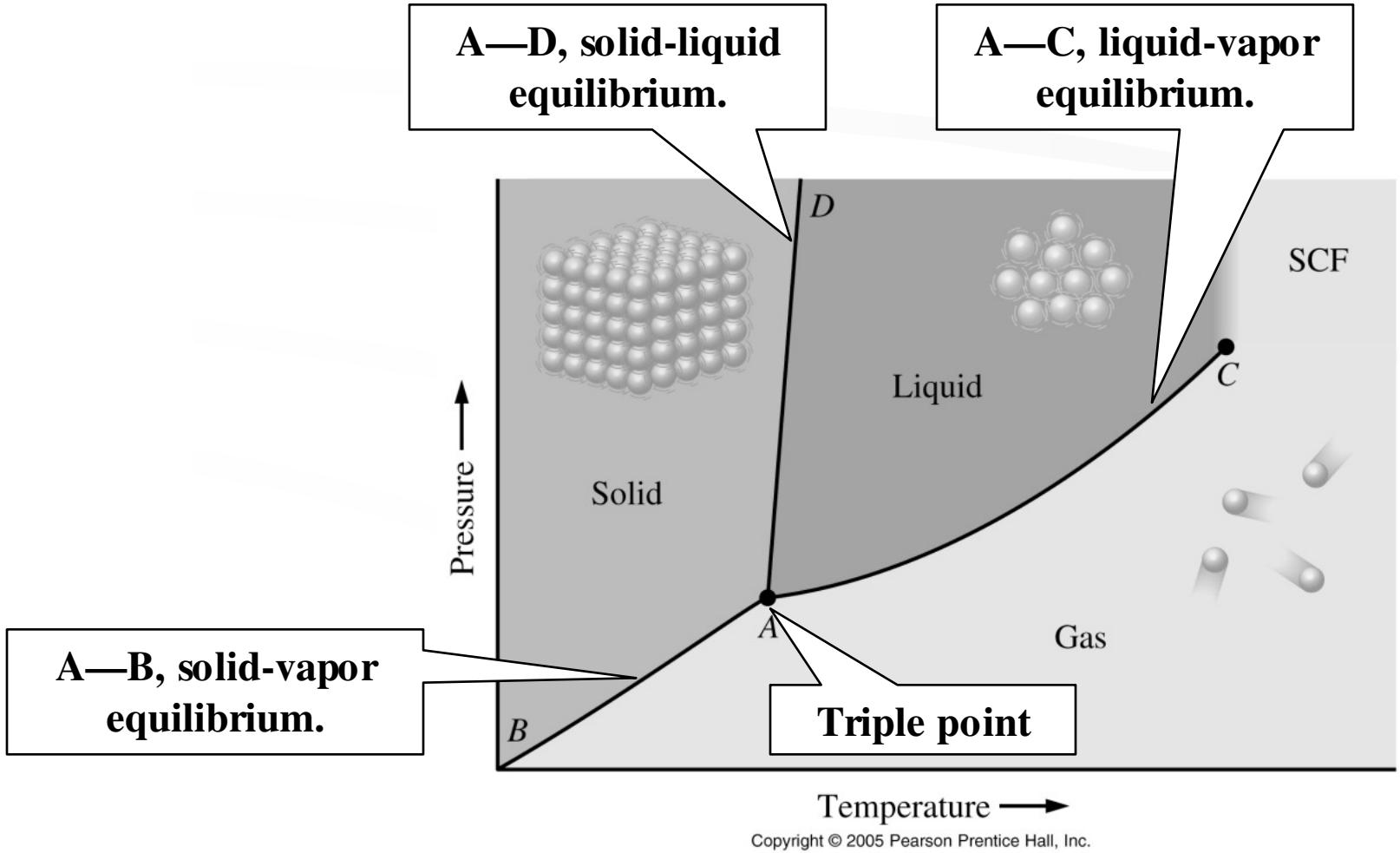
Heating curve for water



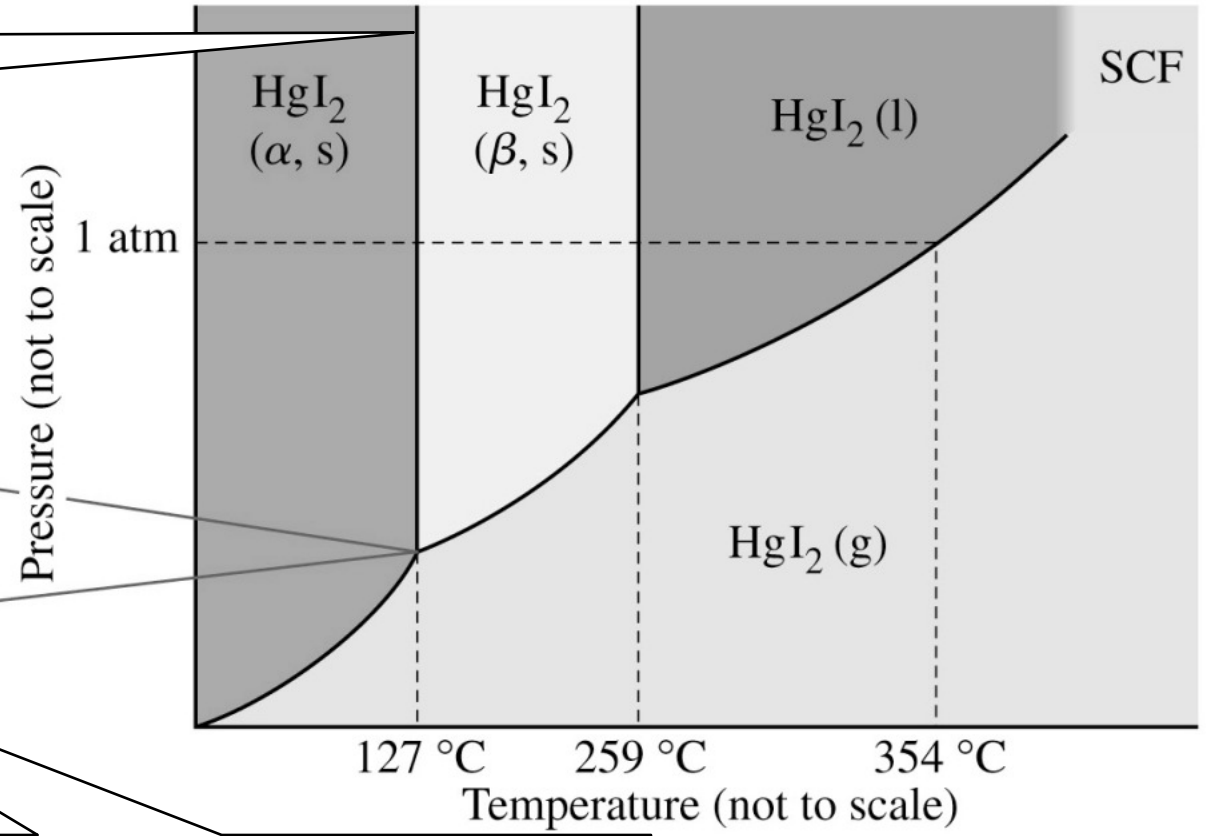
Phase diagram

- Shows phases of a substance at various temperatures and pressures
- Polymorphs can exist in more than one form per phase (examples??)



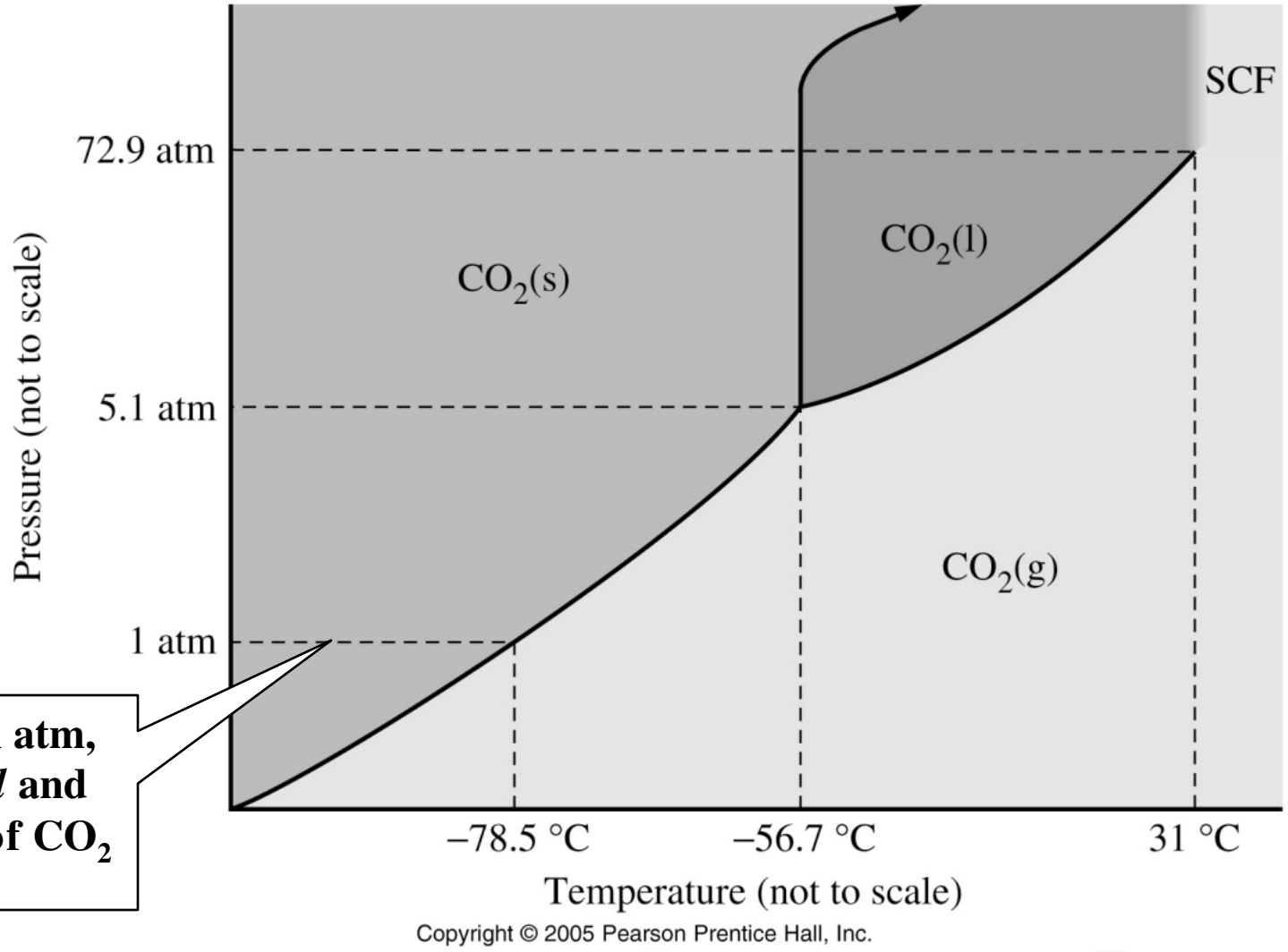
Phase diagram for HgI_2

HgI_2 has *two* solid phases, red and yellow.



As the vessel is allowed to cool, will the contents appear more *red* or more *yellow*?

Phase diagram for CO_2



Note that at 1 atm, only the *solid* and *vapor* phases of CO_2 exist.

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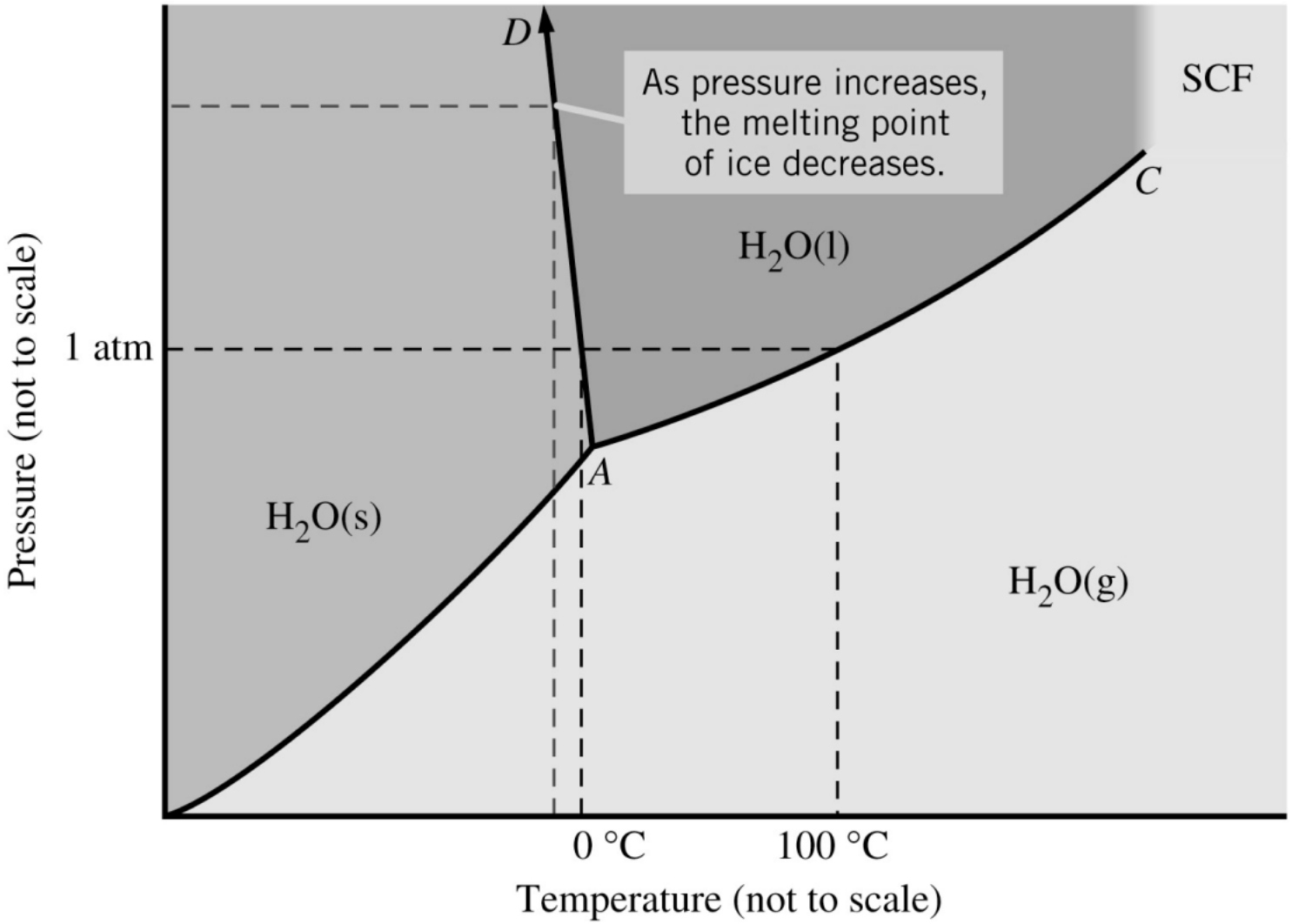
Phase diagram for H_2O



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van der Waals forces

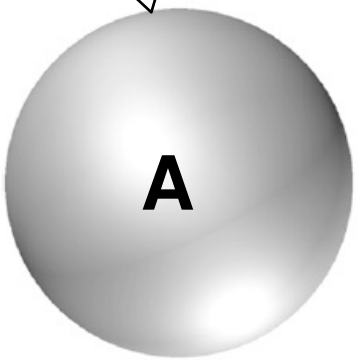
- Due to polarizability of electron clouds
- Dispersion forces (induced dipole-induced dipole forces)
- Dipole-dipole forces
- Ion-dipole forces

Dispersion forces

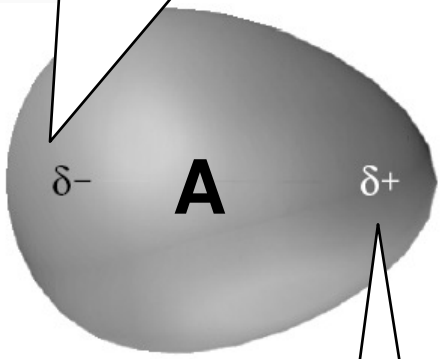
- … exist between any two particles.
- Also called *London* forces (after Fritz London, who offered a theoretical explanation of these forces in 1928).
- Dispersion forces arise because the electron cloud is not perfectly uniform.
- Tiny, momentary dipole moments can exist even in nonpolar molecules.
- aka “induced dipole-induced dipole” interactions

Dispersion forces illustrated

At a given instant, electron density, even in a nonpolar molecule like this one, is not perfectly uniform.

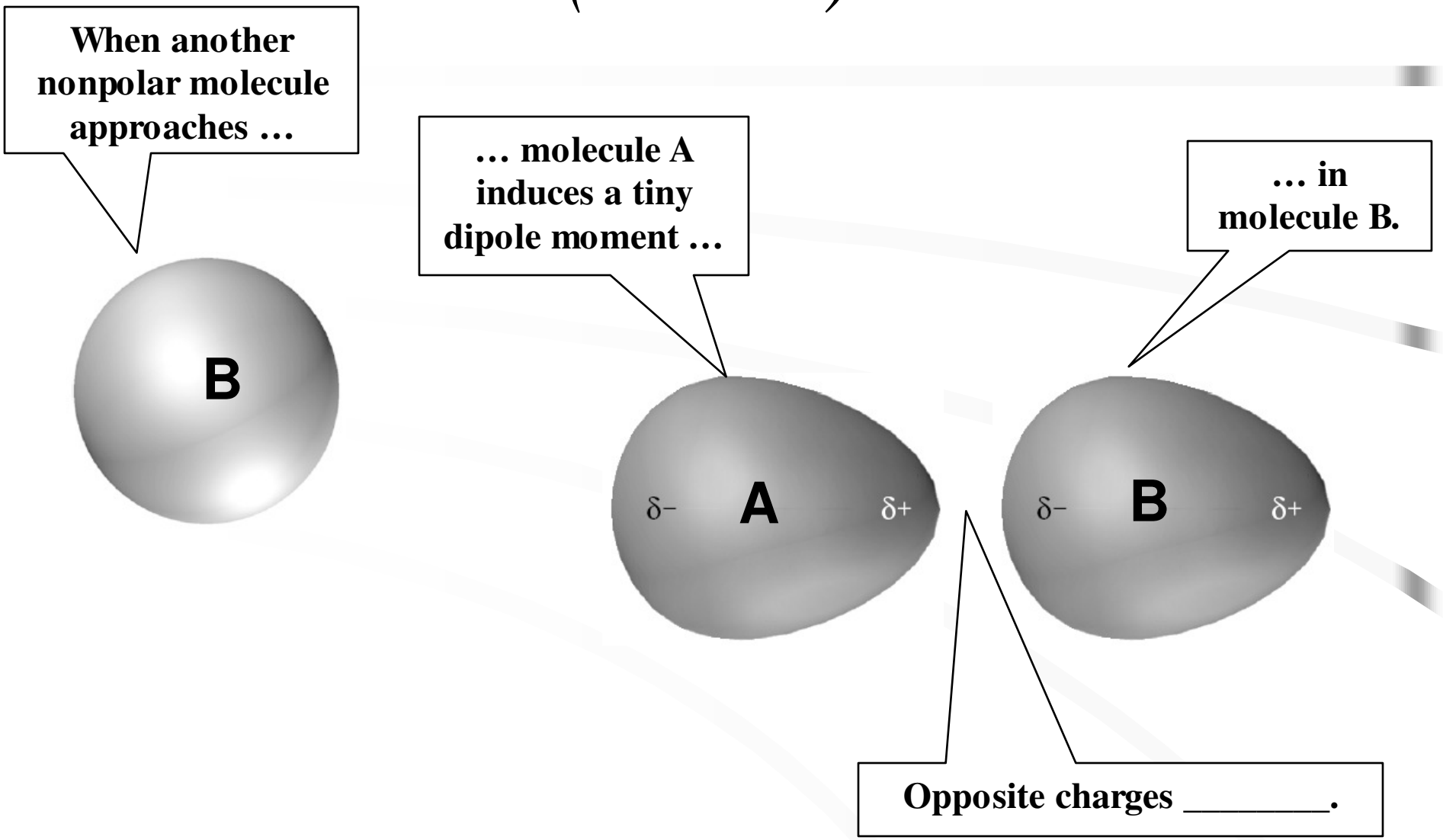


The region of (momentary) higher electron density attains a small (–) charge …



… the other end of the molecule is slightly (+).

Dispersion forces illustrated (cont'd)



Strength of dispersion forces

- Dispersion force strength depends on ***polarizability***: the ease with which the electron cloud is distorted by an external electrical field.
- The *greater* the polarizability of molecules, the *stronger* the dispersion forces between them.
- Polarizability in turn depends on molecular size and shape.
- Heavier molecule => more electrons => a more- polarizable molecule.
- As to molecular shape …

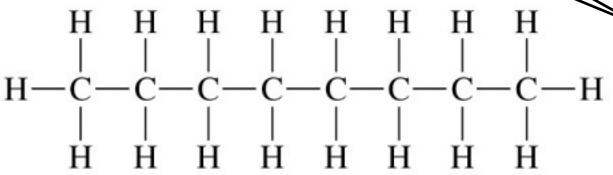
Molecular shape and polarizability

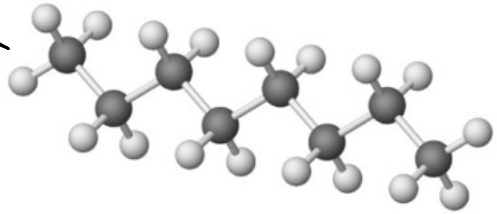
Long skinny molecule …

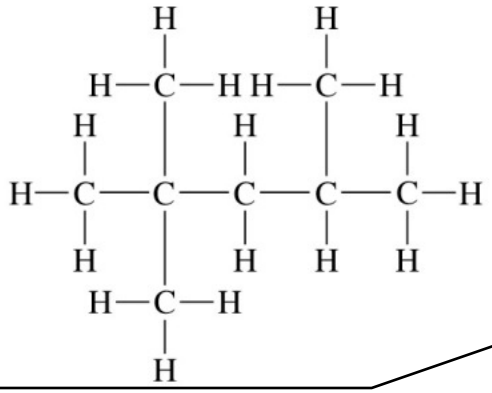
… can have greater separation of charge along its length. Stronger forces of attraction, meaning …

… higher boiling point.

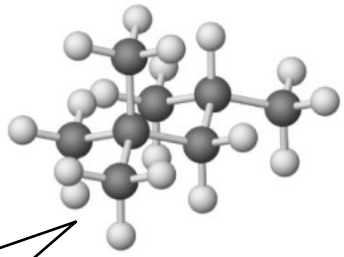
(a) Octane
$CH_3(CH_2)_6CH_3$
melting point −56.8 °C
boiling point 125.7 °C







(b) (Isooctane)
2,2,4-Trimethylpentane
$CH_3C(CH_3)_2CH_2CH(CH_3)_2$
melting point −104.7 °C
boiling point 99.2 °C



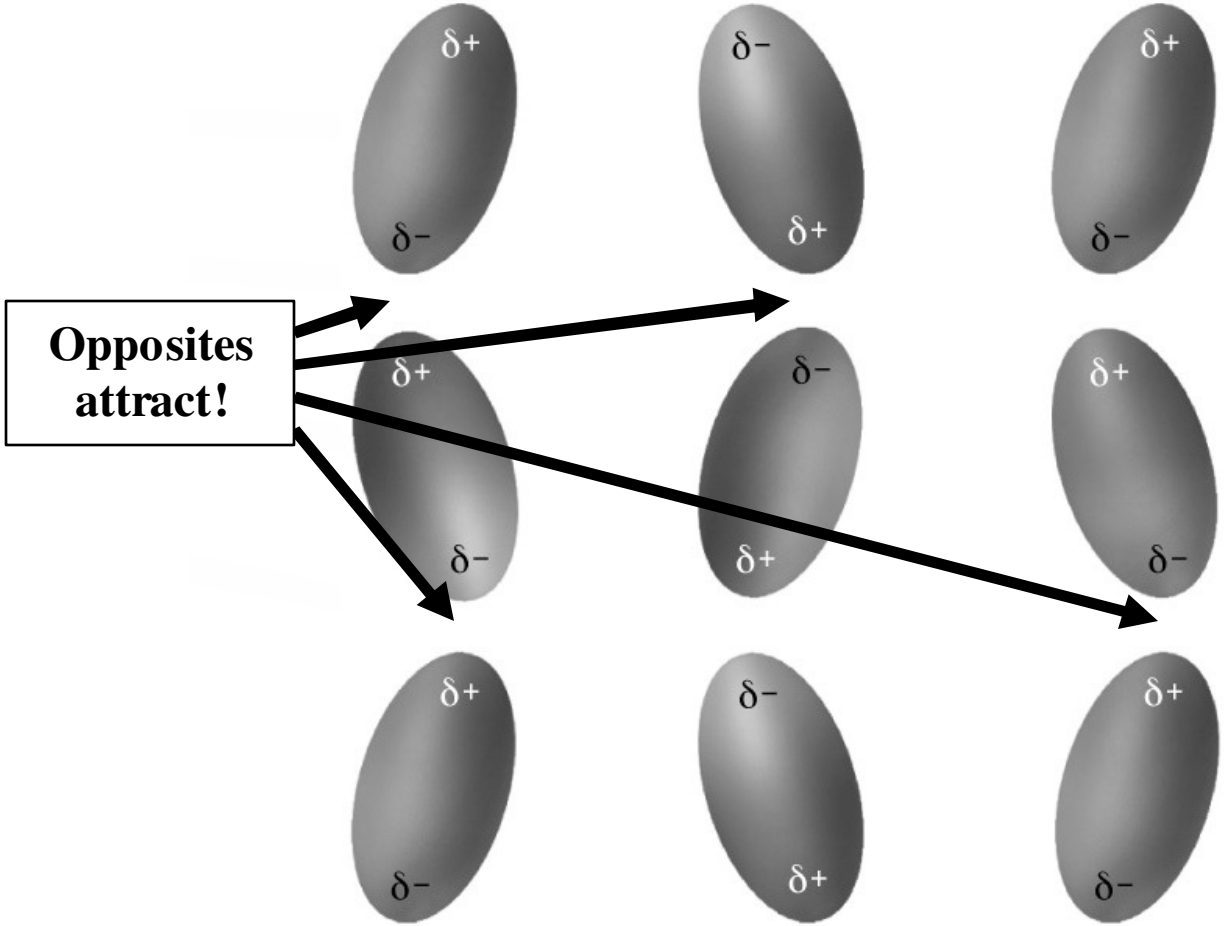
… giving weaker dispersion forces and a lower boiling point.

In the compact isomer, less possible separation of charge …

Dipole–dipole forces

- A polar molecule has a positively charged "end" ($\delta+$) and a negatively charged "end" ($\delta-$).
- When molecules come close to one another, repulsions occur between like-charged regions of dipoles. Opposite charges tend to attract one another.
- The more polar a molecule, the more pronounced is the effect of dipole–dipole forces on physical properties.

Dipole–dipole interactions



Predicting physical properties of molecular substances

- Dispersion forces become stronger with increasing molar mass and elongation of molecules. In comparing nonpolar substances, molar mass and molecular shape are the *essential* factors.
- Dipole–dipole and dipole-induced dipole forces are found in polar substances. The more polar the substance, the greater the intermolecular force is expected to be.
- Because they occur in *all* substances, dispersion forces must always be considered. Often they predominate.

Example

Arrange the following substances in the expected order of increasing boiling point: carbon tetrabromide, CBr_4; butane, $CH_3CH_2CH_2CH_3$; fluorine, F_2; acetaldehyde, CH_3CHO.

Hydrogen bonds

- A ***hydrogen bond*** is an intermolecular force in which:
  - a hydrogen atom that is covalently bonded to a (small, electronegative) nonmetal atom (generally N, O, F) in one molecule …
  - is simultaneously attracted to a (small, electronegative) nonmetal atom of a neighboring molecule (generally lone pairs of N, O, F).

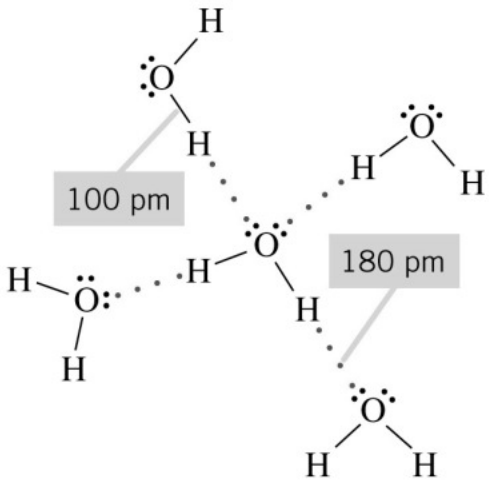
Y — H - - - Z ~~~~

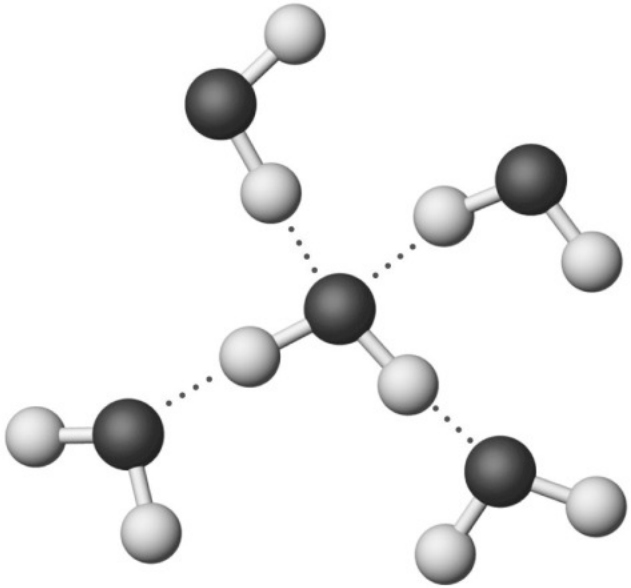
When Y and Z are small and highly electronegative (N, O, F) …

… this force is called a *hydrogen bond*; a special, *strong* type of dipole–dipole force.

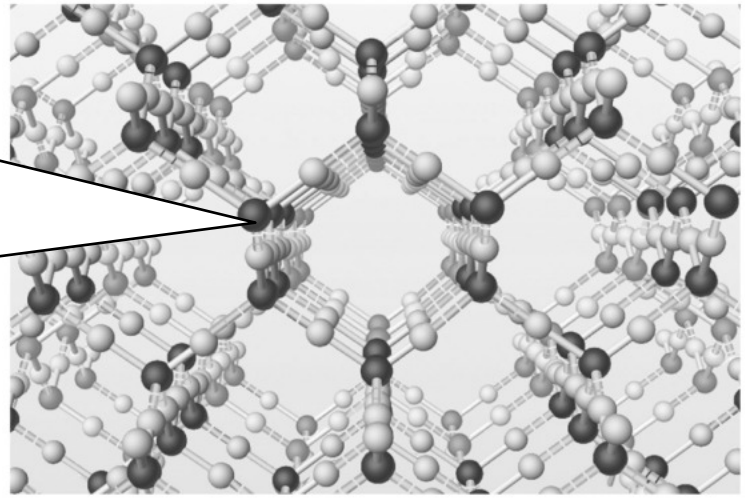
Hydrogen bonds in water

- Why does ice float?

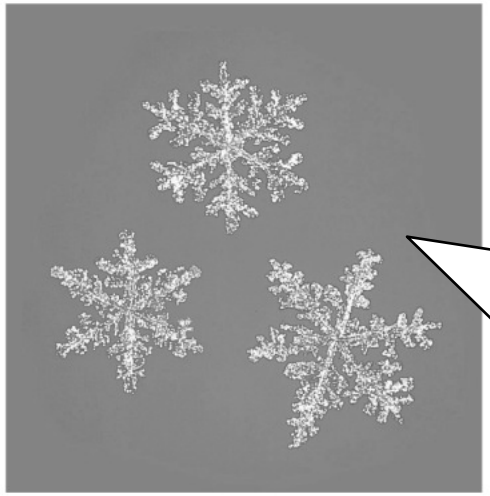




Hydrogen bonding arranges the water molecules into an open hexagonal pattern.



(a)



(b)

"Hexagonal" is reflected in the crystal structure. "Open" means reduced density of the solid (vs. liquid).

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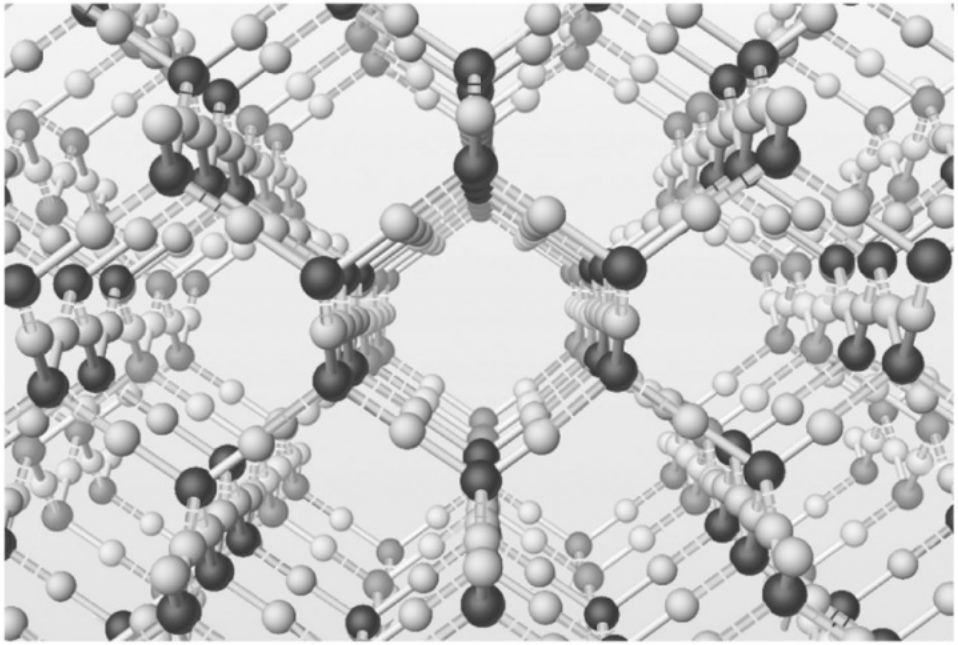
Hydrogen bonding in ice



(a)

(b)

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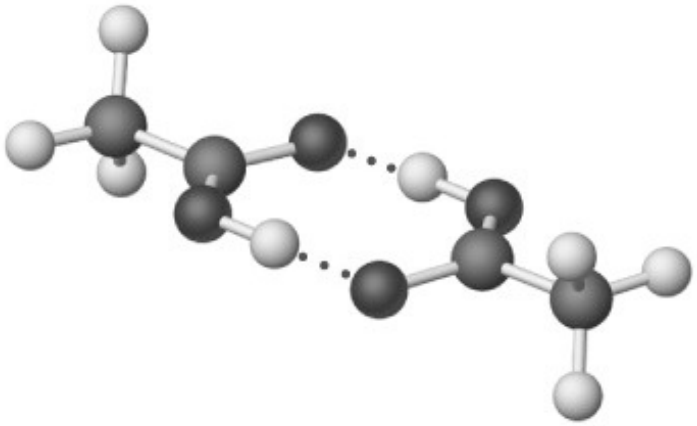
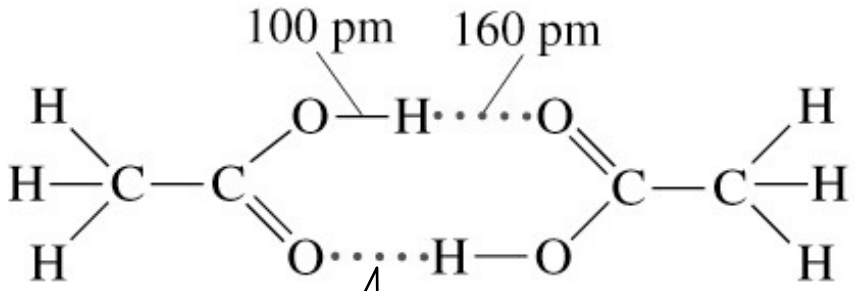
Hydrogen bonding arranges the water molecules into an open hexagonal pattern.

"Hexagonal" is reflected in the crystal structure. "Open" means reduced density of the solid (vs. liquid).

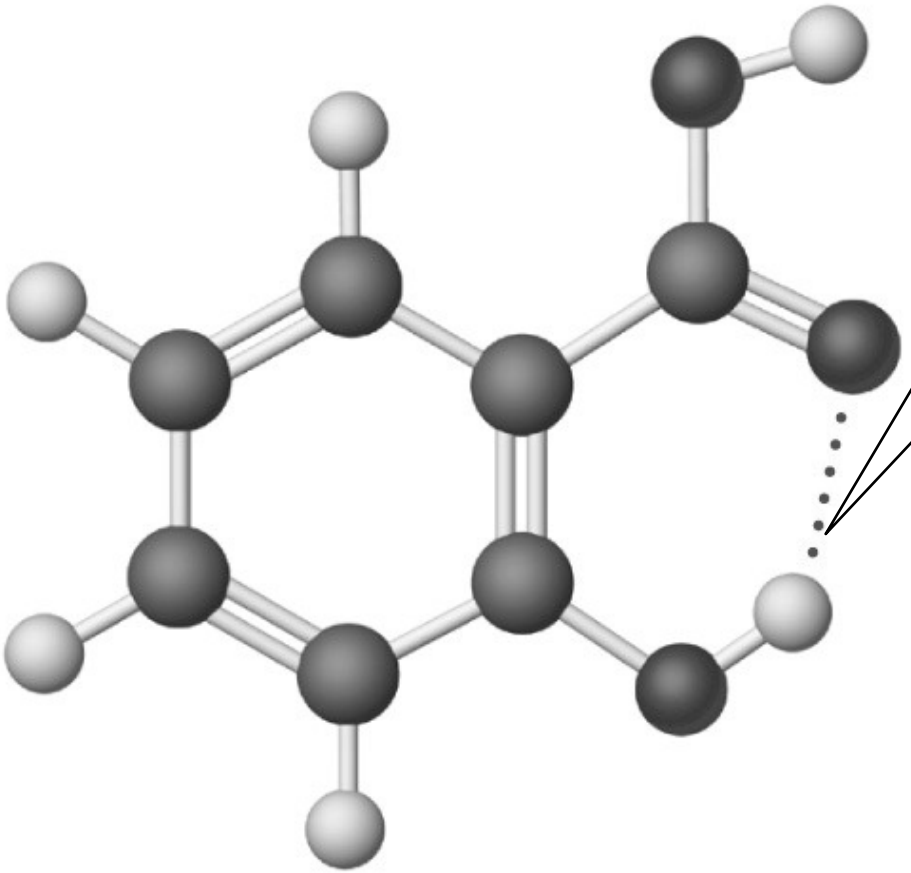
Hydrogen bonding in acetic acid



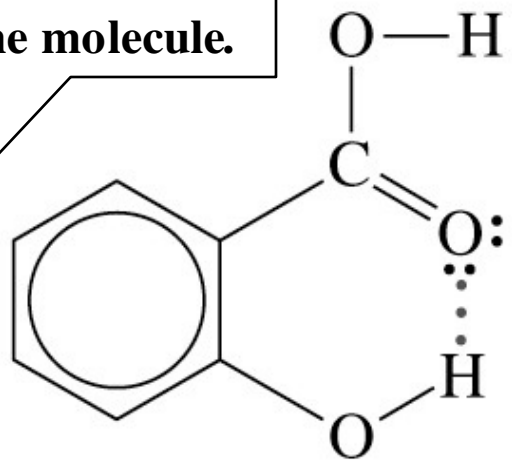


Hydrogen bonding occurs *between* molecules.

Hydrogen bonding in salicylic acid (aka?)

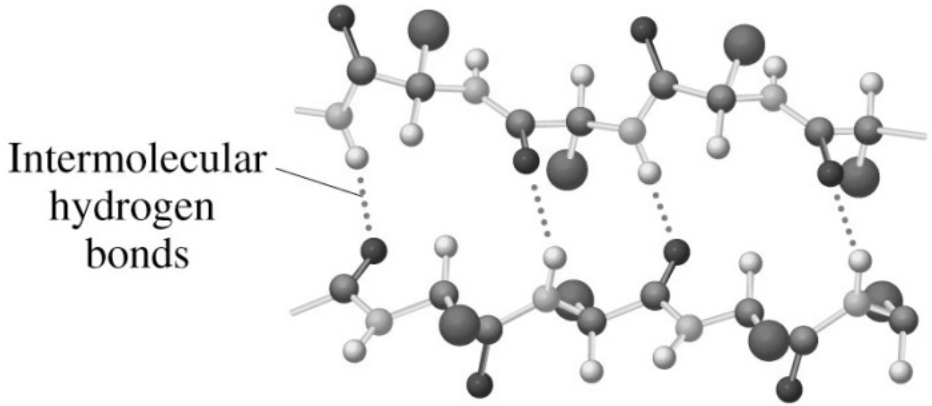


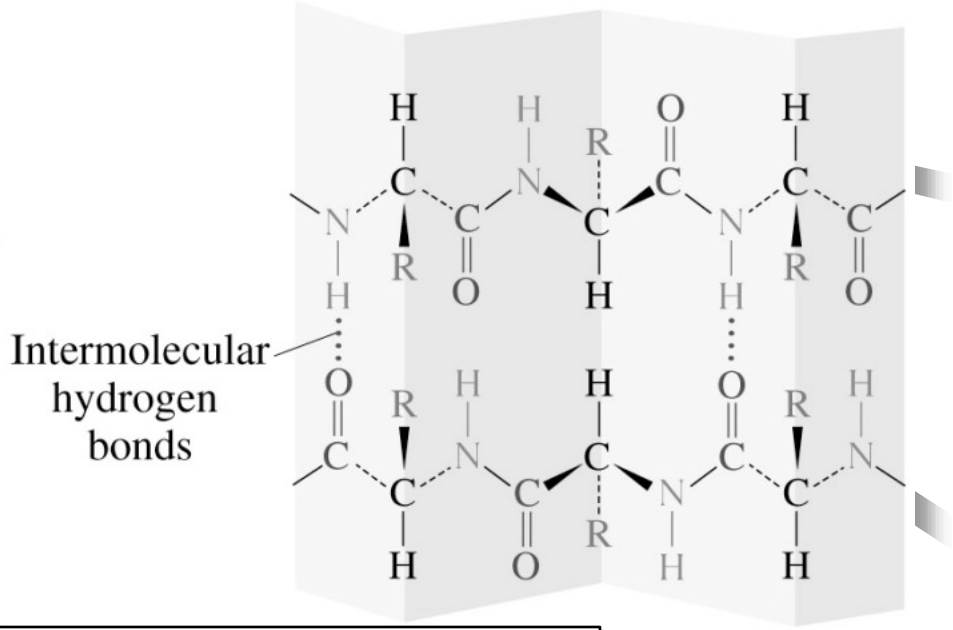
Hydrogen bonding occurs *within* the molecule.



Intermolecular hydrogen bonds

- Can you think of other examples?

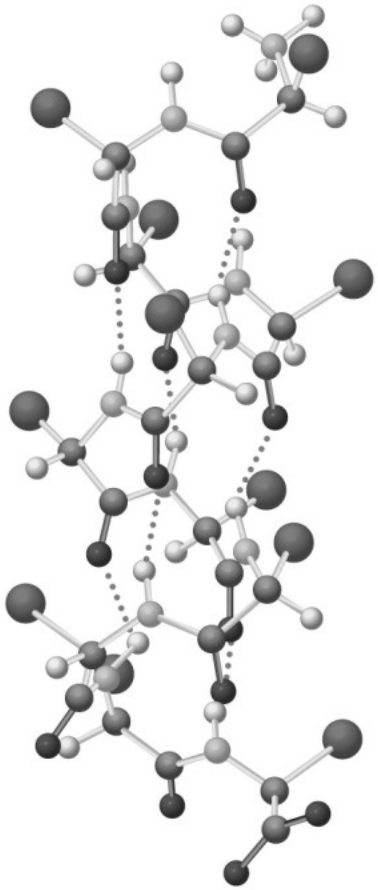


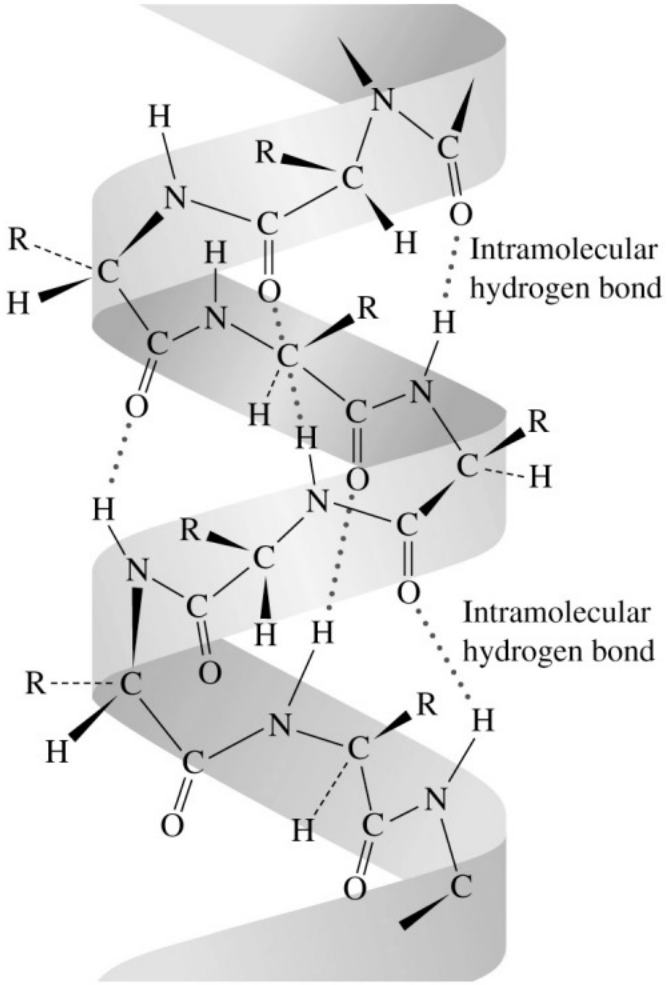


Intermolecular hydrogen bonds give proteins their secondary shape, forcing the protein molecules into particular orientations, like a folded sheet …

Intramolecular H-bonds (cont'd)

… while intramolecular hydrogen bonds can cause proteins to take a helical shape.





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Example

In which of these substances is hydrogen bonding an important intermolecular force: N_2, HI, HF, CH_3CHO, and CH_3OH? Explain.

Homology

- A series of compounds whose formulas and structures vary in a regular manner also have ***properties*** that vary in a predictable manner.
- This principle is called ***homology***.
- Example: both densities and boiling points of the straight-chain alkanes increase in a continuous and regular fashion with increasing numbers of carbon atoms in the chain... a homologous series.
- Trends result from the regular increase in molar mass, which produces a fairly regular increase in the strength of dispersion forces.
- Different from an element which can exist in more than one basic structure known an an *allotrope*.

An Estimation Example

The boiling points of the straight-chain alkanes pentane, hexane, heptane, and octane are 36.1, 68.7, 98.4, and 125.7 °C, respectively. Estimate the boiling point of the straight-chain alkane decane.

Liquid crystals

- The thrust of your instructor's thesis
- Not quite solid, not quite liquid....a true 5th phase of matter

Crystals

- A solid substance with a regular shape and plane surfaces with sharp edges that intersect at fixed angles.
- Made up of a small number of atoms, ions, or molecules in a repeating unit.
- The repeating unit in the *crystal lattice* is the *formula unit*.

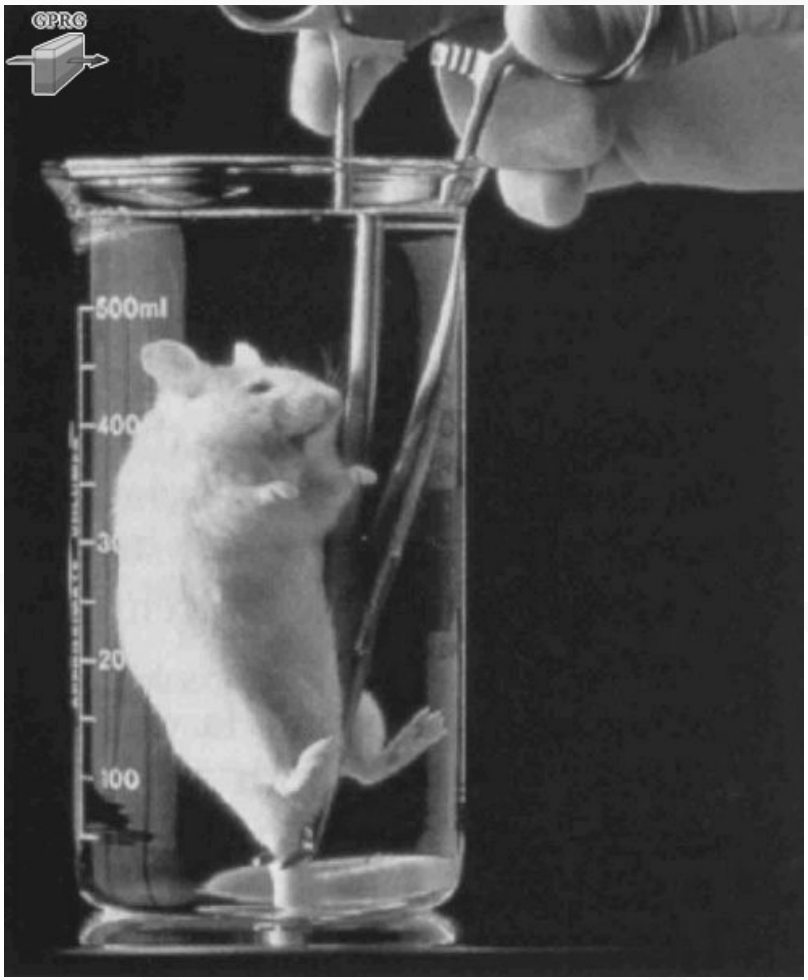
Other stuff

- Surface tension (this is how Rain-X© works)- OMIT
- Viscosity- OMIT
- Network covalent solids- example: C_{60} which is another allotrope of carbon
- Ionic bonds- just common sense- strength of interaction increases as charges increase and distance decreases- OMIT
- Crystals- OMIT

the end

More on solutions

- Earlier, we explored general terminology and reactions of solutions.
- We now return back to solutions to explain some physical phenomena, such as why impure water (a solution of ethylene glycol, aka antifreeze) is used as a car coolant instead of just pure water.
- Solutions can be of several types: gas-gas, gas-liquid, liquid-liquid, solid-liquid, gas-solid, solid-solid (and, for completeness, one would suppose, combinations with the other 2 phases of matter as well)
- How can the compound the mouse is breathing be fluorine-containing when F is a highly toxic cumulative bone-marrow attacker?

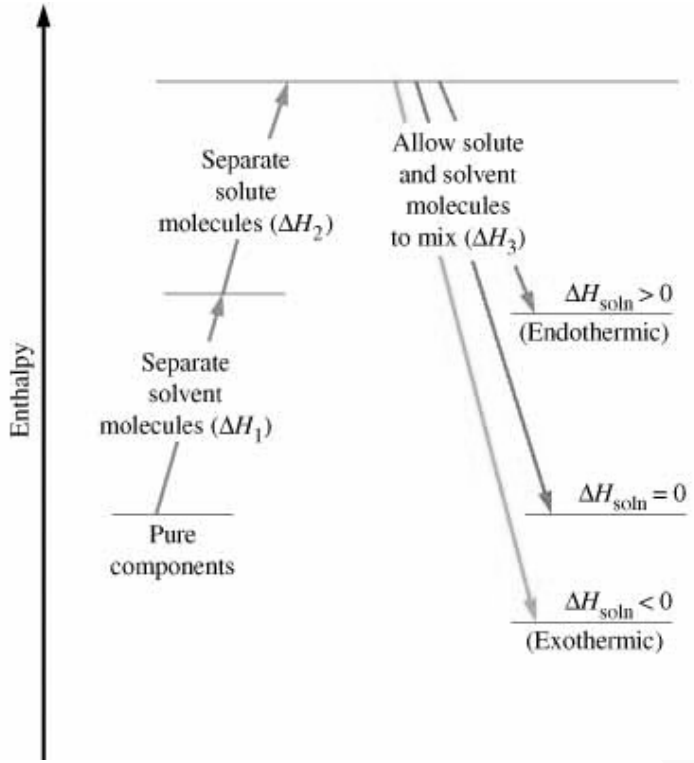


Molarity revisited

- For mass percent, volume percent, mole percent or mole fraction, ppm and ppb calculations, DON'T FORGET THE UNITS!
- ppm = mg/L
- ppb = ug/L
- ppt = ng/L
- Analysis of low concentrations can be challenging…
- Femtomolar (10^{-15}) analysis IS possible, luckily, since sometimes compounds are toxic at ppq levels!! (e.g.- dioxin)

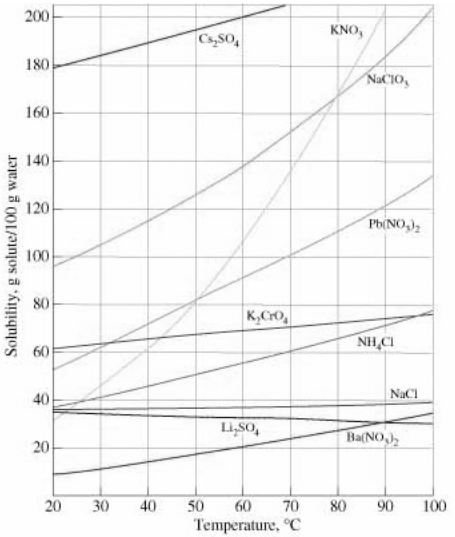
Dissolution

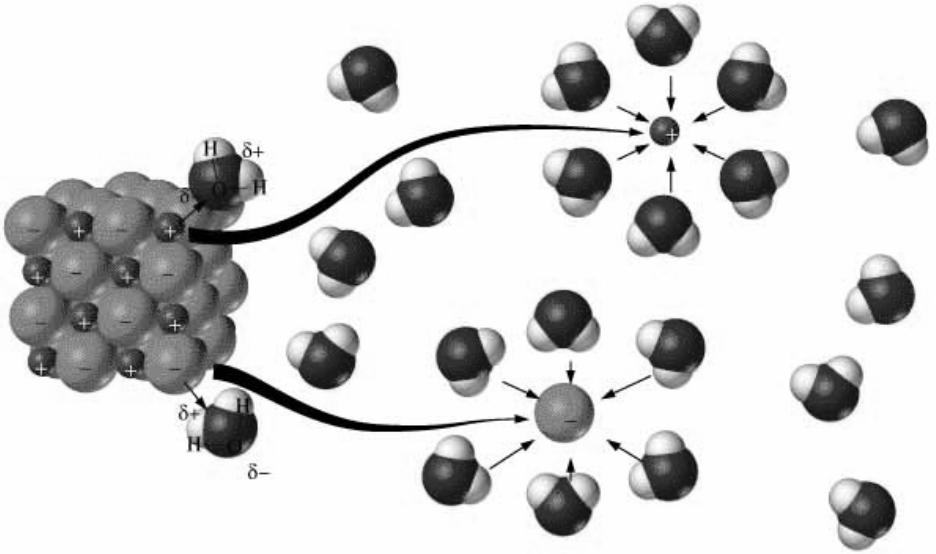
- Can be endothermic or exothermic
  - "cold packs" (NH_4NO_3) (what else is this used for?)
  - "hot packs" ($MgSO_4$)
- Enthalpy of solution (below)
- Nonideal solutions can expand or contract upon dissolution.....why??
- Thus, M is T dependent.

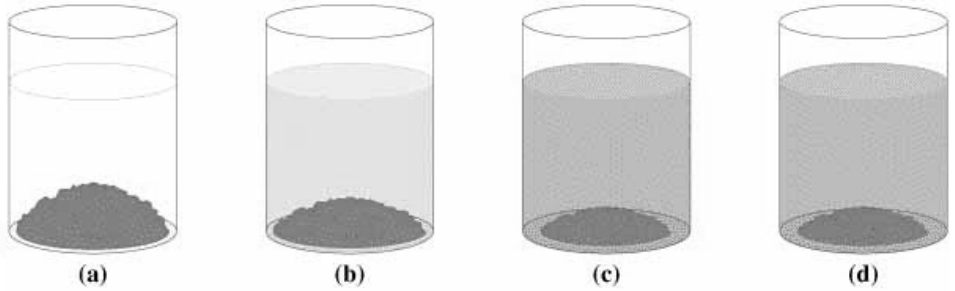


Why do things dissolve?

- LIKE DISSOLVES LIKE
- Fully dissolving compounds are said to be MISCIBLE
- Saturated solution- dynamic equilibrium
- Solubility vs. temperature- supersaturation
- Purification by supersaturation







Solubility rules (again!)

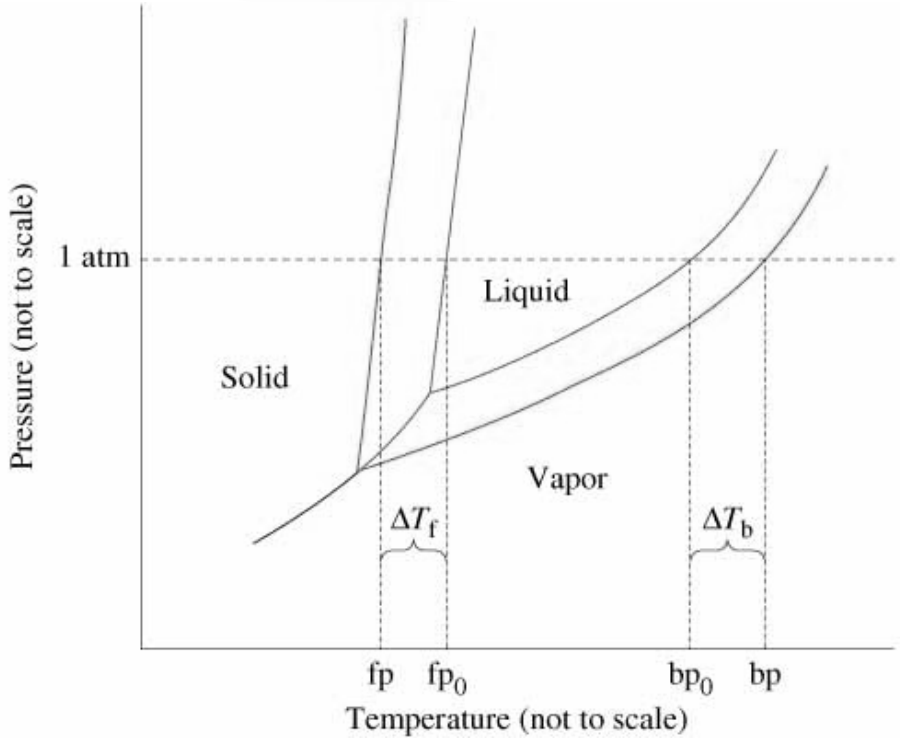
- Group I cation and NH^{4+} salts are soluble (some Li^{+} exceptions)
- Nitrates, acetates, perchlorates are soluble
- Chlorides, bromides, iodides are soluble
- Sulfates are soluble except for Ca, Sr, Ba.
- Ag, Pb, Hg(I) salts are insoluble
- Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of Group II cations and hydroxides of Ca^{2+}, Sr^{2+} and Ba^{2+} are slightly soluble)

Gas solubility

- Temperature dependence
  - No general rule though most gases are less soluble in water at higher temperature
- Pressure dependence
  - Higher pressure = higher solubility due to equilibrium = Henry's Law (1803)... very common example?

Colligative properties

- Depend on the number of solute particles present, NOT their identity
- Vapor pressure- lowered by presence of solute
  - Raoult's Law- $P_{soln} = x_{soln} P^{o}_{soln}$
  - Important application in fractional distillation.
  - Used in chemical purification, oil refining, ethanol production, etc.
- Freezing point depression $\Delta T = K_f m$ (m = moles solute / kg solvent)
- Boiling point elevation $\Delta T = K_b m$

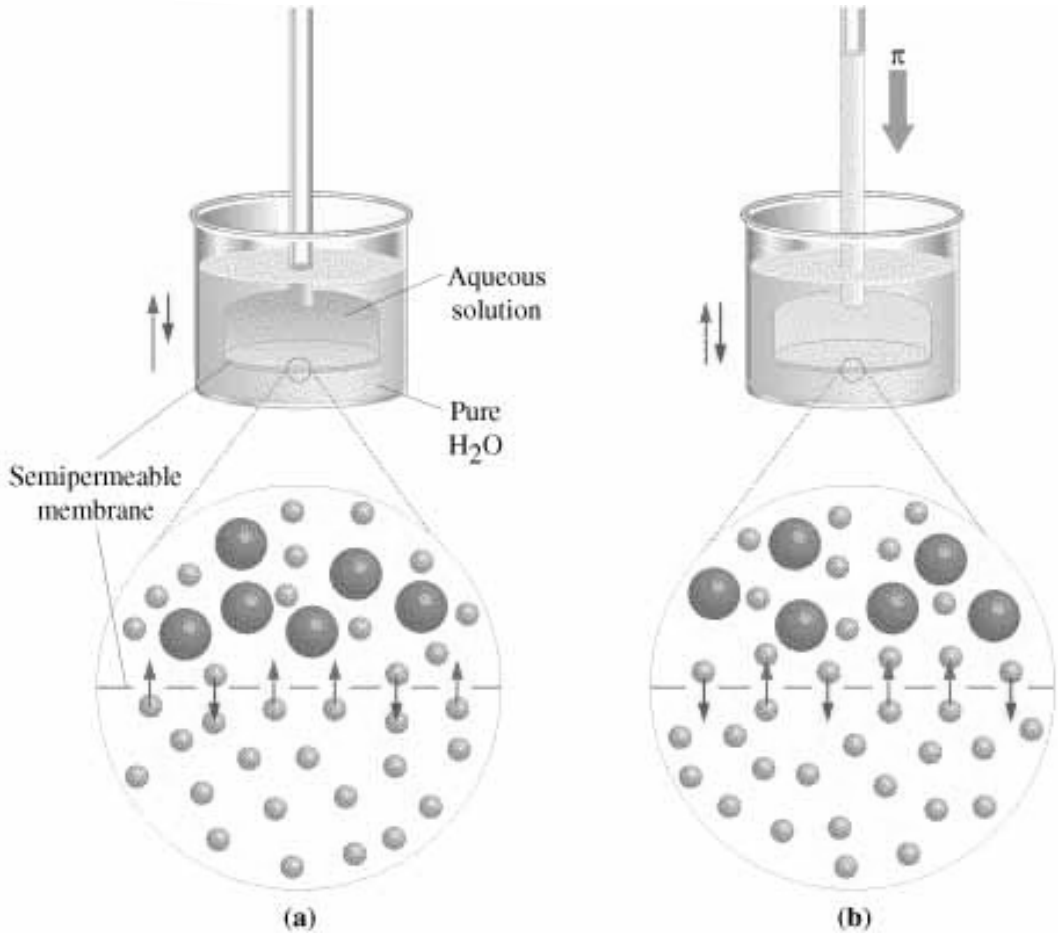


Osmotic pressure

- OSMOSIS is the net flow of solvent molecules from pure solvent through a semipermeable membrane (small solvent molecules may pass through, but not large solute molecules) into a solution.
- For a 20% sucrose solution, osmosis can lift the solution 150m!
- ie- dilution of a solution by solvent through a barrier
- Can reduce solvent flow into solution by increasing flow of solvent out of the solution by applying pressure to it.
- At the OSMOTIC PRESSURE, osmosis ceases.
- (About 15 atm for the 20% sugar solution.)

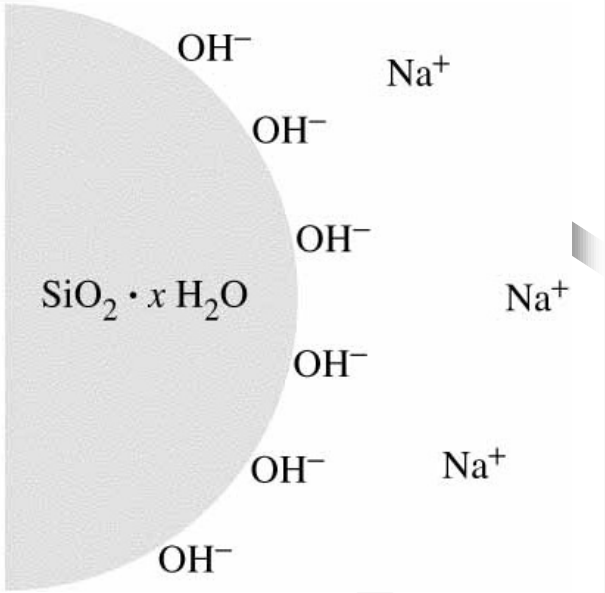
Osmotic pressure (cont'd)

- $\pi = MRT$
- (yes, molarity even though it's a colligative property)



Colloids

- Between a solution and a suspension
- Based on particle size (1-1000nm)
- Too small to see with regular microscope or settle out (can often COAGULATE-PRECIPITATE with an electrolyte)
- Large enough to diffract light (Tyndall effect)
- A SOL is a solid in a liquid
- An EMULSION is a liquid in a liquid
- An AEROSOL is a solid or liquid in a gas



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Reaction rate

- Speed of reaction
- Change in concentration of reactant or product with time
- Moles per liter per second ($ML^{-1}s^{-1}$)
- Appearance of product
- Disappearance of reactant

Rate law

- For aA + bB → cC + dD, the rate law is Rate = k $[A]^m[B]^n$
- Little k = rate constant
- NOT big K (equilibrium constant)
- Exponents *usually* small positive integers
- Exponents determined experimentally
- Exponents do NOT come from the balanced equation
- Repeat, exponents do NOT come from the balanced equation

Order of reaction

- Exponents in rate law give the order
- 0 = zero order
  - Changing concentration has no effect on rate
- 1 = first order
  - Double concentration, double rate
- 2 = second order
  - Double concentration, quadruple rate

Rate constant

- A proportionality constant
- Units vary with overall order of reaction
  - Zero Ms^{-1}
  - First s^{-1}
  - Second $M^{-1}s^{-1}$
  - Third $M^{-2}s^{-1}$

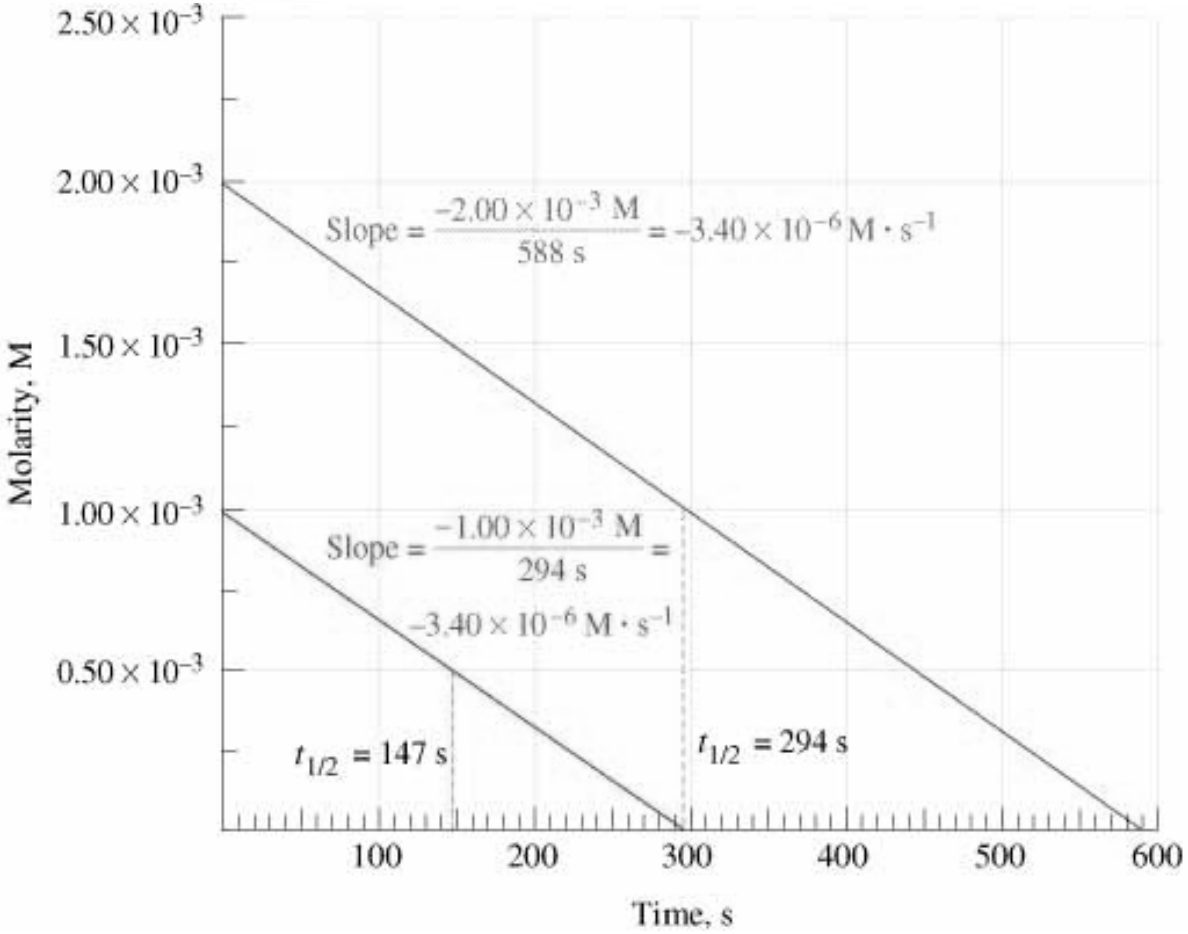
Problem solving

[NO]	$[Cl_2]$	rate
3	3	3
6	3	12
3	6	6

- $2NO\ (g) + Cl_2\ (g) \rightarrow 2NOCl\ (g)$
- Rate = $k[NO]^2[Cl]$

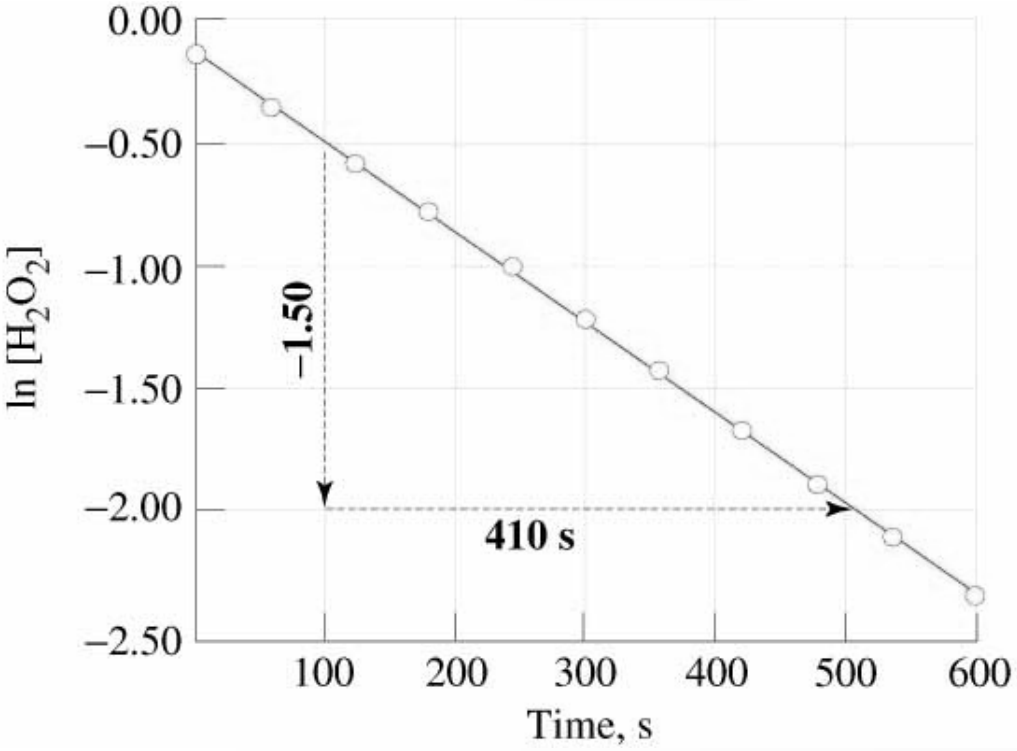
Zero order reactions

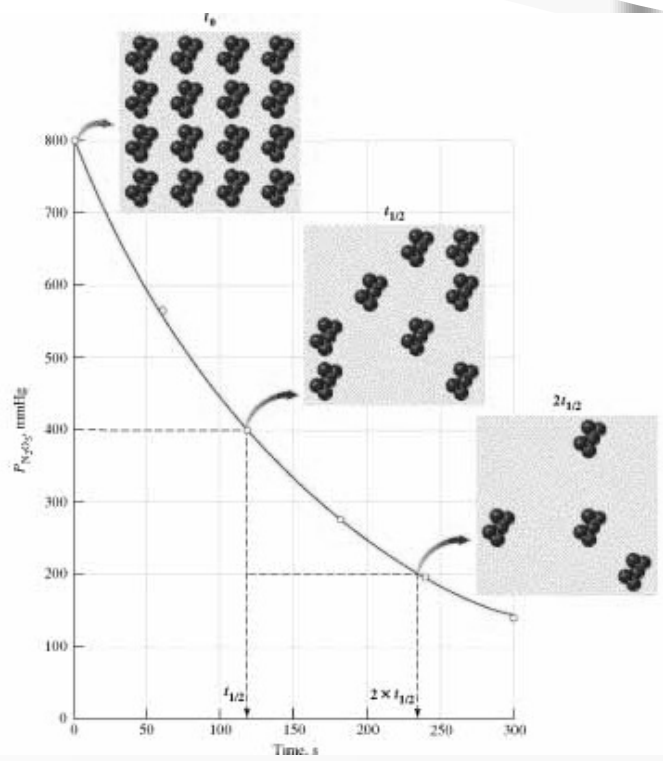
- Rate = k
- Plot of M vs t is a line with slope = $-k$



First order reactions

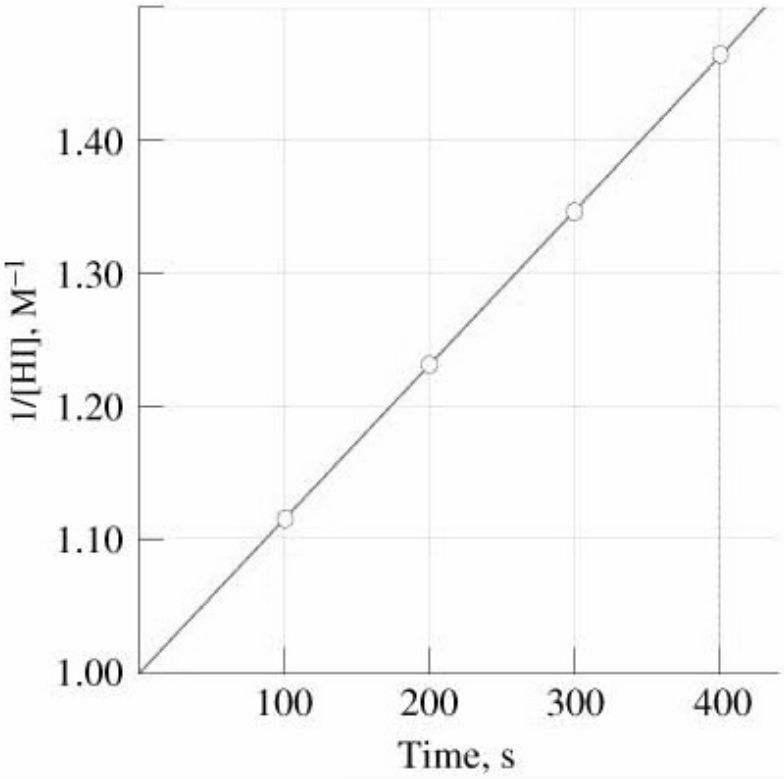
- Radioactive decay
- Integrated rate law = $\ln([A]_t/[A]_o) = -kt$
- Plot of ln[A] vs t = straight line with slope $-k$
- Half life $t_{1/2} = 0.693/k$
- After n half lives, $(1/2)^n$ of the initial concentration remains





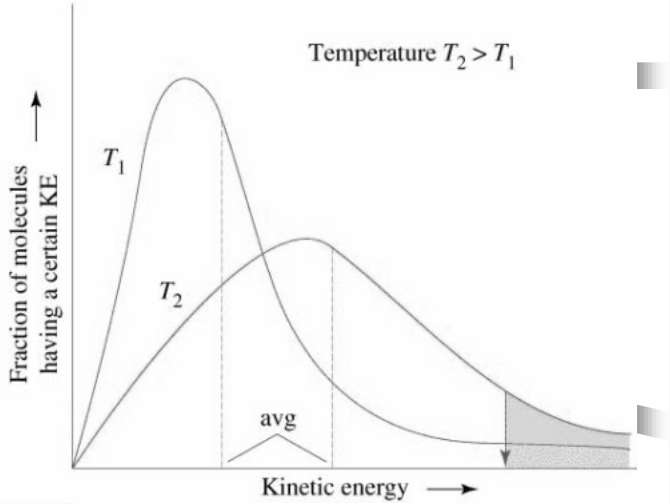
Second order reactions

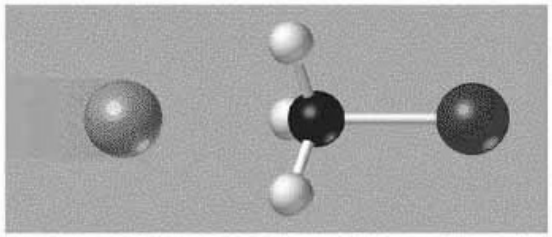
- $1/[A]_t = kt + 1/[A]_o$
- Plot of 1/[A] vs *t* is a straight line with slope = *k*



Collision theory

- Atoms and molecules must collide in order to react (form/break bonds)
- Not all collisions are effective; more are with increased T
- The ACTIVATION ENERGY is the minimum energy that must be supplied by a collision for a reaction to occur
- Orientation can also be important





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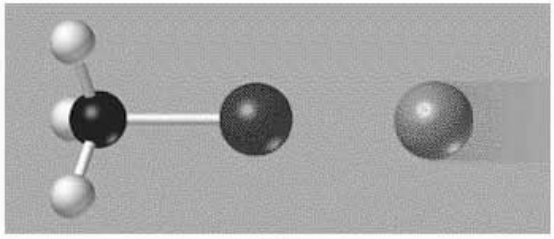

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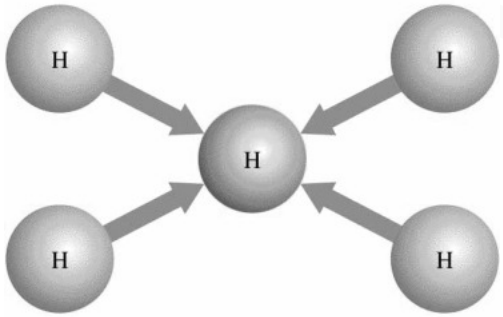
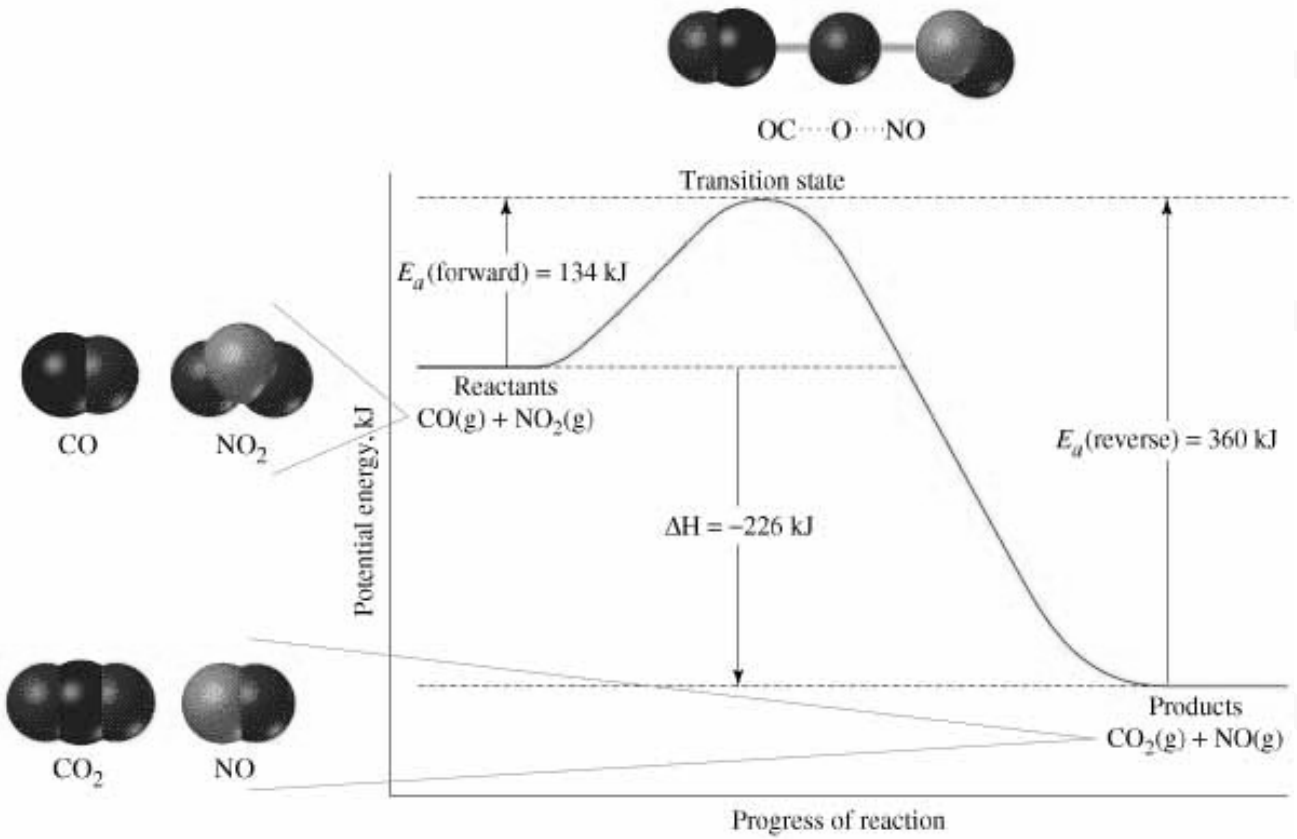


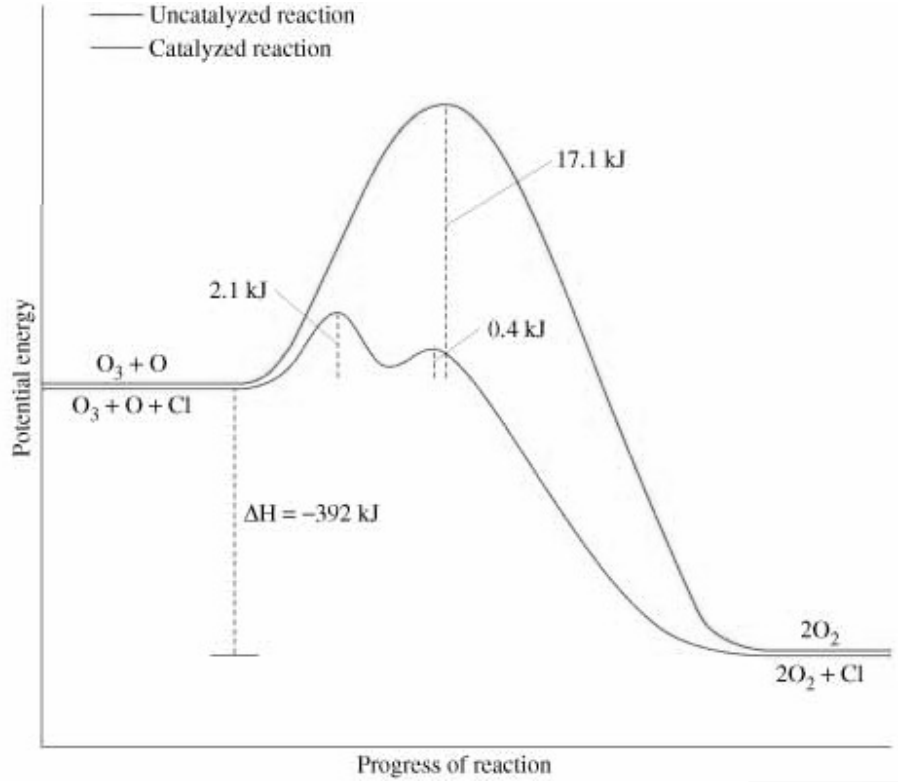
Transition state theory

- A REACTION PROFILE shows the movement from reactants to products through the ACTIVATED COMPLEX at the TRANSITION STATE



Catalysis

- A CATALYST lowers the activation energy of the reaction but is not consumed during the reaction
- An enzyme is a biological (protein) catalyst



end of section

Equilibria

- We have mentioned the dynamic nature of a reaction at equilibrium several times before, and now explore the topic in detail
  - In an equilibrium, the forward and reverse processes are occurring at the same rate
  - Reactant and product concentrations are constant
  - The dynamic nature of an equilibrium (eq) can be demonstrated using radioactive tracers (why?)

Table 14.1 Three Experiments Involving the Reaction $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at 698 K

Experiment Number	Initial Concentrations, M	Equilibrium Concentrations, M	$\frac{[H_2][I_2]}{[HI]}$	$\frac{[H_2][I_2]}{2\,[HI]}$	$\frac{[H_2][I_2]}{[HI]^2}$
1	[HI]: 1.000 $[H_2]$: 0.000 $[I_2]$: 0.000	0.786 0.107 0.107	0.0146	0.00728	0.0185
2	[HI]: 0.000 $[H_2]$: 1.000 $[I_2]$: 1.000	1.573 0.213 0.213	0.0288	0.0144	0.0183
3	[HI]: 1.000 $[H_2]$: 1.000 $[I_2]$: 1.000	2.360 0.320 0.320	0.0434	0.0217	0.0184

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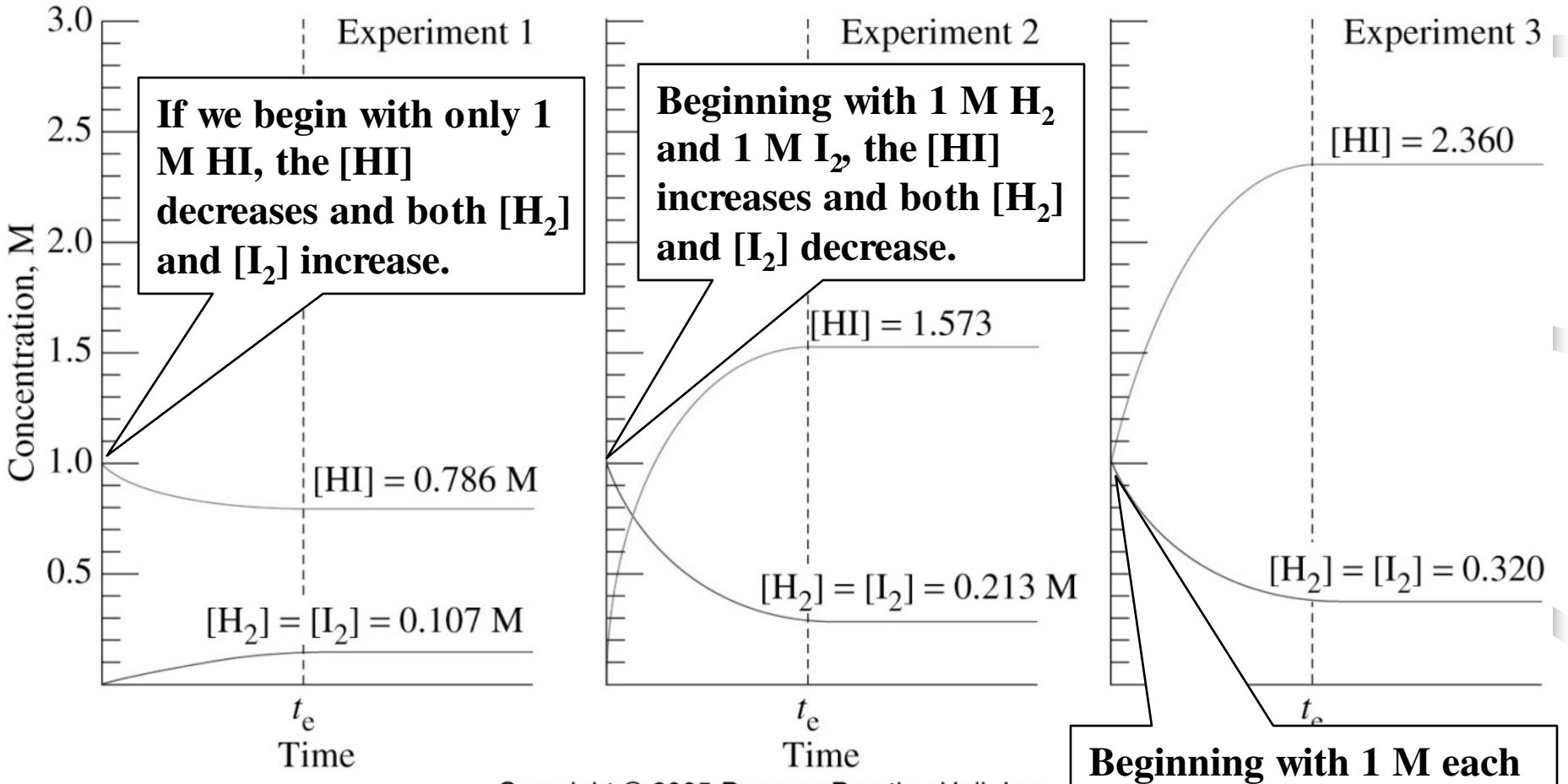
Regardless of the starting concentrations; once equilibrium is reached …

… the expression with products in numerator, reactants in denominator, where each concentration is raised to the power of its coefficient, appears to give a constant.

Concentration vs. *time*



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Equilibrium constants

- Product concentrations divided by reactant concentrations gives the EQUILIBRIUM CONSTANT EXPRESSION or equation
- Ex: for 2 $NO(g) + O_2(g) \Leftrightarrow 2\ NO_2(g)$, $K_c = [NO_2]^2 / [NO]^2\ [O_2] = 4.67 \times 10^{13}$
- Exponents equal the stoichiometric coefficients
- Given some of the variables, you can solve for the missing one

Reaction rates at equilibrium

- For the previous reaction, the forward rate = $k_f[NO]^2\ [O_2]$ where k is the rate constant
- The reverse rate = $k_r[NO_2]^2$
- At eq, forward rate = reverse rate
- So, the equilibrium constant $K_{eq} = k_f / k_r$
- Effect of reversing equation or multiplying whole system by a number
- For multi-step reactions, the overall rate depends only upon the slow step

Reaction rates at equilibrium (cont'd)

- Partial pressures can be used in place of concentrations for gas equations
- Pure solids and liquids DO NOT appear in equilibrium constant expressions since their CONCENTRATIONS don't change during the reactions (AMOUNTS of course change, but not concentrations)
- Extreme values for K indicate non-reversible reactions

Example: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_c = \frac{[CaO]\,[CO_2]}{[CaCO_3]}$$

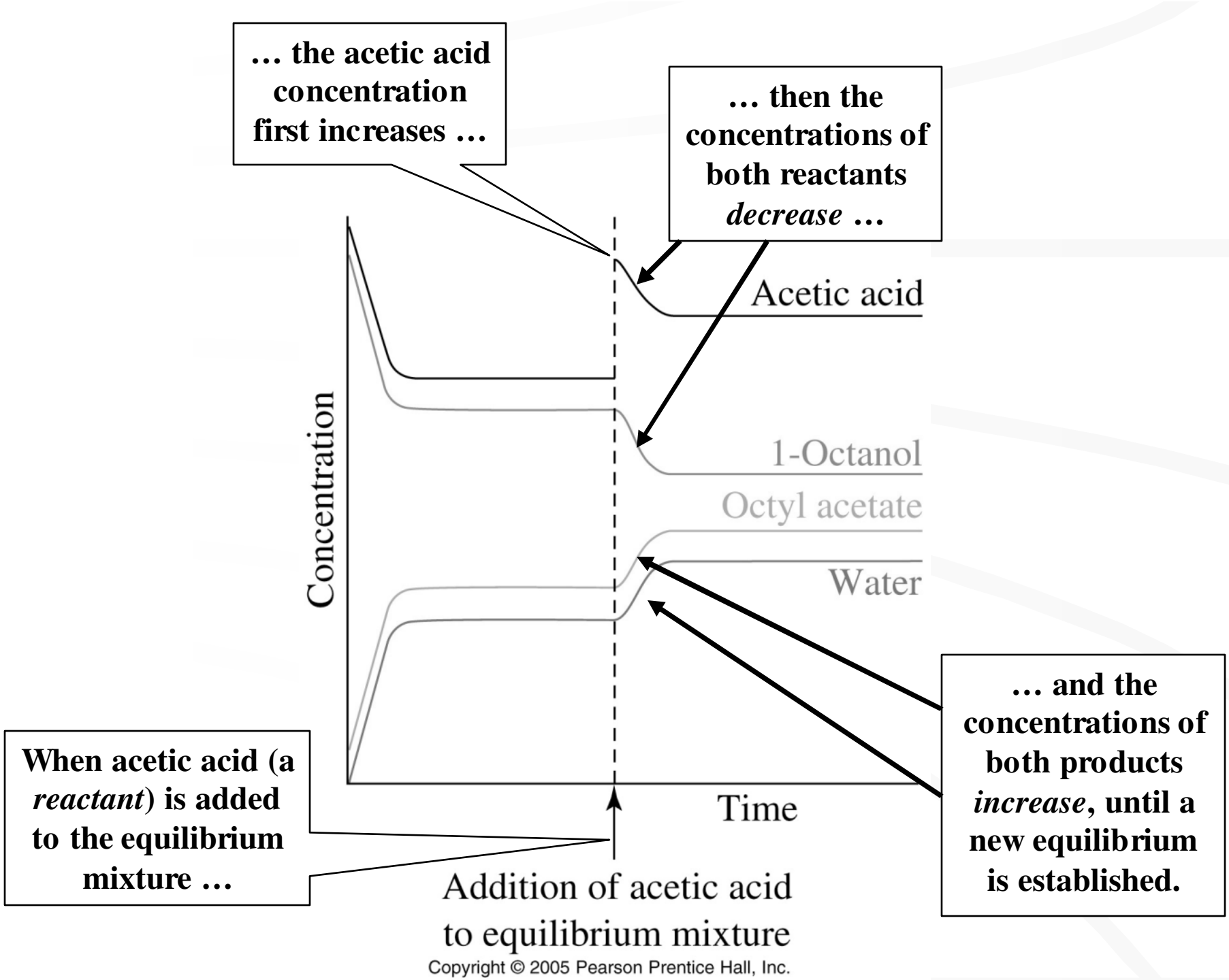
$$\boldsymbol{K_c = [CO_2]}$$

Reaction quotient

- An examination of the K type for a reaction NOT at eq
- For ***non***equilibrium conditions, the expression having the same form as K_c or K_p is called the ***reaction quotient***, $\boldsymbol{Q_c}$ or $\boldsymbol{Q_p}$.
- The reaction quotient is not constant for a reaction, but is useful for *predicting the direction* in which a net change must occur to establish equilibrium.
- To determine the direction of net change, we compare the magnitude of Q_c to that of K_c.

LeChatelier's principle

- A stress placed on a reaction system at equilibrium is minimized
- Addition of products or removal of products
- Changing pressure (4 slides ahead)
- Changing temperature
- Addition of catalyst
  - A common word very few understand...
  - Enzymes



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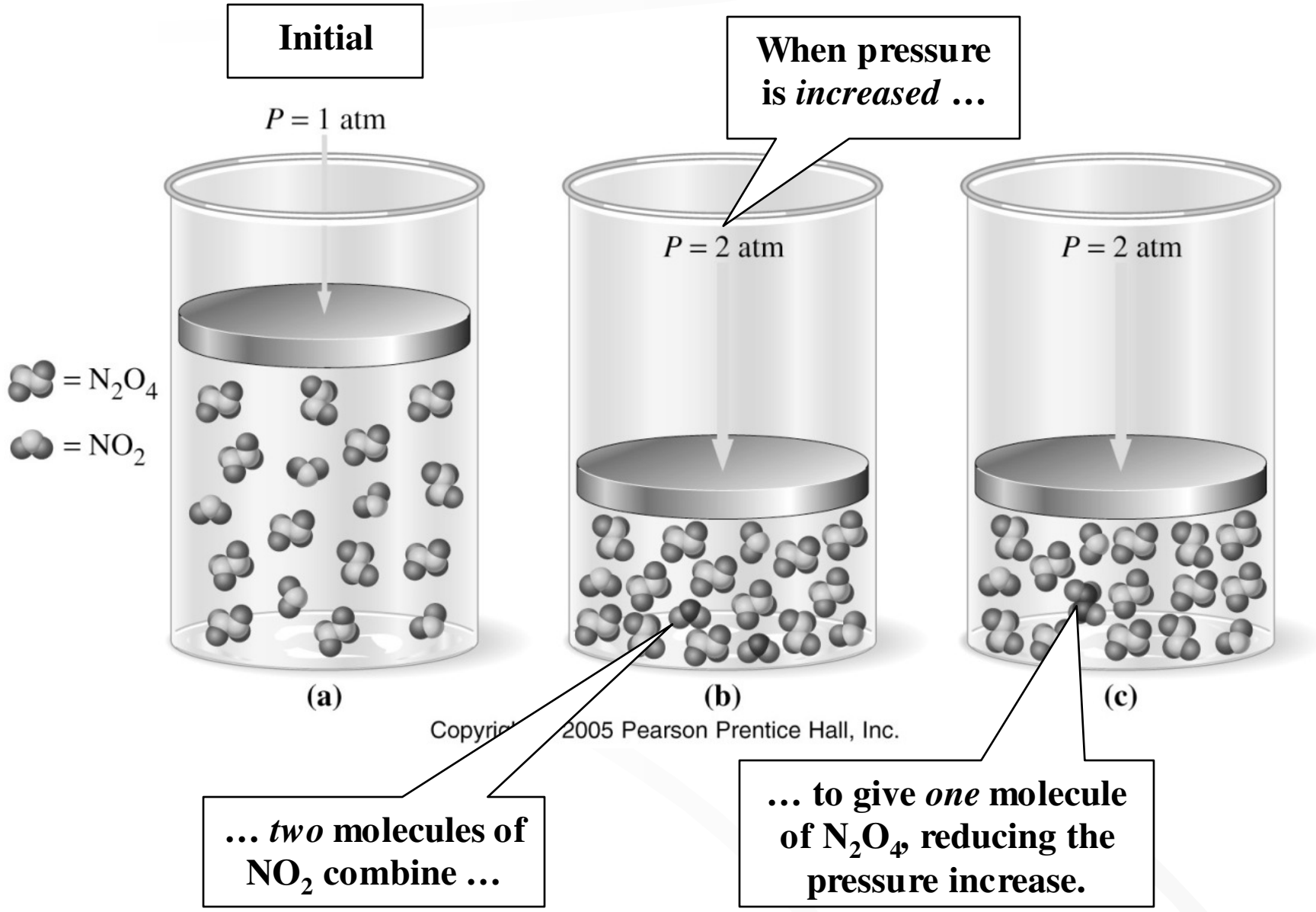
Initial
When pressure is *increased* …
P = 1 atm
P = 2 atm
P = 2 atm
= N_2O_4
= NO_2
(a)
(b)
(c)
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… *two* molecules of NO_2 combine …
… to give *one* molecule of N_2O_4, reducing the pressure increase.

end of section

Quick review of topics

- Solutions can incorporate the various states of matter
- Definitions of, calculations with molarity/molality
- Solutions can expand or contract upon dissolution, thus M is T dependent
- Dissolution can be exo- or endothermic
- Like dissolves like
- Colligative properties- specifically boiling point elevation and freezing point depression

Quick review (cont'd)

- Rate constants (little k) and are experimentally determined
- Reaction rate is how fast a reaction occurs
- At equilibrium, forward and reverse rates are equal
- Reactant and product concentrations are constant at equilibrium, even though eq is DYNAMIC
- Product concentrations divided by reactant concentrations gives the equilibrium constant expression or equation (big K), with exponents equal to the stoichiometric coefficients from the balanced equation (pure solids and liquids do not appear)
- Size of K (either in terms of concentration or pressure) gives the extent of reaction ("how far to the left or right the reaction lies")
- The reaction quotient Q starts at zero and goes to K
- Use LeChatelier to predict effects of changing P, V or T
- Catalysts (enzymes, biologically) lower activation energy and speed up reactions… they do not effect eq

Acids and bases expanded

- Must know 3 definitions
- Must know common strong/weak acids/bases
- Using your knowledge of acid-base reactions and reaction equilibria, mathematical expressions of acid-base equilibria can be given

Review

- Remember, Arrhenius said acids donated protons and bases donated hydroxide ions
- Bronsted said that acids are proton donors and bases are proton acceptors
- (Lewis definitions involve electron pairs)
- Bronsted theory required no water

Conjugate acid-base pairs are apparent in an acid-base reaction at equilibrium

- Ex. $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
- NH_4^+ is the conjugate acid of the base NH_3
- OH^- is the conjugate base of the acid H_2O
- So a conjugate base is an acid minus a proton
- And a conjugate acid is a base plus a proton
- A substance that can act as both an acid and a base is called amphoteric (or amphiprotic)

K_a and K_b

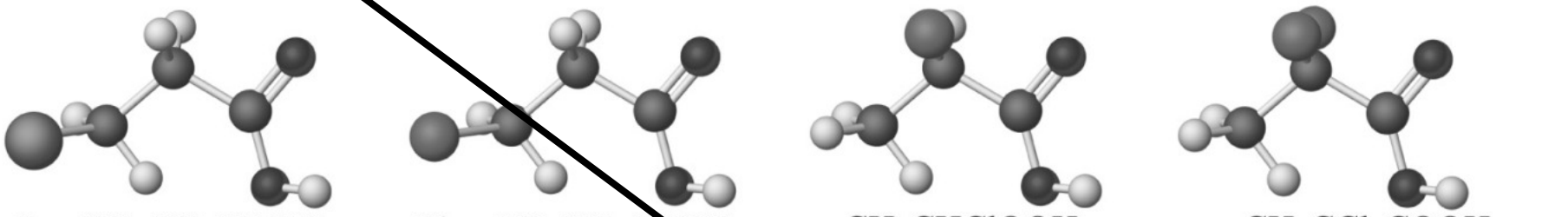
- The K for an acid-base equilibrium is called either the acid or base ionization constant (depending on the molecules involved)
- Strong acids have a large K_a and strong bases have a large K_b (why???)
- A strong acid has a weak conjugate base (why???)
- A strong base has a weak conjugate acid
- Explanations of the acidity/basicity of salts tend to be longwinded and unnecessary… what do you *know* to determine whether NH_4Cl and Na_2CO_3 are acidic or not?

Factors affecting acid strength for binary acids

- Bond strength
- Atomic radius
- Ionic or covalent character
  - electronegativity differences

Factors affecting acid strength for other acids and bases

- Electron Withdrawing Groups (EWG's) attached to carboxylic acids



$I—CH_2CH_2COOH$	$Cl—CH_2CH_2COOH$	$CH_3CHClOOH$	CH_3CCl_2COOH
3-Iodopropanoic acid	3-Chloropropanoic acid	2-Chloropropanoic acid	2,2-Dichloropropanoic acid
$K_a = 8.3 \times 10^{-5}$	$K_a = 1.0 \times 10^{-4}$	$K_a = 1.4 \times 10^{-3}$	$K_a = 8.7 \times 10^{-3}$

Increasing acid strength →

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- EWG's on amines
  - Aromatic amines are much weaker bases than aliphatic amines.
  - This is due in part to the fact that the π electrons in the benzene ring of an aromatic molecule are *delocalized* and can involve the nitrogen atom's lone-pair electrons in the resonance hybrid.
  - As a result, the lone-pair electrons are much less likely to accept a proton.
  - Electron-withdrawing groups on the ring further diminish the basicity of aromatic amines relative to aniline.

The pH scale

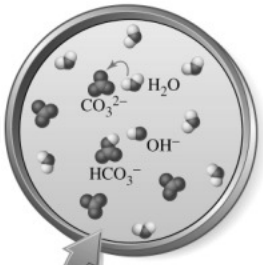
- Concentration of H_3O^+ can vary over a wide range in aqueous solution, from about 10 M to about 10^{-14} M.
- A more convenient expression for H_3O^+ is **pH**. Lowercase "p" and uppercase "H"
- $$pH = -\log [H_3O^+] \quad \text{and so} \quad [H_3O^+] = 10^{-pH}$$
- The "negative logarithm" function of pH is so useful that it has been applied to other species and constants.

  pOH $= -\log [OH^-]$ and so $[OH^-] = 10^{-pOH}$

  pK_w $= -\log K_w$
- At 25 °C, $pK_w = 14.00$
- $pK_w = pH + pOH = 14.00$
- Calculations
- Polyprotic acids – values of K_a decrease successively for a given polyprotic acid. $K_{a1} > K_{a2} > K_{a3}$, etc.

Other topics

- Ions as acids and bases
- Common ion effect (LeChatelier revisited)
- Buffers (use in lab)
- Indicators (use in lab)
- Neutralization reactions and titration curves (use in lab)



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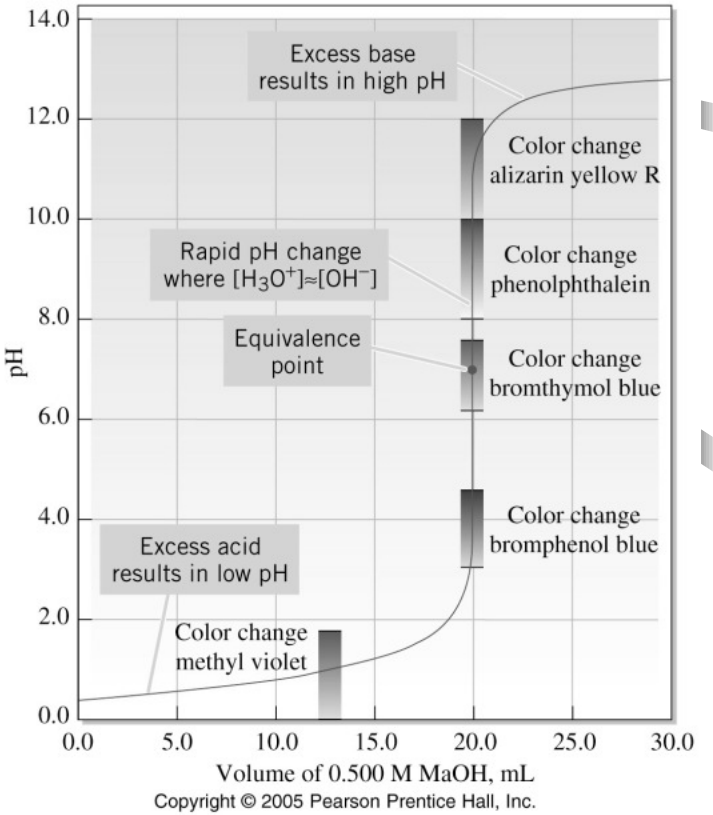

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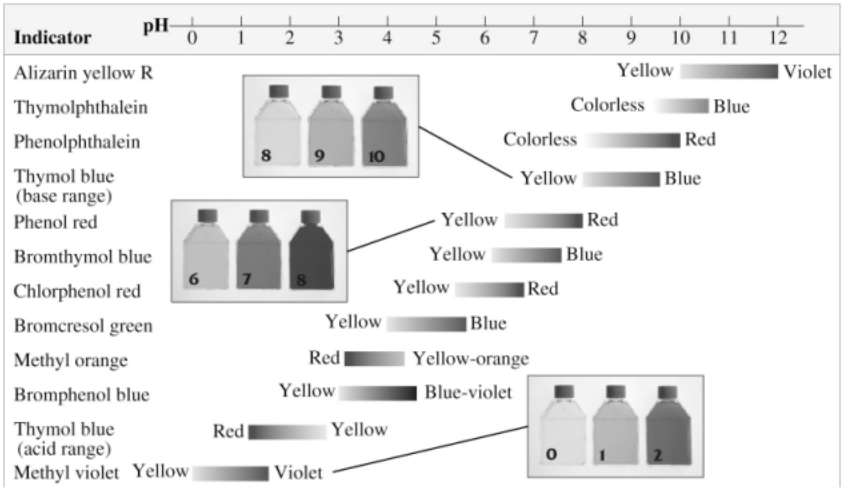

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Neutralization reactions

- At the equivalence point in an acid–base titration, the acid and base have been brought together in precise stoichiometric proportions.
- The endpoint is the point in the titration at which the indicator changes color.
- Ideally, the indicator is selected so that the endpoint and the equivalence point are very close together.
- The endpoint and the equivalence point for a neutralization titration can be best matched by plotting a titration curve, a graph of pH versus volume of titrant.

end of section

Review

- Solubility was introduced earlier with the formation of precipitates
- LeChatelier's Principle tells us that formation of a solid from aqueous reactants drives a reaction in the forward direction
- Using what we learned about equilibrium constants, we can discuss how soluble something is

Example

- $BaSO_4(s) \Leftrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$
- The equilibrium constant (or *solubility product constant* here),
  $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ at 25°C
  since solids don't appear in the expression
- ....not very soluble, which is why it can be taken prior to being X-rayed
- K_{sp}s are influenced by a complex set of factors
- Given K_{sp}, you can calculate an ion concentration and *vice versa*

Table 16.1 Some Solubility Product Constants at 25 °C

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\ OH^-(aq)$	1.3×10^{-33}
Barium carbonate	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.1×10^{-9}
Barium sulfate	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
Calcium carbonate	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	2.8×10^{-9}
Calcium fluoride	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$	5.3×10^{-9}
Calcium sulfate	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	9.1×10^{-6}
Calcium oxalate	$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$	2.7×10^{-9}
Chromium(III) hydroxide	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\ OH^-(aq)$	6.3×10^{-31}
Copper(II) sulfide	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	8.7×10^{-36}
Iron(III) hydroxide	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\ OH^-(aq)$	4×10^{-38}
Lead(II) chloride	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$	1.6×10^{-5}
Lead(II) chromate	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.8×10^{-13}
Lead(II) iodide	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$	7.1×10^{-9}
Magnesium carbonate	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
Magnesium fluoride	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^-(aq)$	3.7×10^{-8}
Magnesium hydroxide	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$	1.8×10^{-11}
Magnesium phosphate	$Mg_3(PO_4)_2(s) \rightleftharpoons 3\ Mg^{2+}(aq) + 2\ PO_4^{3-}(aq)$	1×10^{-25}
Mercury(I) chloride	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\ Cl^-(aq)$	1.3×10^{-18}
Mercury(II) sulfide	$HgS(s) \rightleftharpoons Hg^{2+}(aq) + S^{2-}(aq)$	2×10^{-53}
Silver bromide	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Silver chloride	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Silver iodide	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.5×10^{-17}
Strontium carbonate	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	1.1×10^{-10}
Strontium sulfate	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}
Zinc sulfide	$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$	1.6×10^{-24}

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K_{sp} *and molar solubility*

- K_{sp} is an equilibrium constant
- ***Molar solubility*** is the number of moles of compound that will dissolve per liter of solution.
- Molar solubility is ***related*** to the value of K_{sp}, but molar solubility and K_{sp} are ***not*** the same thing.
- In fact, "smaller K_{sp}" doesn't always mean "lower molar solubility."
- Solubility depends on both K_{sp} and the form of the equilibrium constant expression.

Example

At 20 °C, a saturated aqueous solution of silver carbonate contains 32 mg of Ag_2CO_3 per liter of solution. Calculate K_{sp} for Ag_2CO_3 at 20 °C. The balanced equation is

$$Ag_2CO_3(s) \rightleftharpoons 2\,Ag^+(aq) + CO_3^{2-}(aq)$$

K_{sp} = ?

Example

From the K_{sp} value for silver sulfate, calculate its molar solubility at 25 °C.

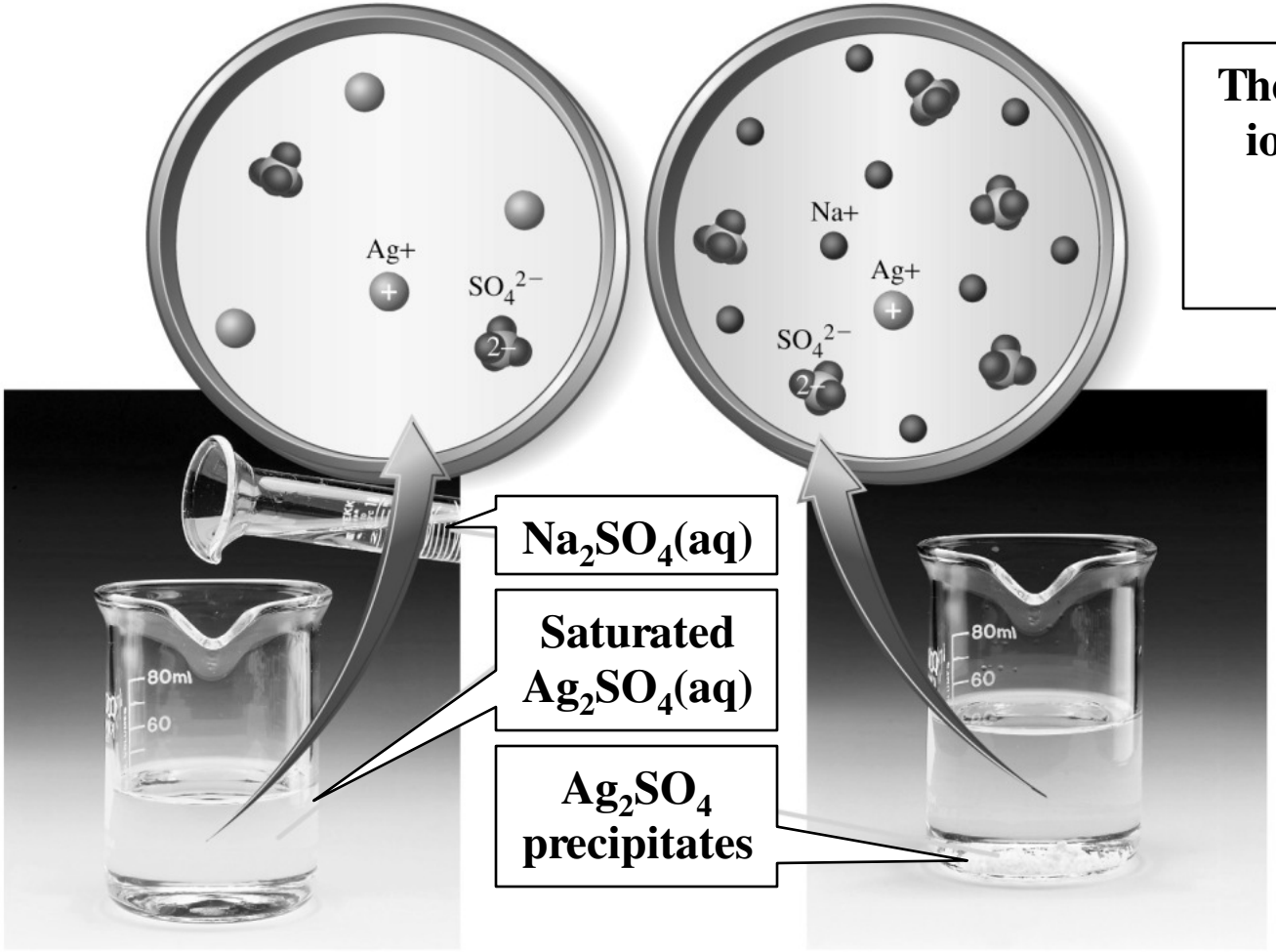
$$Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)$$

$K_{sp} = 1.4 \times 10^{-5}$ at 25 °C

Common ion effect revisited

- LeChatelier's Principle re-revisited
  - The common ion effect affects solubility equilibria as it does other aqueous equilibria.
  - The solubility of a slightly soluble ionic compound is lowered when a second solute that furnishes a common ion is added to the solution.

Common ion effect illustrated



The added sulfate ion *reduces* the solubility of Ag_2SO_4.

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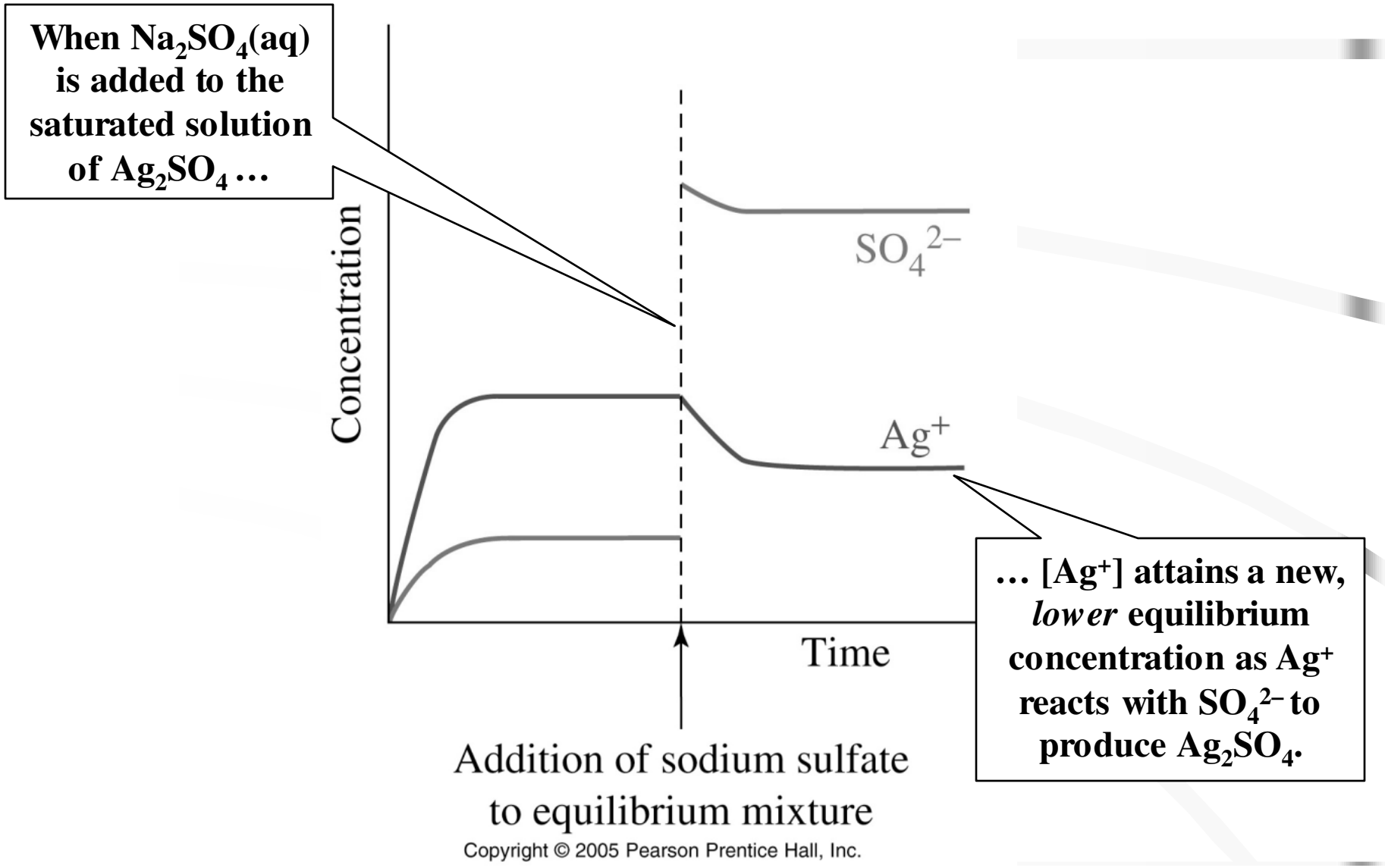
Common ion effect illustrated (cont'd)



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Solubility and activities

- Ions that are not common to the precipitate can also affect solubility.
  - CaF_2 is more soluble in 0.010 M Na_2SO_4 than it is in water.
- Increased solubility occurs because of interionic attractions.
- Each Ca^{2+} and F^- is surrounded by ions of opposite charge, which impede the reaction of Ca^{2+} with F^-.
- The effective concentrations, or activities, of Ca^{2+} and F^- are lower than their actual concentrations.
- Again, activities will not be explored in detail

Q versus K (again)

- Reaction (or Ion Product) quotient, Q_{ip}
- Comparing Q_{ip} to K_{sp} tells whether precipitation will occur
- For $Q_{ip} > K_{sp}$, precipitation of the supersaturated solution should occur
- For $Q_{ip} < K_{sp}$, precipitation of the unsaturated solution cannot occur
- For $Q_{ip} = K_{sp}$, the solution is saturated
- In applying the precipitation criteria, the effect of dilution when solutions are mixed must be considered.

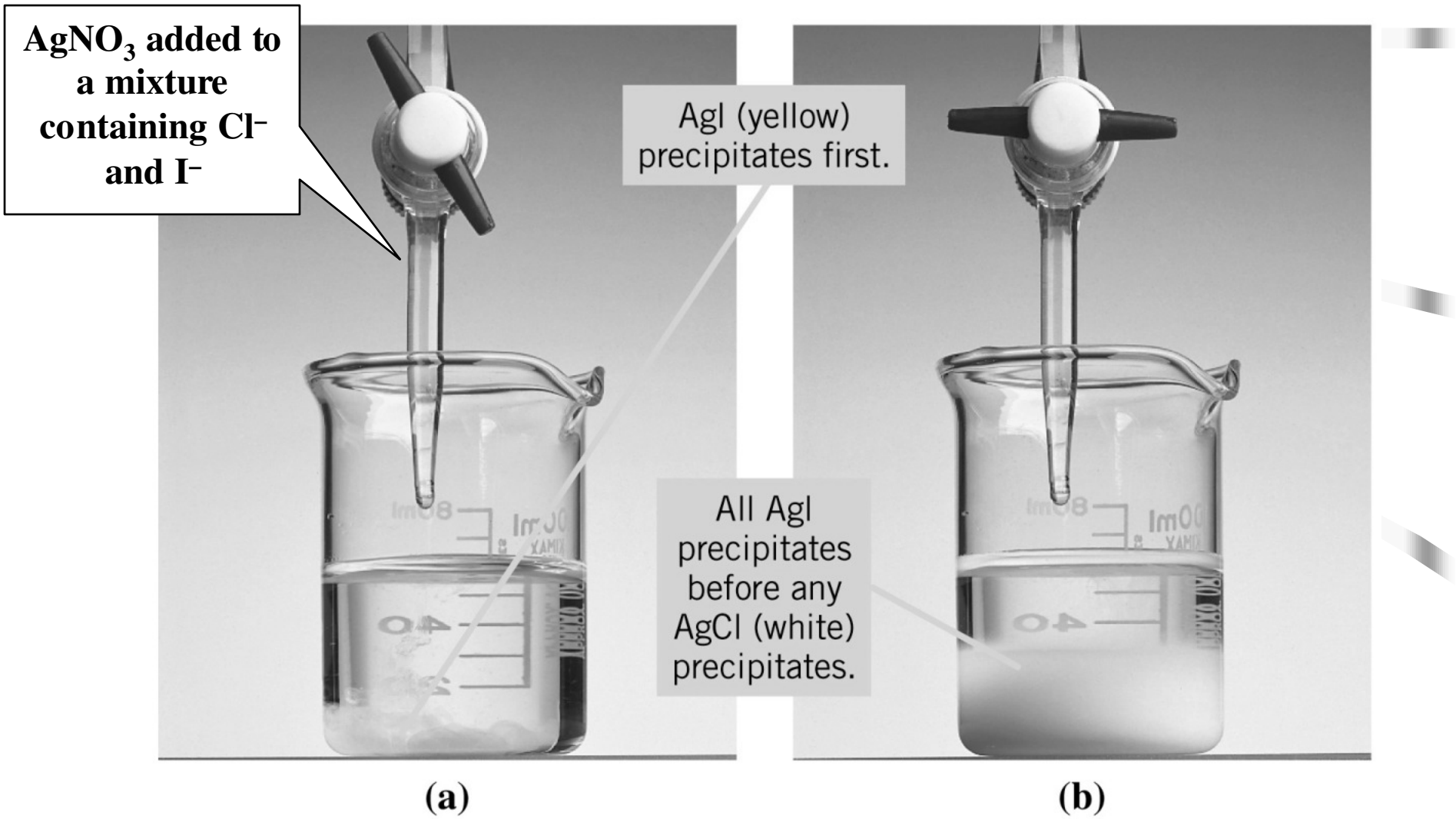
Example

If 1.00 mg of Na_2CrO_4 is added to 225 mL of 0.00015 M $AgNO_3$, will a precipitate form?

$$Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$$

$K_{sp} = 1.1 \times 10^{-12}$

Selective precipitation



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Example

An aqueous solution that is 2.00 M in $AgNO_3$ is slowly added from a buret to an aqueous solution that is 0.0100 M in Cl^- and also 0.0100 M in I^-.

a. Which ion, Cl^- or I^-, is the first to precipitate from solution?

b. When the second ion begins to precipitate, what is the remaining concentration of the first ion?

c. Is separation of the two ions by selective precipitation feasible?

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_{sp} = 8.5 \times 10^{-17}$$

pH effect

- If the anion of a precipitate is that of a weak acid, the precipitate will dissolve somewhat when the pH is lowered:

Added H^+ reacts with, and *removes,* acetate; LeChâtelier's principle says more acetate forms.

- If, however, the anion of the precipitate is that of a strong acid, lowering the pH will have no effect on the precipitate.

H^+ does not consume Cl^- ; acid does not affect the equilibrium.

Example

What is the molar solubility of $Mg(OH)_2(s)$ in a buffer solution having $[OH^-] = 1.0 \times 10^{-5}$ M, that is, pH = 9.00?

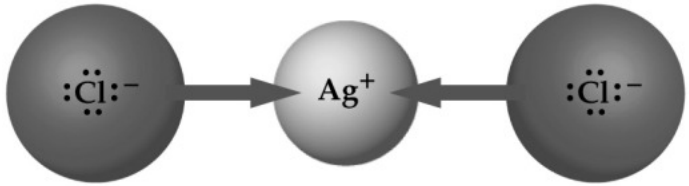
$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq) \qquad K_{sp} = 1.8 \times 10^{-11}$$

Complex ion formation

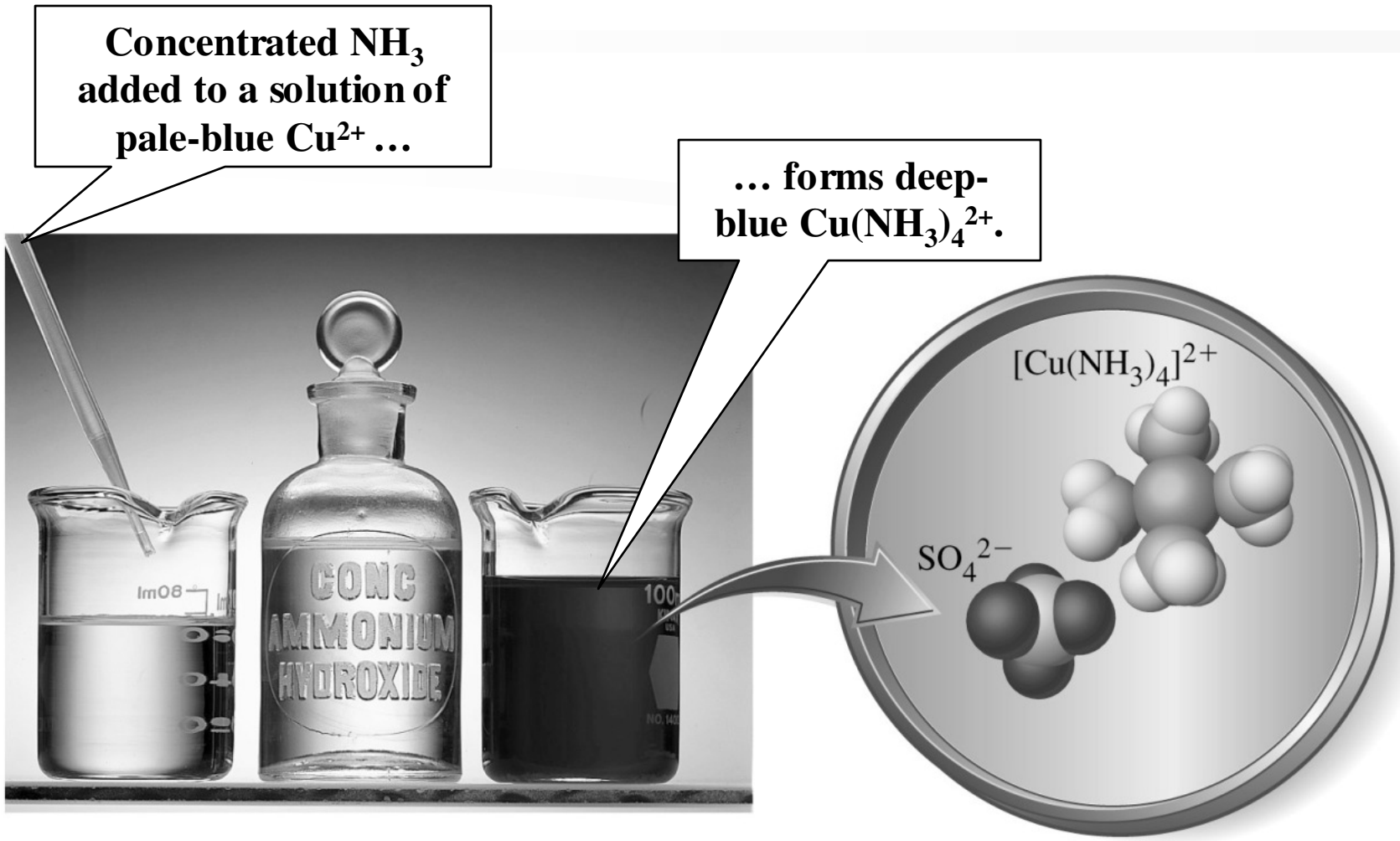
- KEY POINT– A ***complex ion*** consists of a central metal atom or ion, with other groups called ***ligands*** bonded to it.
- The metal ion acts as a Lewis acid (accepts electron pairs).
- Ligands act as Lewis bases (donate electron pairs).
- The equilibrium involving a complex ion, the metal ion, and the ligands may be described through a ***formation constant, K_f***:

$$Ag^+(aq) + 2\,Cl^-(aq) \rightleftharpoons [AgCl_2]^-(aq)$$

$$K_f = \frac{[AgCl_2]^-}{[Ag^+][Cl^-]^2} = 1.2 \times 10^8$$



Complex ion formation (cont'd)



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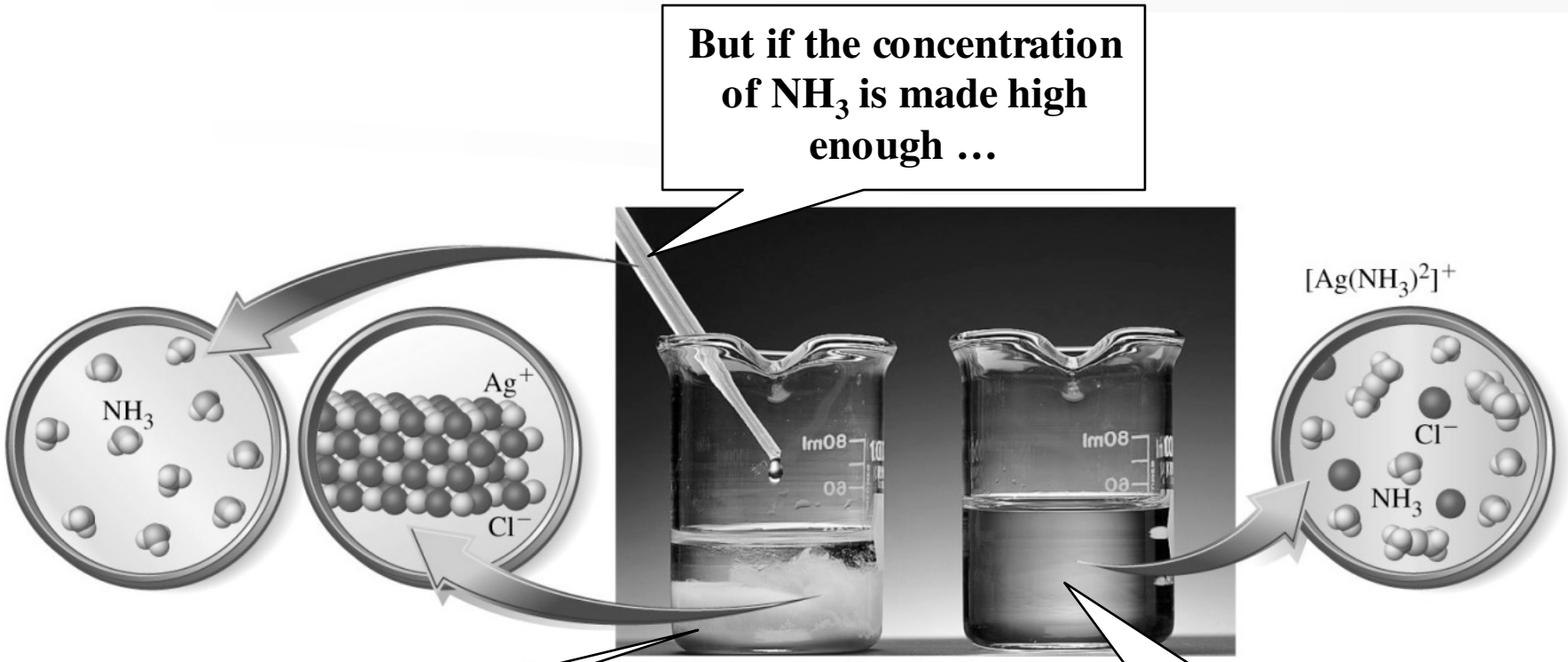
Complex ion formation and solubility



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Complex ions in acid–base reactions

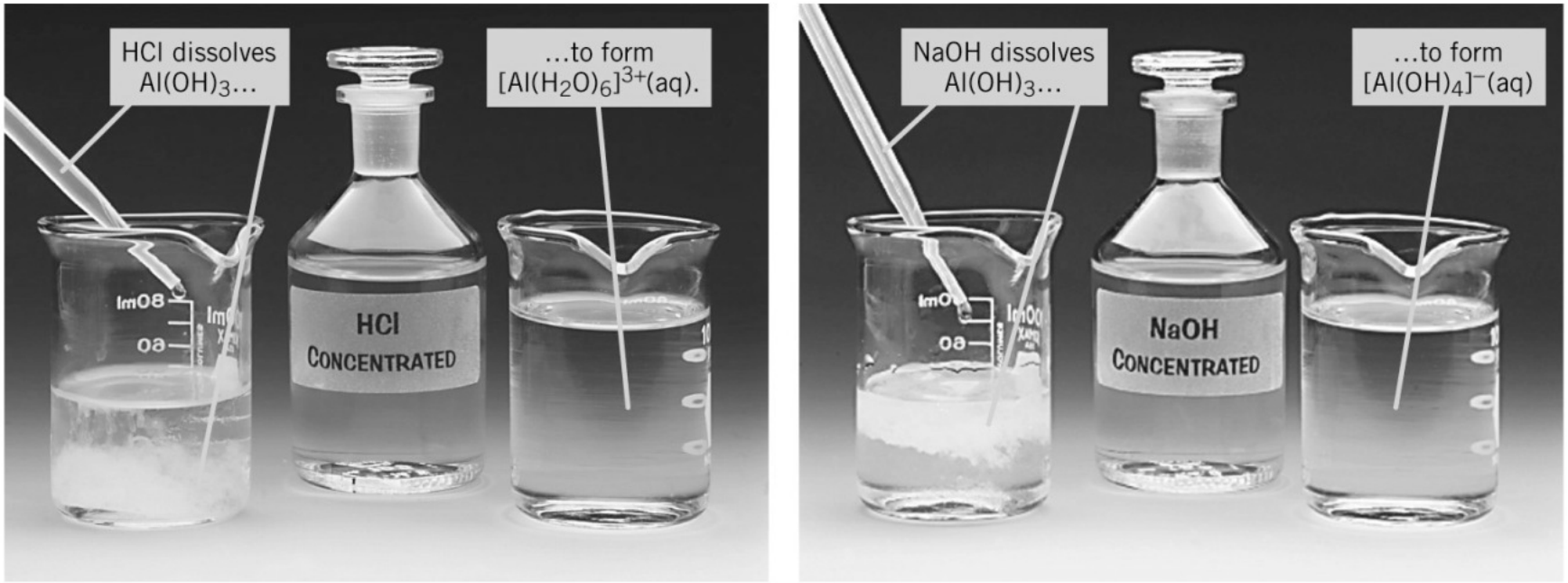
- Water molecules are commonly found as ligands in complex ions (H_2O is a Lewis base).

$[Na(H_2O)_4]^+$ $[Al(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{3+}$

- The electron-withdrawing power of a ***small***, ***highly charged*** metal ion can weaken an O—H bond in one of the ligand water molecules.
- The weakened O—H bond can then give up its proton to another water molecule in the solution.
- The complex ion acts as an ***acid***.

Amphoteric compounds

- Certain metal hydroxides, insoluble in water, are ***amphoteric***; they will react with both strong acids and strong bases.
- $Al(OH)_3$, $Zn(OH)_2$, and $Cr(OH)_3$ are amphoteric.



(a) (b)

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end of section

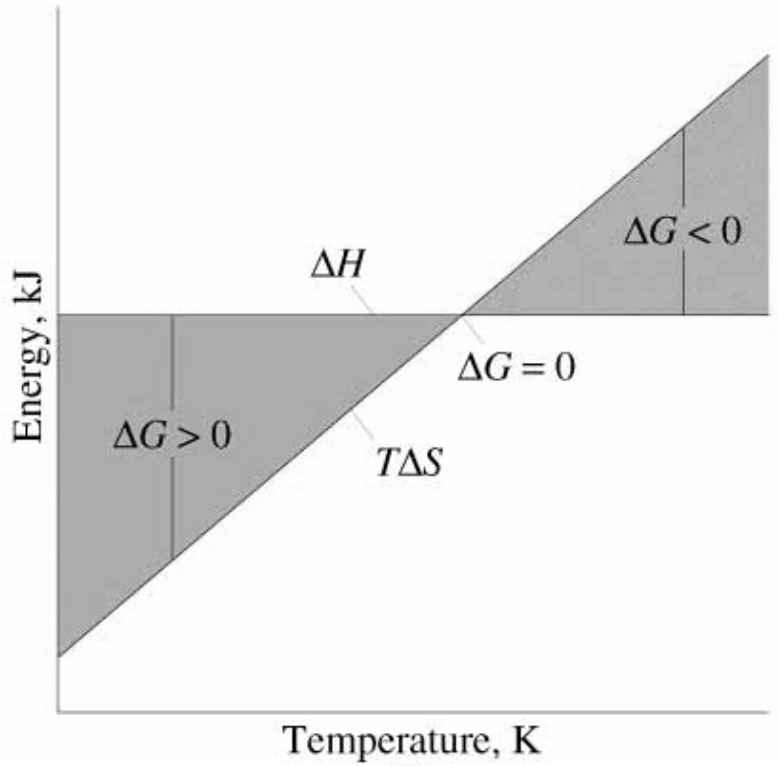
Thermodynamics

Jargon

- SPONTANEITY- whether or not a process can occur unassisted
  - If forward reaction is spontaneous, then reverse reaction is not and vice versa
- ENTROPY- measure of randomness
  - $\Delta S_{univ} > 0$
- ENTHALPY- heat of reaction
- FREE ENERGY- relates enthalpy and entropy to spontaneity
  - $\Delta G = \Delta H - T\Delta S$

Free energy

- ΔG<0 spontaneous
- ΔG>0 nonspontaneous
- ΔG=0 equilibrium
- ΔH neg, ΔS pos, ΔG neg, spont
- ΔH pos, ΔS neg, ΔG pos, nonspont
- ΔH pos, ΔS pos, spont at high T
- ΔH neg, ΔS neg, spont at low



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