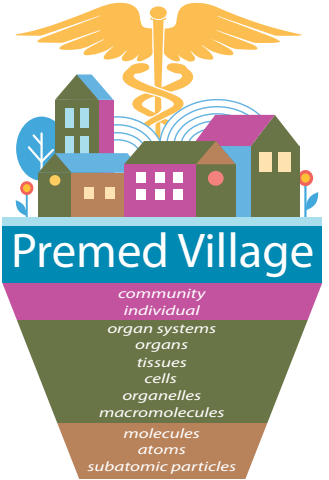

Chemistry Notes

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Physics

MECHANICS

- Kinematics ✔
- Newton's Laws ✔
- Work, Energy, and Power ✔
- Harmonic Motion
- Elastic Properties of Solids
- Fluid Mechanics

WAVES

- Waves

GRAVITATION

- Gravitation

THERMODYNAMICS

- Heat & Temperature
- The Ideal Gas and Kinetic Theory preview
- The First Law of Thermodynamics
- The Second Law of Thermodynamics and Heat Engines

ELECTRICITY & MAGNETISM

- Electricity ✔
- DC Current
- Magnetism

LIGHT & OPTICS

- The Properties of Light
- Geometric Optics
- Wave Optics

MODERN PHYSICS & NUCLEAR PHYSICS

- Modern Physics
- Nuclear Physics

General Chemistry

THE STRUCTURE OF MATTER

- Atomic Theory ✔
- Periodic Properties ✔
- The Chemical Bond ✔
- Intermolecular Forces ✔

STOICHIOMETRY

- Stoichiometry

CHEMICAL THERMODYNAMICS AND CHEMICAL KINETICS

- Thermochemistry
- The States of Matter
- Chemical Thermodynamics and the Equilibrium State
- Chemical Kinetics

SOLUTIONS AND AQUEOUS SYSTEMS

- Water
- Solutions
- Acids and Bases

OXIDATION REDUCTION AND ELECTROCHEMISTRY

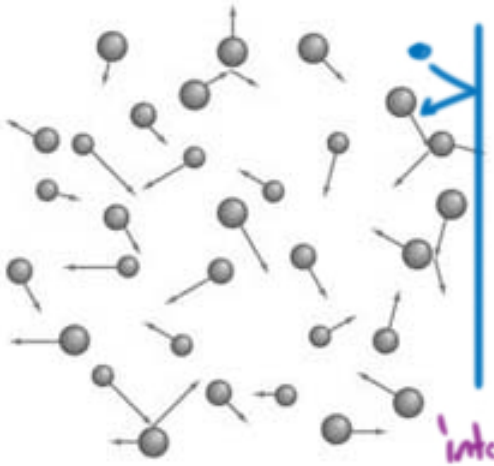
- Oxidation/Reduction
- Electrochemistry

COORDINATION CHEMISTRY

- Coordination Chemistry

The Internal Energy of an Ideal Gas Depends on Temperature

only the kinetic energy of the particles ie. thermal energy



- point masses
- no action at a distance forces
- only elastic collisions

'internal energy'

$\frac{U}{N} = \frac{3}{2}kT$

$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$

$$U = \frac{3}{2}NkT$$

U = internal energy
N = number of molecules
k = Boltzmann's constant
= R / Avogadro's number
T = temperature

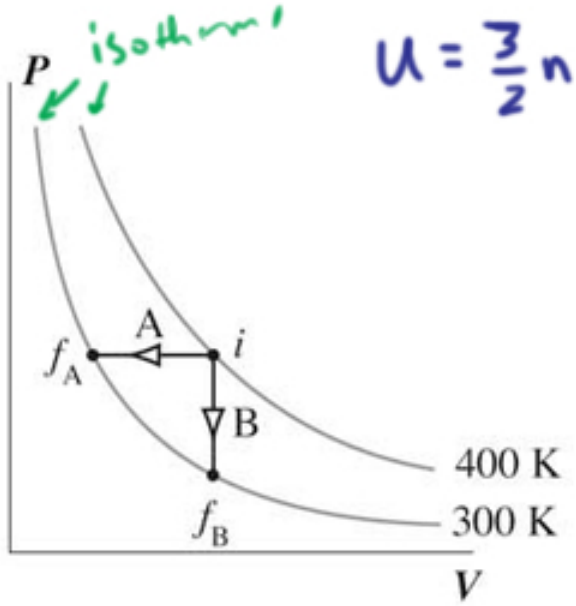
$$U = \frac{3}{2}nRT$$

n = moles of gas
R = ideal gas constant

Kelvin

Our starting point to understand internal energy

The graph at right shows two isotherms corresponding to pressure vs. volume of a sample of ideal gas at 400K and 300K respectively. Path A shows the *isobaric* compression of the gas from initial state i to final state f_A. Path B shows *isovolumetric* cooling from initial state i to final state f_B. Which of the two transformations represents the greatest internal energy decrease for the gas?



$U = \frac{3}{2} nRT$

a. Path A

b. Path B

c. The internal energy changes are equal

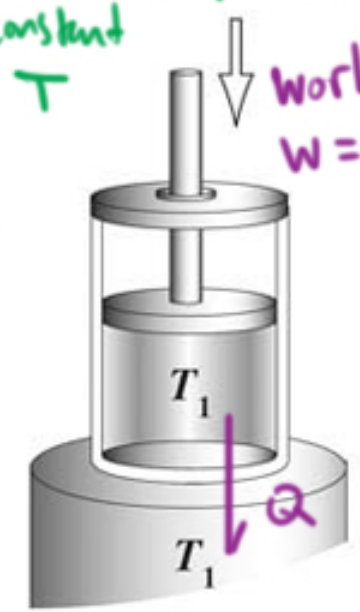
d. Both paths increase internal energy

isothermal compression

constant T

A piston containing ideal gas is slowly compressed in thermal contact with a heat reservoir. Constant temperature is maintained throughout the compression. Which of the following must have occured?

$\Delta U = 0$



a. Heat flowed into the reservoir.

b. The pressure of the gas decreased.

c. The internal energy of the gas increased.

d. The internal energy of the gas decreased.

$\Delta U = Q - W$

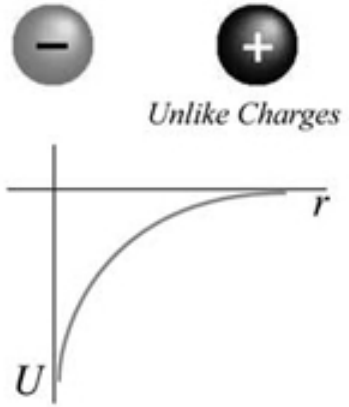
$\Delta U = 0$

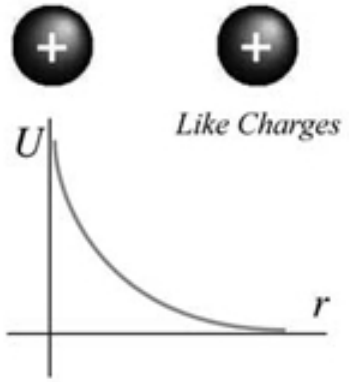
$W = Q$

Real substances

$$U_e = k\frac{q_1 q_2}{r}$$

ΔU may involve changes in terms of electrostatic potential energy.

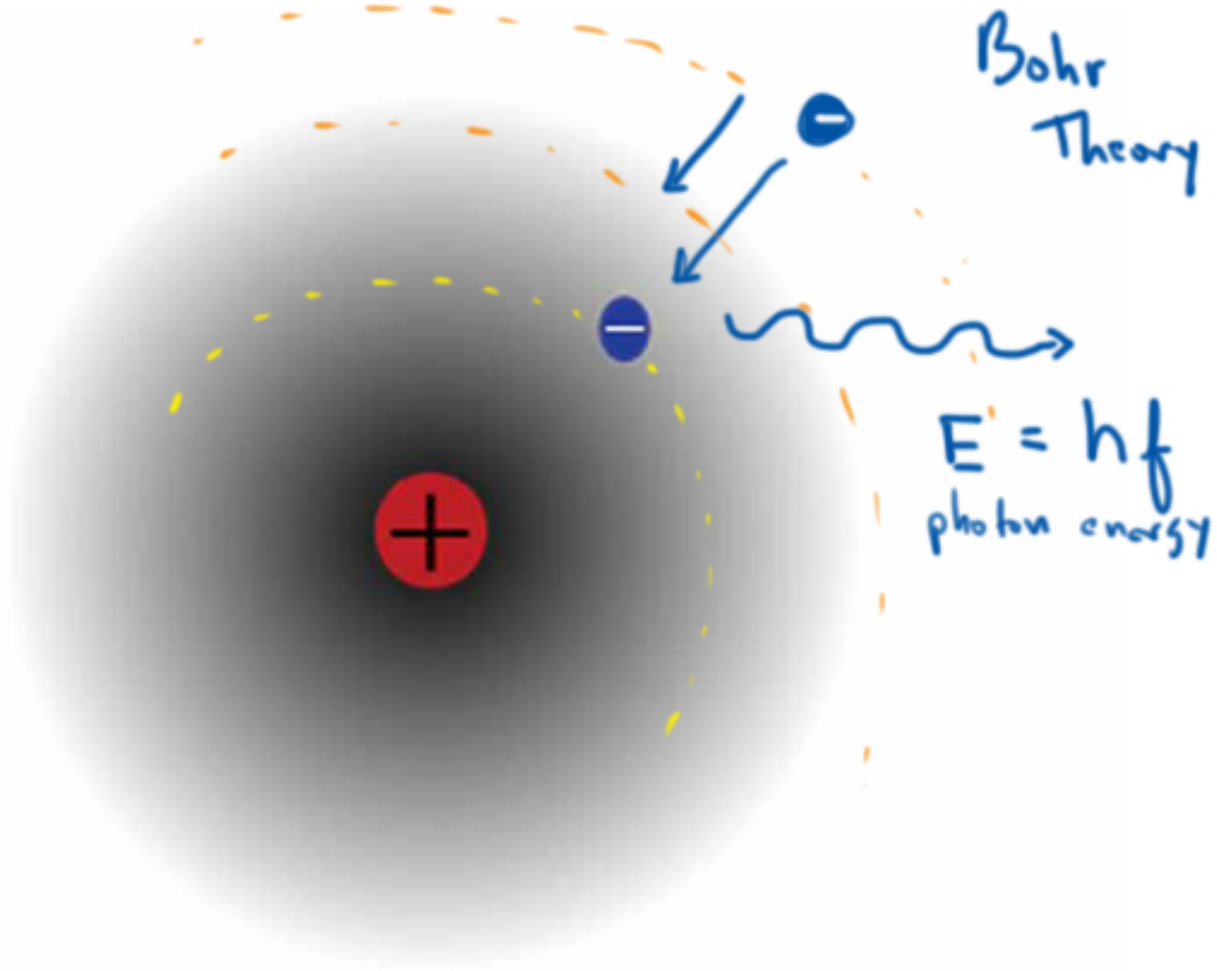




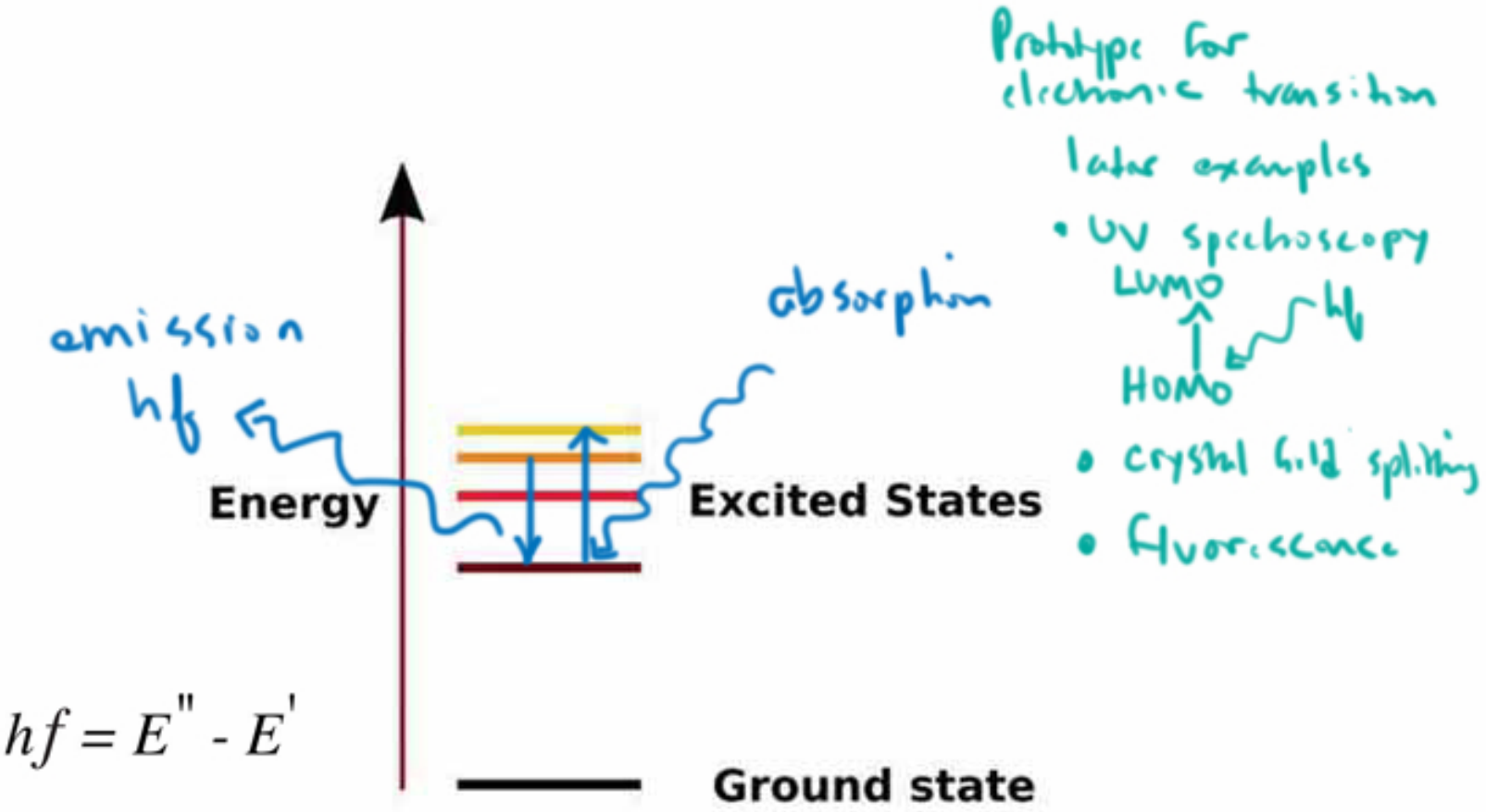
classical

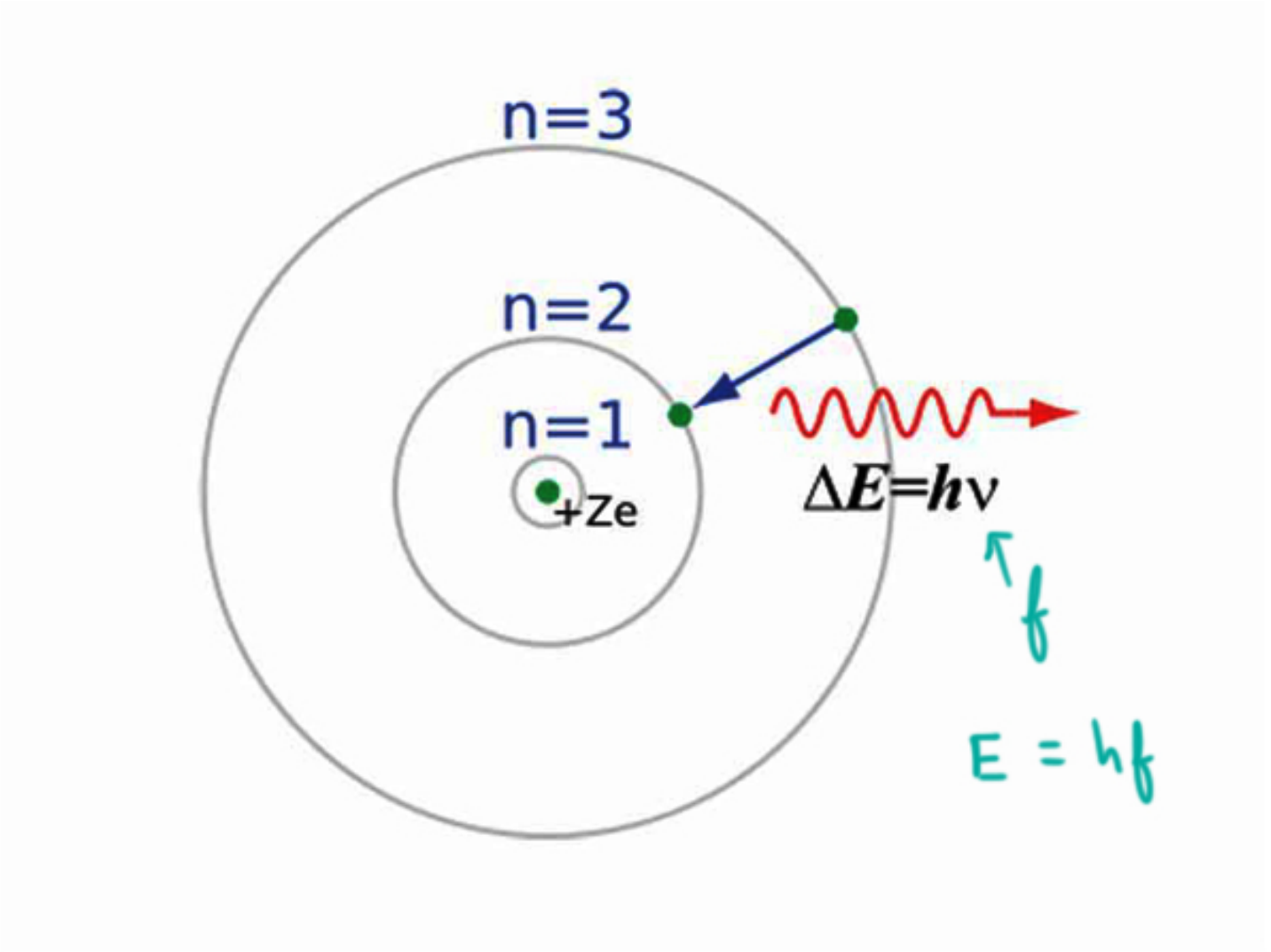
$U = \frac{kq_1q_2}{r}$

Quantized



Line Spectrum


Prototype for electronic transition
later examples
• UV spectroscopy
LUMO
HOMO
hf
• crystal field splitting
• fluorescence
absorption
emission
hf
Energy
Excited States
$hf = E'' - E'$
Ground state


n=3
n=2
n=1
+Ze
ΔE=hν
f
E = hf

In the Bohr theory of the atom the energy of the n-th level for any atom is given by the following equation

$$E \approx \frac{-13.6Z^2}{n^2} \text{ eV}$$

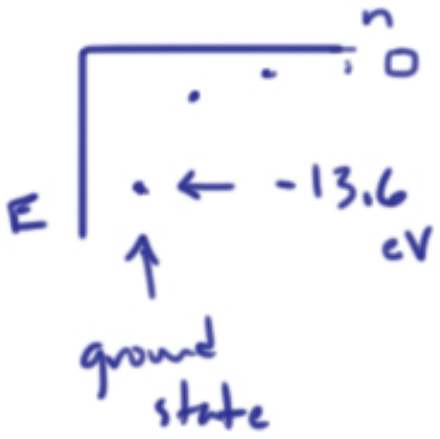
where Z is the atom's atomic number. Which of the following is a true statement according to the theory?

A. A ground state hydrogen electron has about 13.6 eV less energy than an electron far from the nucleus.

B. The ionization energy of hydrogen is approximately 50 eV.

C. The minimum energy possible for a hydrogen electron is zero.

D. Less energy is required to elevate an electron from the ground state to the 2nd energy level than from the 2nd to the 3rd.



Ionization energy of hydrogen is 13.6 eV

Quantum Numbers and Atomic Orbitals

n = principle quantum number

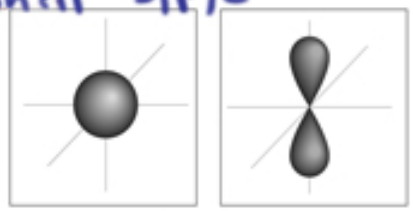
shell

Electron energy within an atom mainly depends on the principle quantum number, n, which can have values of 1, 2, 3 . . . Orbitals with the same principle quantum number are said to belong to the same *shell*. Shells are designated with the letters 1 = K, 2 = L, 3 = M, and so on.

l = angular momentum quantum number

subshell s,p,d

l determines what kind of *subshell* contains the electron. l values are constrained by n. For a given value of n, l can be any integer: 0, 1, 2 . . . n - 1. The subshell determines the shape of the electron orbital. Subshells are designated with letters corresponding to 0 = *s*, 1 = *p*, 2 = *d*, 3 = *f*, *etc.*

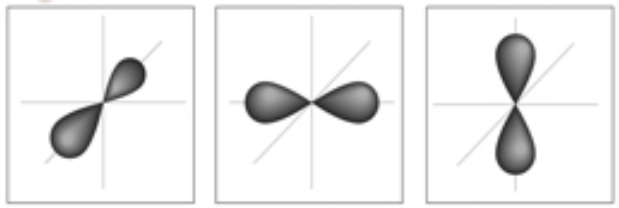


s subshell orbital | *p subshell orbital*

m_l = magnetic quantum number

orbital

m_l, determines the *orbital* within a subshell. It's values are constrained by l. For a given l, m_l can be any integer between -l and l. Thus, an *s* subshell (l = 0) has one orbital, while a *p* subshell (l = 1) has three (m_l = -1, 0 or 1).



The three orbitals of a p subshell.

m_s = spin quantum number

spin

In addition to orbital angular momentum, characterized by l, electrons possess quantized angular momentum corresponding to rotation about their own axis. The values of electron spin are designated by the spin quantum number, m_s, which can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

- de Broglie - wave nature of electrons
- Schroedinger - the wave equation
- Pauli exclusion
  - an orbital holds 2 electrons max
- Aufbau principle

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

- Hund's rule

$\lambda = \frac{2L}{n}$

$n = 1, 2, 3$ etc

$$Li\,(g) \xrightarrow{IE} Li^{+} + e^{-}$$

ionization energy increases

ionization energy decreases

FA decreases

$C(g) + e^{-} \longrightarrow C^{-}(g)$

electron affinity

atomic radius decreases

Periods	Groups IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**	104 Unq	105 Unp	106 Unh												

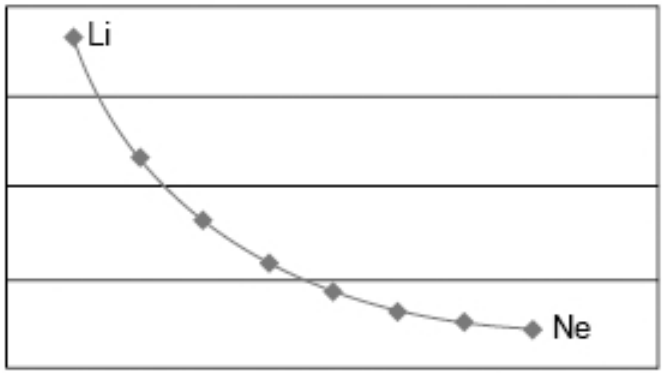
*Lanthanide series

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

**Actinide series

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

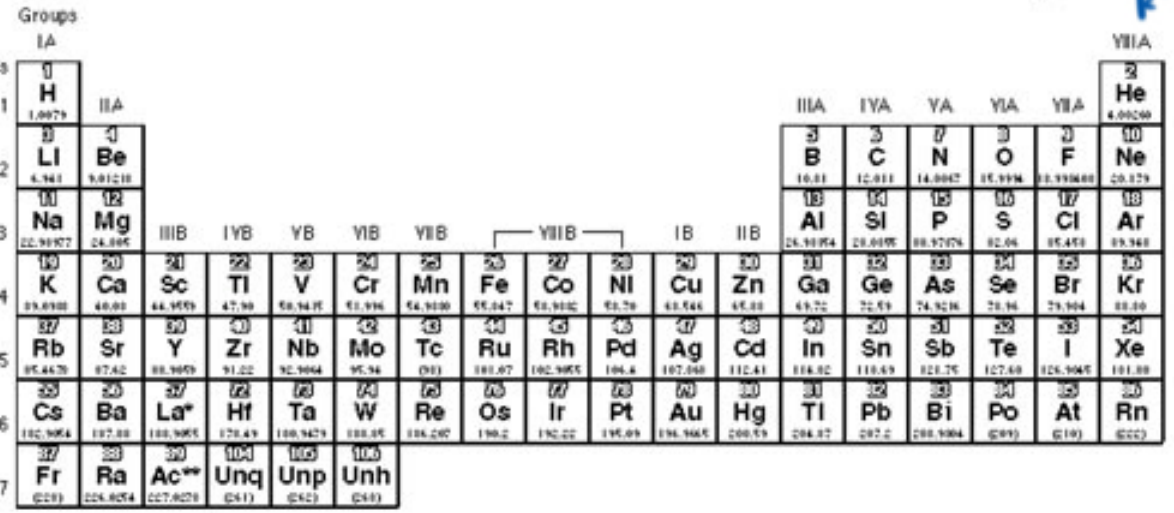
The graph below shows the variation across the 2nd period of the periodic table of this property



A. ionization energy
B. electron affinity
C. atomic radius
D. electronegativity

relative strength of attraction an atom has for electrons shared in chemical bonding

electronegativity increases



electroneg-ativity decreases

Relevance

δ− Is a bond nonpolar polar ionic?

H C H (δ+)

δ− H C H− (δ+) (δ−)

what kind of intermolecular force?

Physical Properties

Solubility

δ− O

H3C C CH3

Nu: Reactivity

Oxidation Reduction

ox # −4 H C H H ox # +1

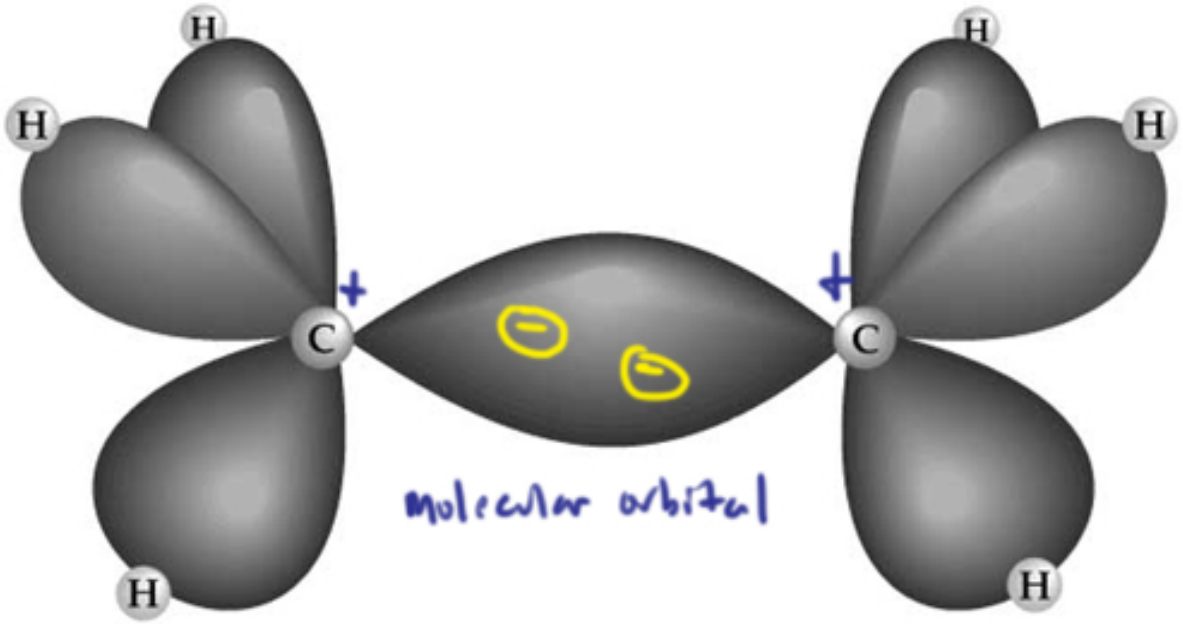
2 O=O (ox # 0) → O=C=O (ox # +4) + 2 H−O−H (ox # −2)

R− C(δ+) O(δ−) H

C - 2.5
H - 2.1
O - 3.5
N - 3.0
Cl - 3.0
Br - 2.8
F - 4.0
S - 2.6

Li, Na, Mg ~ 1.0

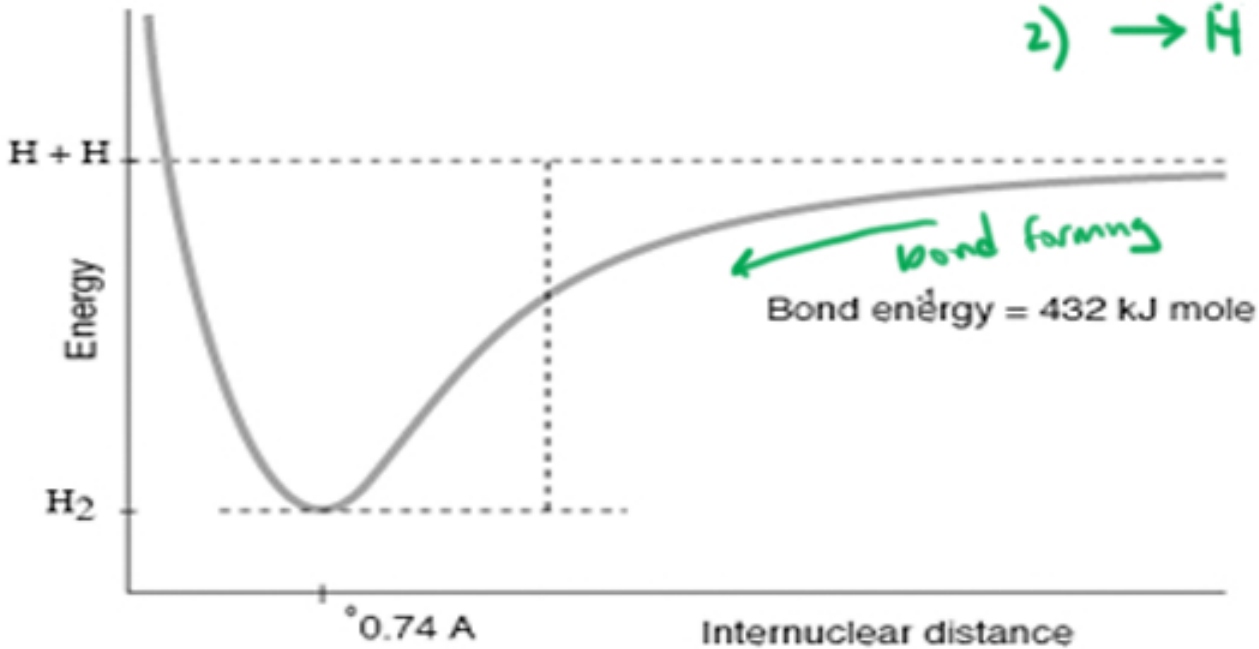
Covalent Bonding



molecular orbital

Ethane

$2H \longrightarrow H_2 + 432\ kJ$



bond length

$1\text{ Å} = 10^{-10}\ m \quad 10\text{ Å} = 1\ nm$

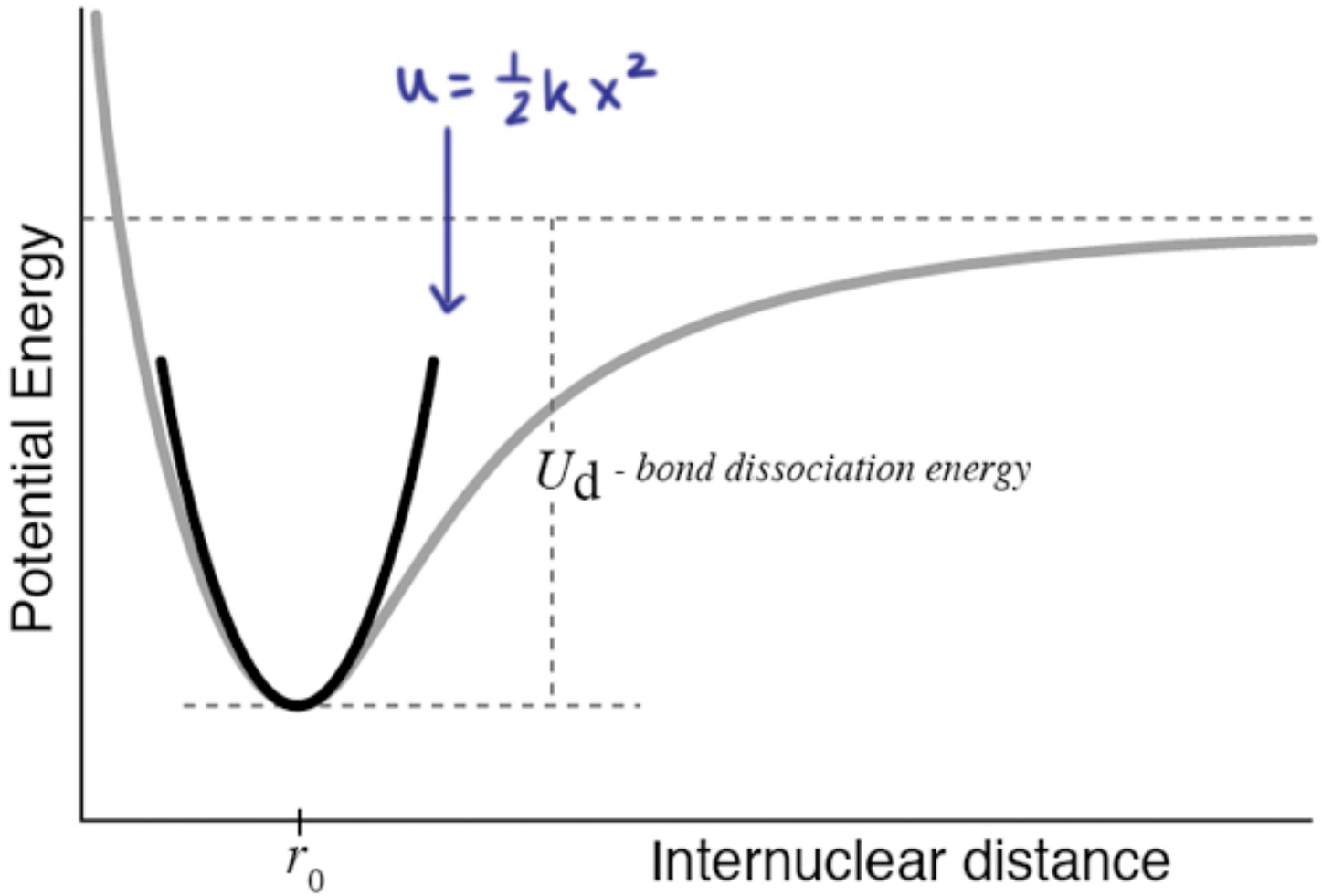
1) H H

2) → H ⊖ ⊖ H ←

3) H ⊖⊖ H

Molecular orbital Theory

H σ H


$u = \frac{1}{2} k x^2$
Potential Energy
U_d - bond dissociation energy
r_0
Internuclear distance

Covalent bonds vibrate

- partition for thermal energy
- IR spectroscopy

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

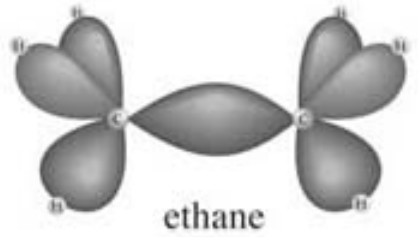
The stretching vibrations along the bond axis of a C–H bond in ethane absorb infrared radiation of lower frequency than the IR radiation absorbed by a C–H bond of ethylene. Which of the following statements can be deduced from this evidence?

a. The carbon-hydrogen bonds in ethylene are stronger than the carbon-hydrogen bonds in ethane

b. Ethane has free rotation about the C–C bond axis

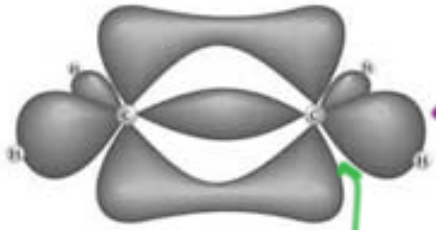
c. The C–H bonds are shorter in ethane.

d. The percent composition of ethane is greater for hydrogen.



ethane

C-H stretch ← 2990 cm^{-1}



ethylene

CH stretch ← 3010 cm^{-1}

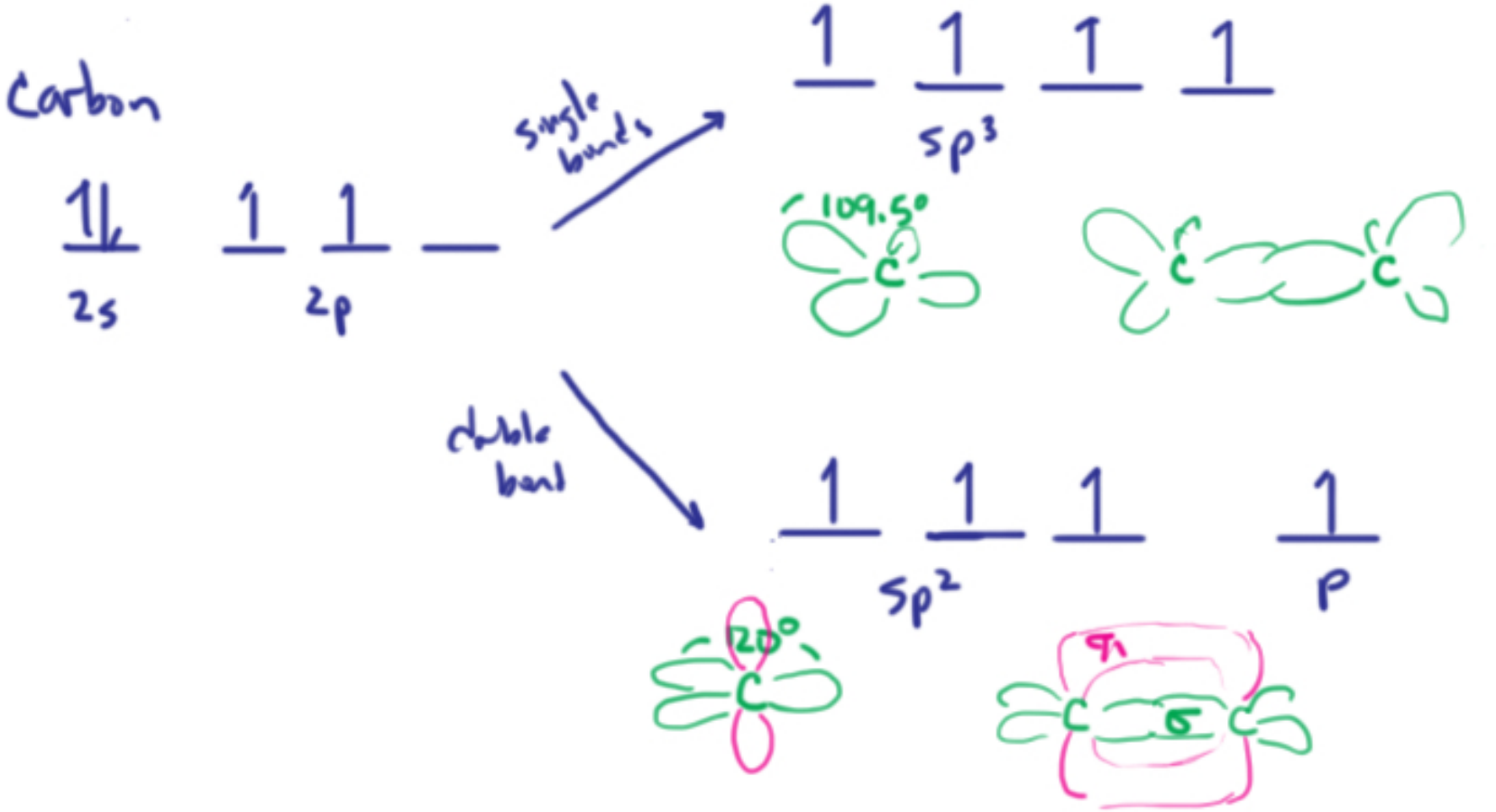
greater s character

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

spring constant

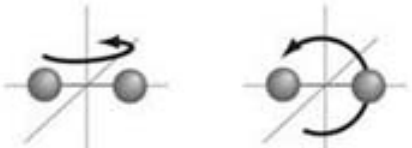
increasing k / bond strength

orbital hybridization

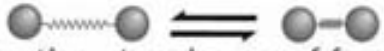


A monotomic gas molecule such as **He** possesses only kinetic energy deriving from its linear motion. A diatomic gas molecule, like Cl_2, in addition to translational motion, can also rotate and vibrate. What does this difference tell us?

translational motion - three degrees of freedom



rotational motion - two degrees of freedom



vibration - two degrees of freedom

a. Helium is a noble gas.

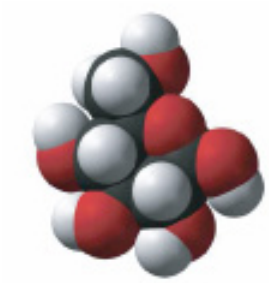
b. Chlorine has a higher molar heat capacity than helium.

c. At a given temperature, helium molecules have greater average translational kinetic energy than chlorine molecules.

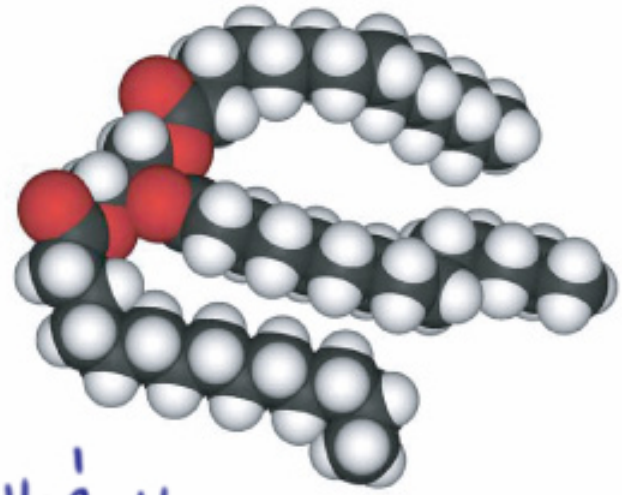
d. The chlorine molecules have greater average translational kinetic

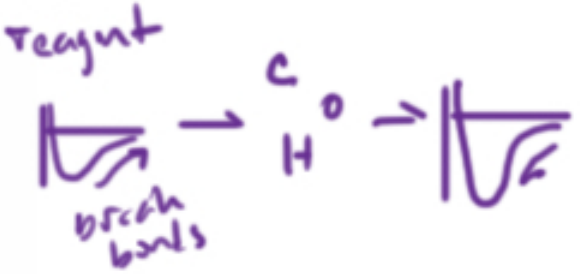
Heats of Combustion of Nutrient Molecules

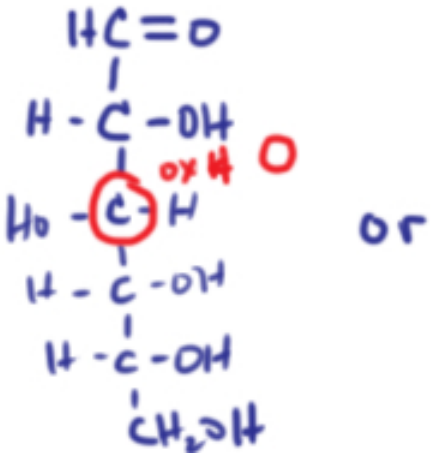
Glucose 466 kJ/mol carbon



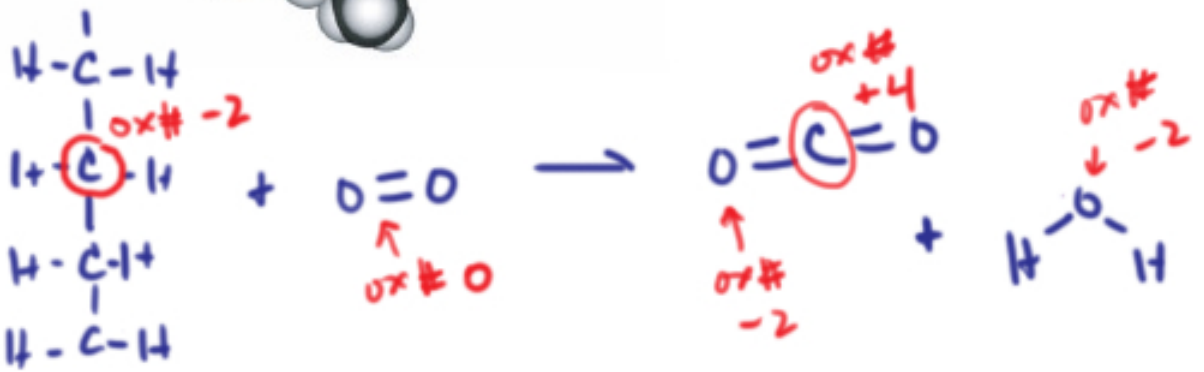
Triglyceride 626 kJ/mol carbon

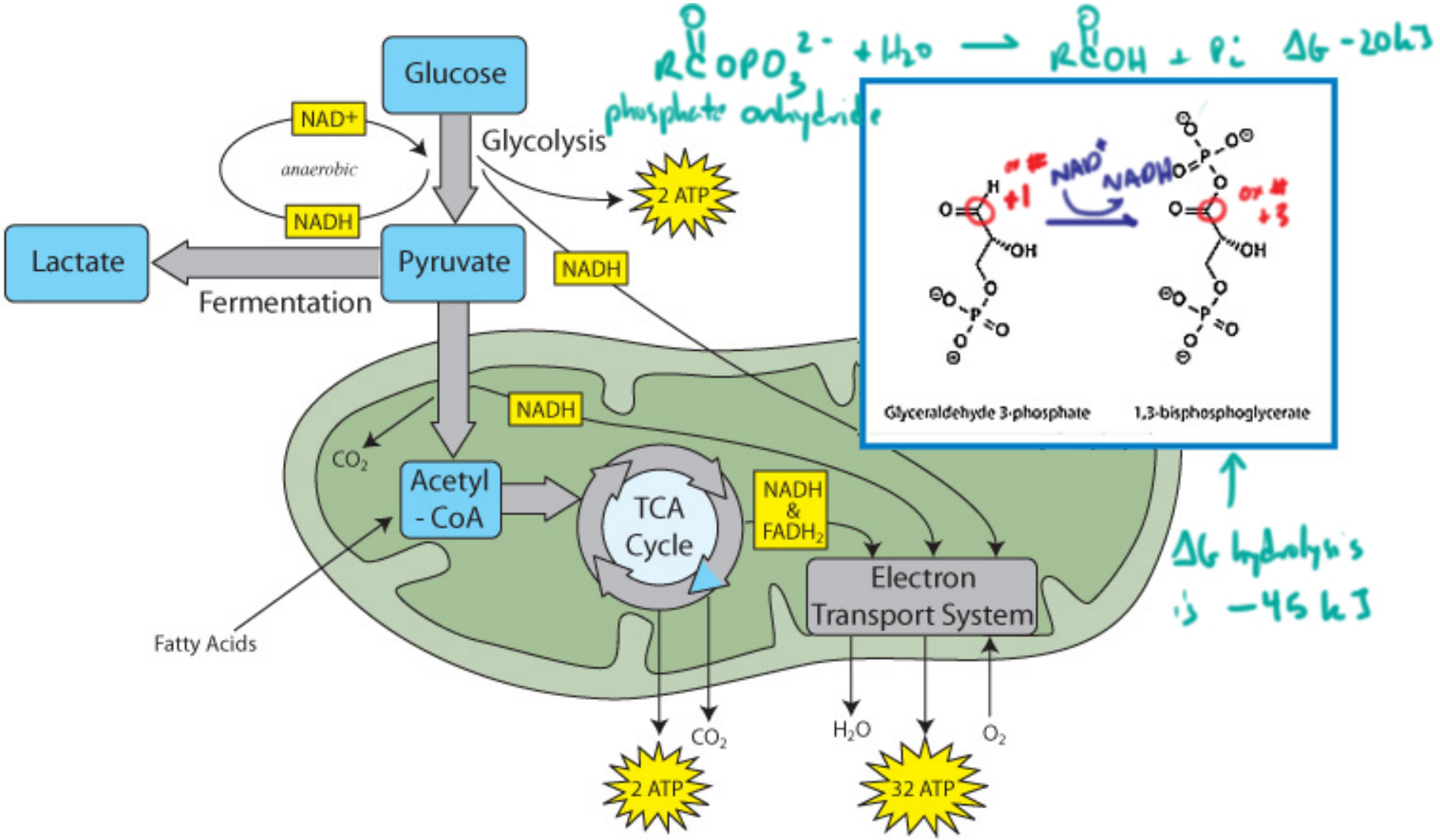


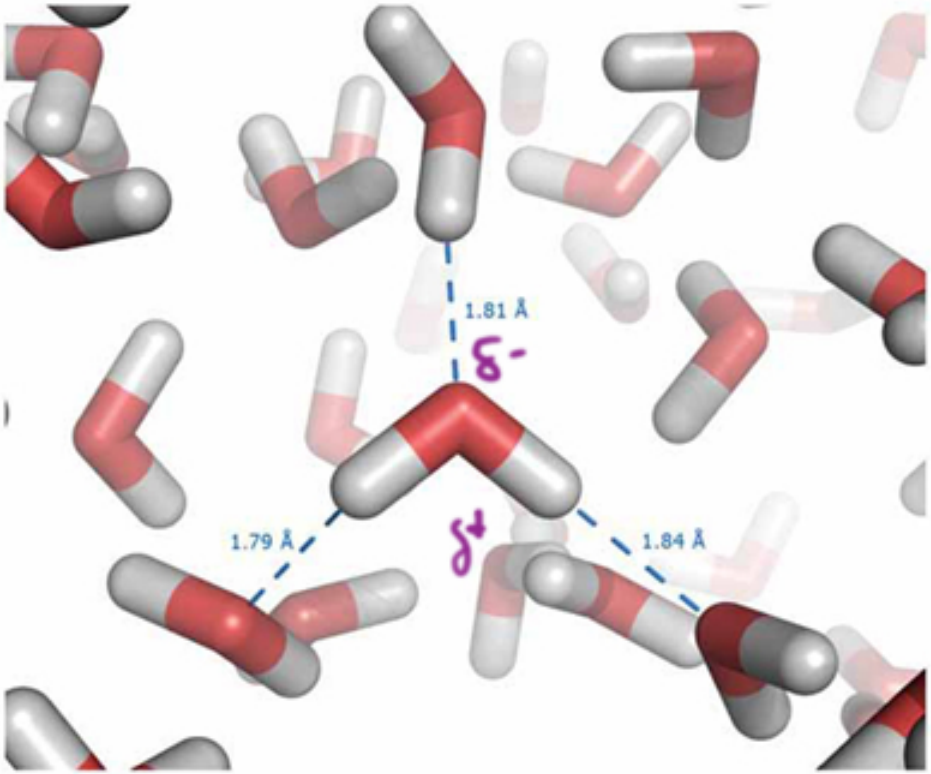


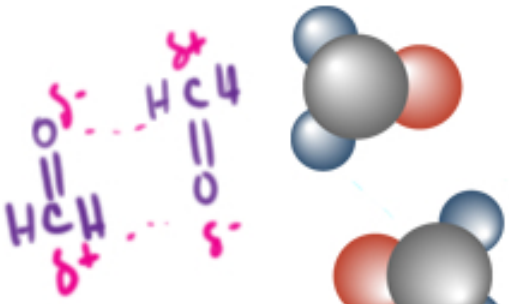


or




Glucose
NAD+
anaerobic
NADH
Glycolysis
2 ATP
Lactate
Fermentation
Pyruvate
NADH
NADH
CO2
Acetyl - CoA
TCA Cycle
NADH & FADH2
Electron Transport System
Fatty Acids
CO2
H2O
O2
2 ATP
32 ATP
NAD+
NADH
Glyceraldehyde 3-phosphate
1,3-bisphosphoglycerate


1.81 Å
δ-
1.79 Å
δ+
1.84 Å

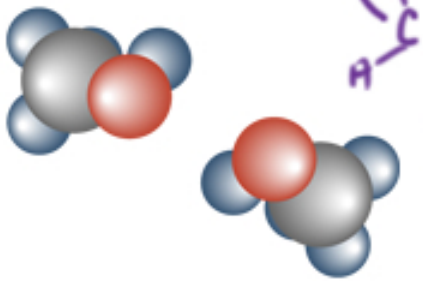


Dipole
Dipole

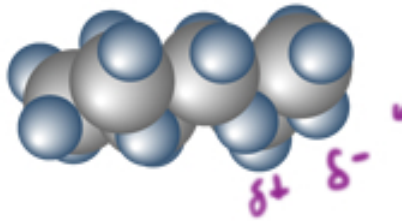
stronger

acetone

butane



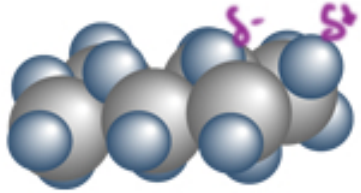
H bonding
strongest



temporary
random
dipole
induced

Van der Vaals
or
London dispersion

Weakest



Undissolved ⇌ Dissolved

Like Dissolves Like

⊕ ΔG

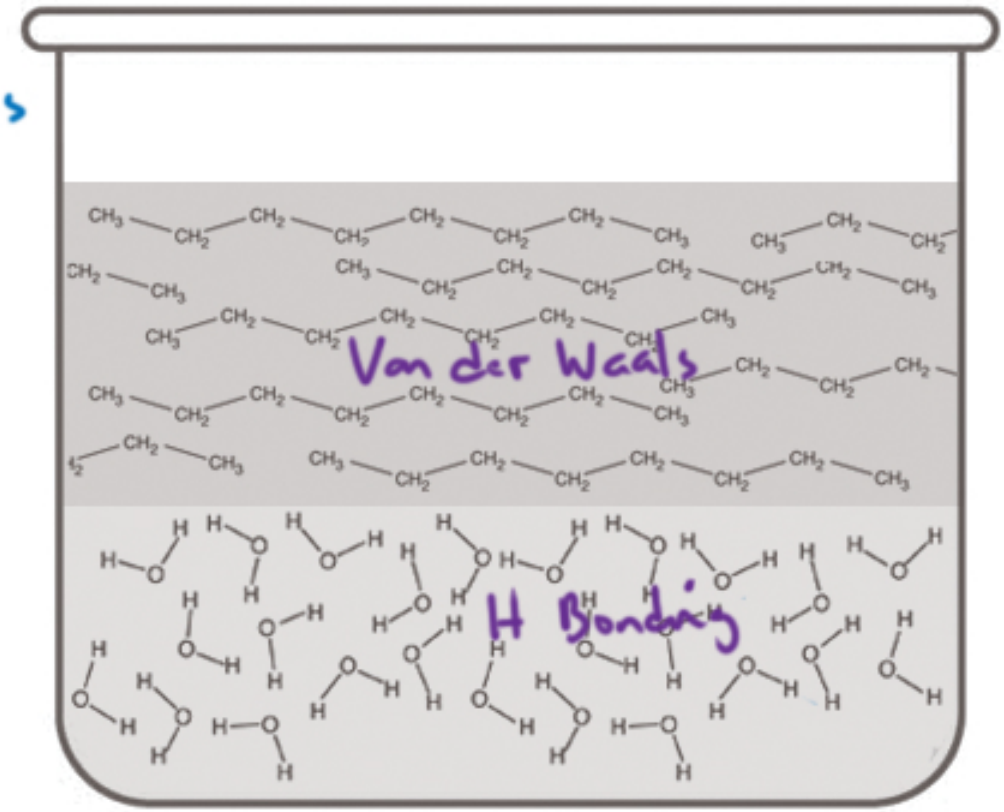
nonspontaneous

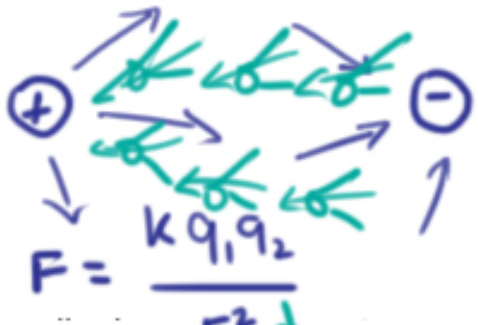
may be

⊕ ΔH

because

⊕ ΔU

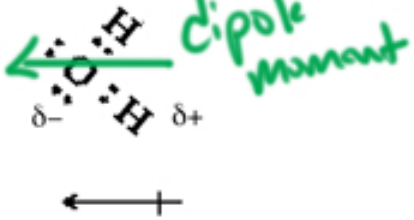




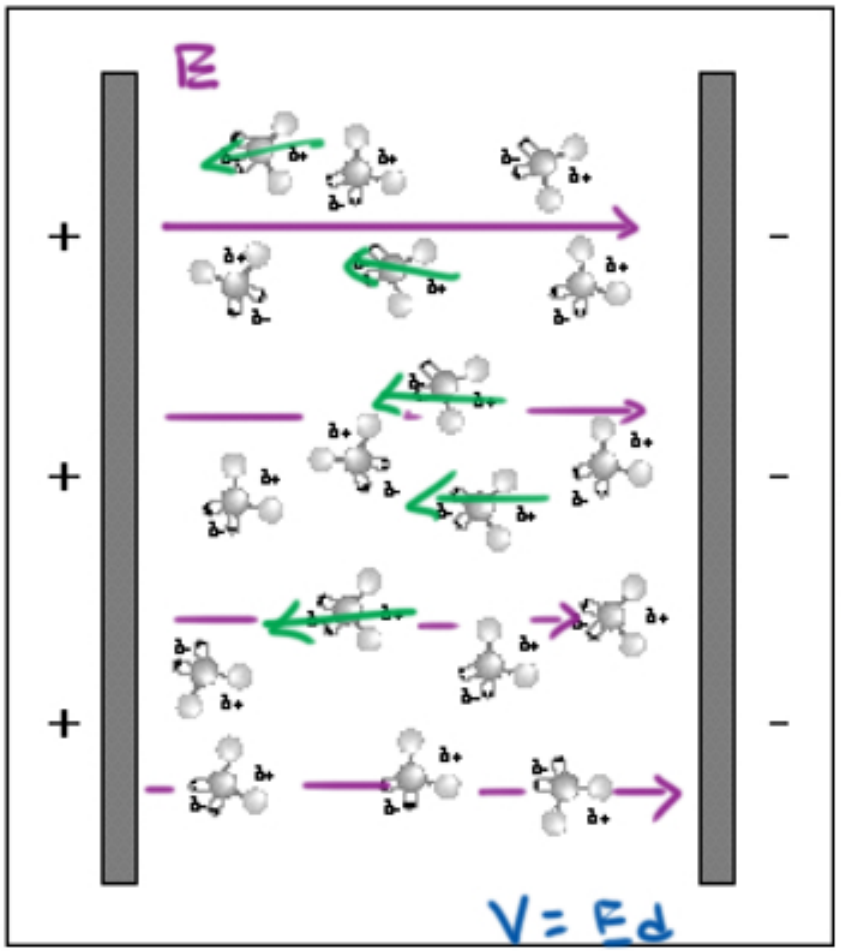
$$F = \frac{k q_1 q_2}{r^2 d_{H_2O}}$$

dielectric constant = 80

dipole moment = qd



dipole moment



A dielectric substance weakens an external field.

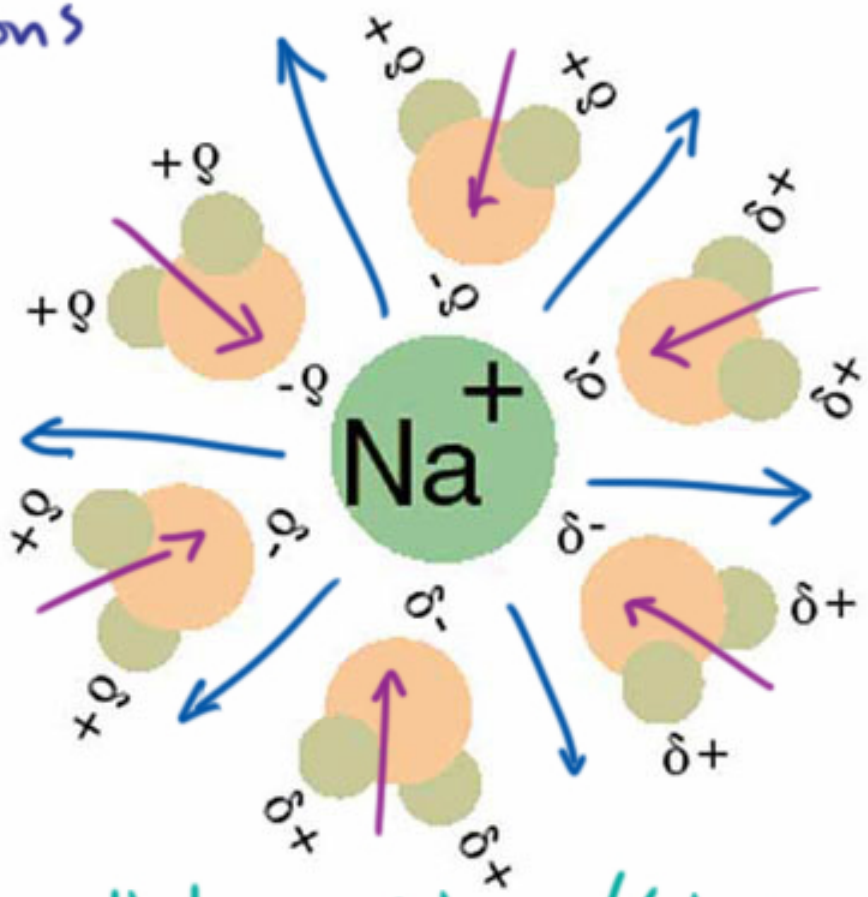
Increases the capacitance

$$C = \frac{Q}{V}$$

Water loves ions

- enthalpy of hydration

Ions love water



Hydration Sphere - (Solvation Shell)

Cl⁻

The First Law of Thermodynamics

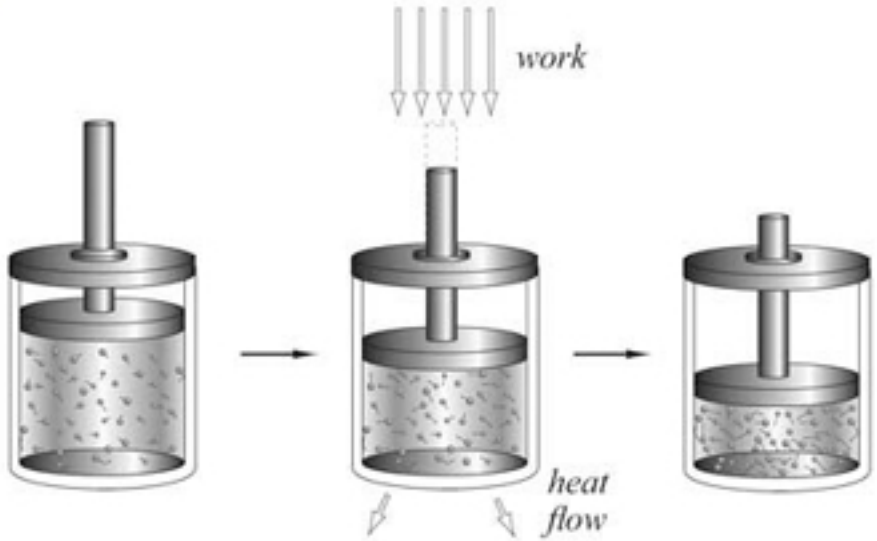
surroundings

system

$$\Delta U = Q - W \quad \text{(pressure-volume work)}$$
$$= Q - P^{*}\Delta V$$

ΔU = internal energy change
Q = heat flow
W = macroscopic work

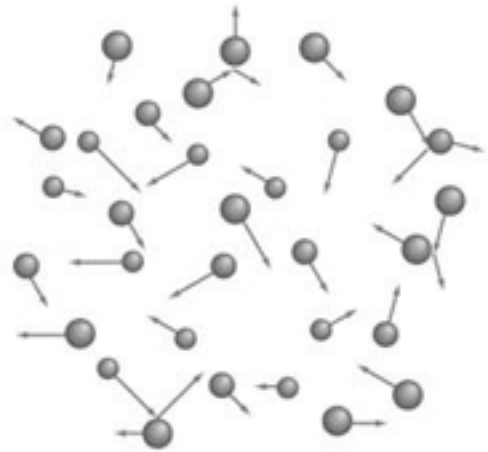
P^{*} = constant pressure
ΔV = volume change



Internal energy change results from the combination of heat flow and work between the system and its surroundings. In this example, the internal energy of our ideal gas system became greater (the particles are moving faster in the final state) because more energy entered the system through work than departed the system as heat flow.

The Internal Energy of an Ideal Gas Depends on Temperature

- internal energy is only the kinetic energy of the particles (translational)
  - thermal energy



- no inter-at.-a. distance forces
- point mass

$$\frac{U}{N} = \frac{3}{2}kT$$

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$$

$$U = \frac{3}{2}NkT$$

U = internal energy
N = number of molecules
k = Boltzmann's constant
= R / Avogadro's number
T = temperature

$$U = \frac{3}{2}nRT$$

n = moles of gas
R = ideal gas constant

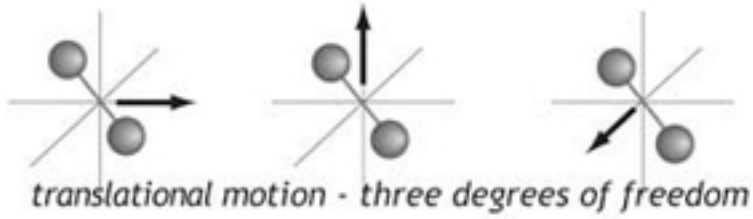
Molar Heat Capacities ($J\ mol^{-1}\ K^{-1}$)

He	20.5	N_2	29.5	H_2O	33.5
Ar	20.5	F_2	31.4	CO_2	37.2

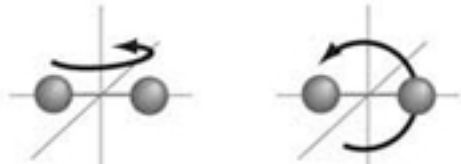
$\frac{J}{mol\ K}$

$$KE_{total} = KE_{trans} + KE_{rot} + KE_{vib}$$

$$U = KE_{total} + PE_{total}$$



translational motion - three degrees of freedom

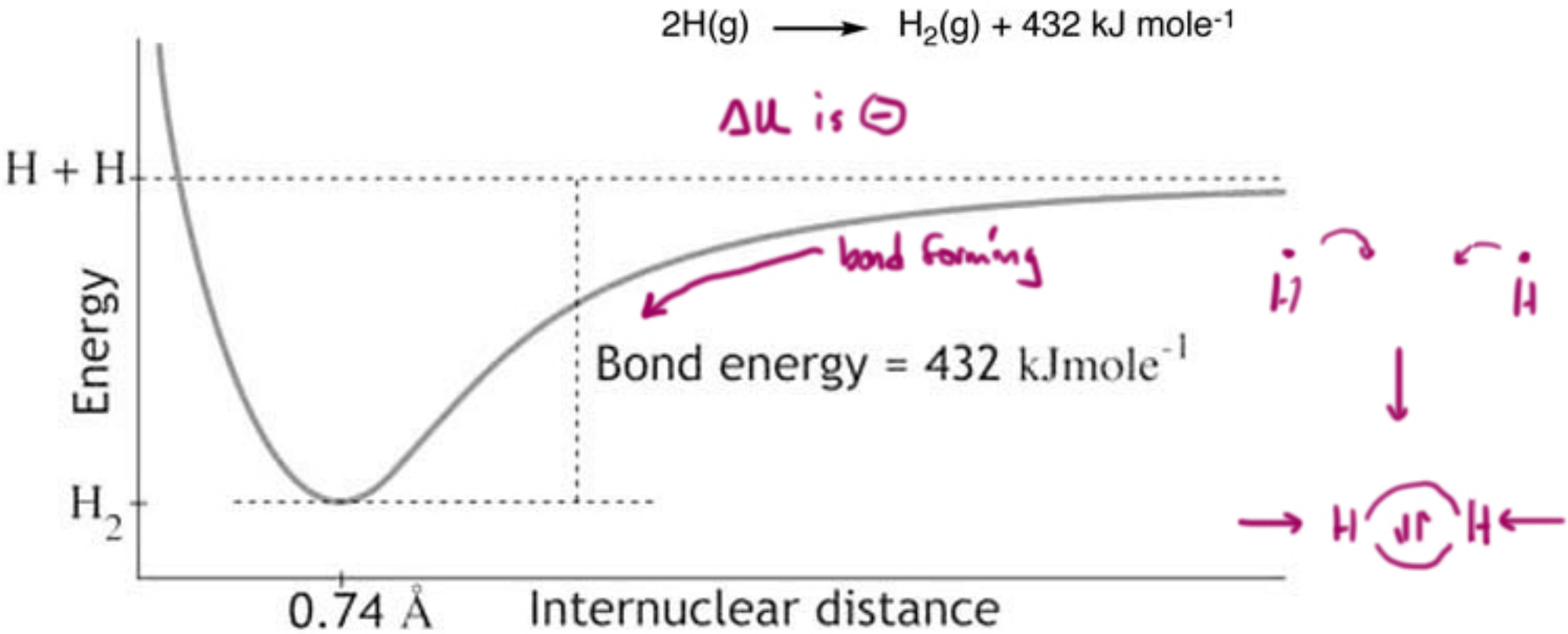


rotational motion - two degrees of freedom

vibration - two degrees of freedom

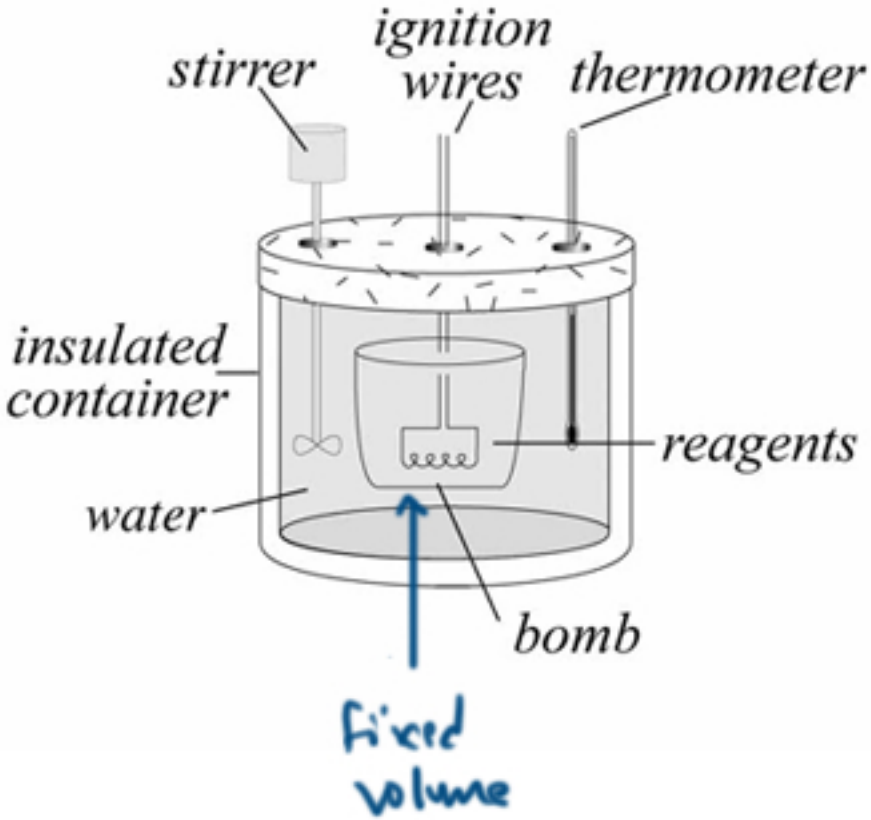
- Real substances may also have vibrational and rotational kinetic energy.

  - even just the thermal energy is more complicated



With real substances, internal energy change can occur along lines of electrostatic potential energy.

$\Delta U = Q - W$



$\Delta U = Q$ (constant volume, $W = 0$)

if $\Delta V = 0$, then $W = 0$

Internal energy change will equal the heat flow

The enthalpy. a state function

$H = U + PV$ ← what about it as a kind of thermal potential

A state function whose change equals heat flow (as long as P is constant)

$\Delta U = Q - W$ (benchtop) 1st law

$H = U + PV$ ← the enthalpy

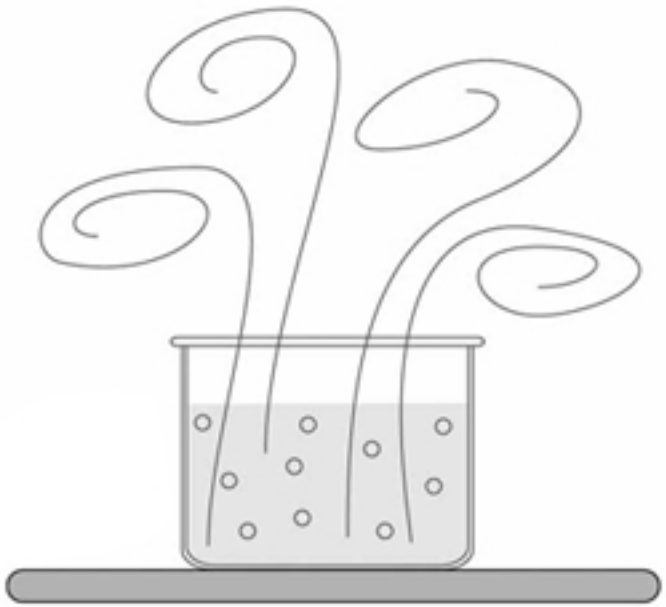
$\Delta H = \Delta U + \Delta(PV)$

if P is constant

$\Delta H = \Delta U + P\Delta V$ ← $P\Delta V$ = work

substitute 1st law

$\Delta H = (Q - W) + P\Delta V$



$\Delta H = Q$ (constant pressure)

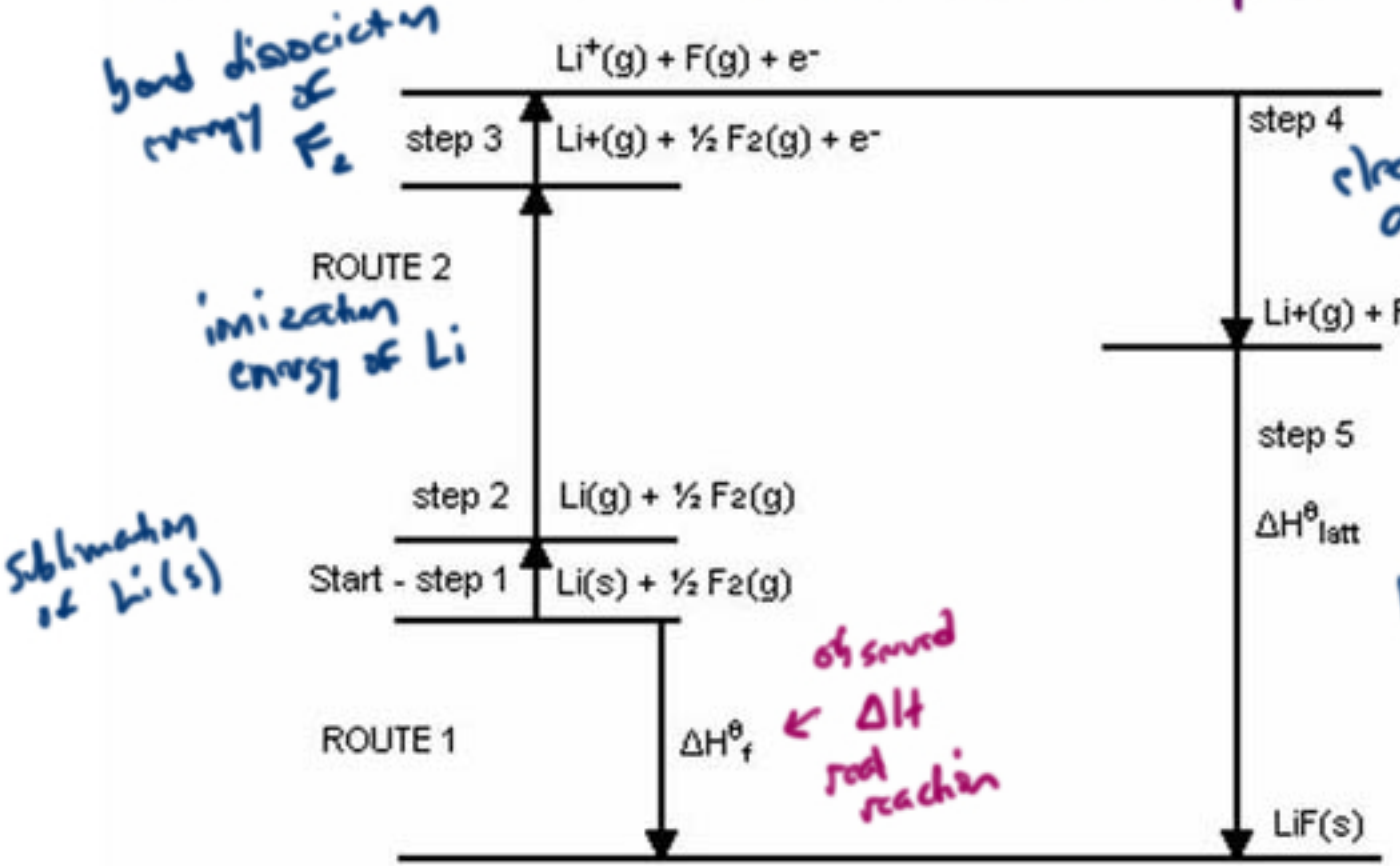
Now we can treat heat flow as path independent.

Hess' Law of Heat Summation

$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$

Born-Haber Cycle

Formation of an ionic compound.



Demonstration of Hess' Law

$H = U + PV$

A positive value of ΔH for a reaction at STP means that:

A. The internal energy of the substance has increased. (only if ΔV is 0)

B. Heat is given off to the environment during the reaction.

C. Heat is absorbed from the environment during the reaction.

D. The reaction is exothermic.

$H = U + PV$

$H = U + PV$

$\ominus \quad \ominus$

Which of the following statements is true about the following exothermic reaction, when carried out at constant temperature and pressure?

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

3 moles 2 moles

A. The magnitude of the change in internal energy over the reaction is greater than the magnitude of the enthalpy change.

B. The magnitude of the change in internal energy over the reaction is less than the magnitude of the enthalpy change.

C. The magnitude of the change in internal energy over reaction is equal to the magnitude of the enthalpy change.

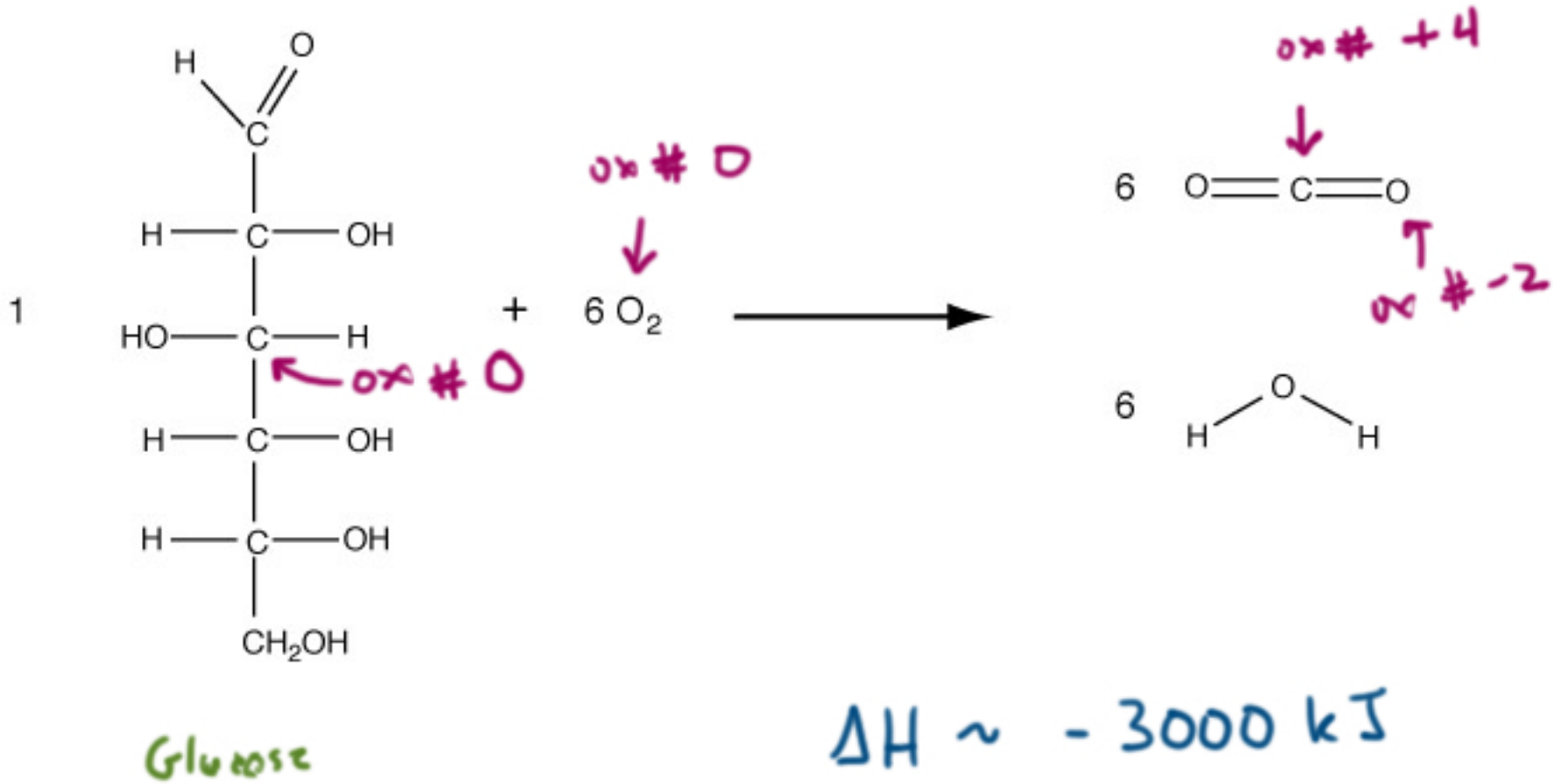
D. Impossible to determine any of the above from given information.

Is ΔH equal here to ΔU?

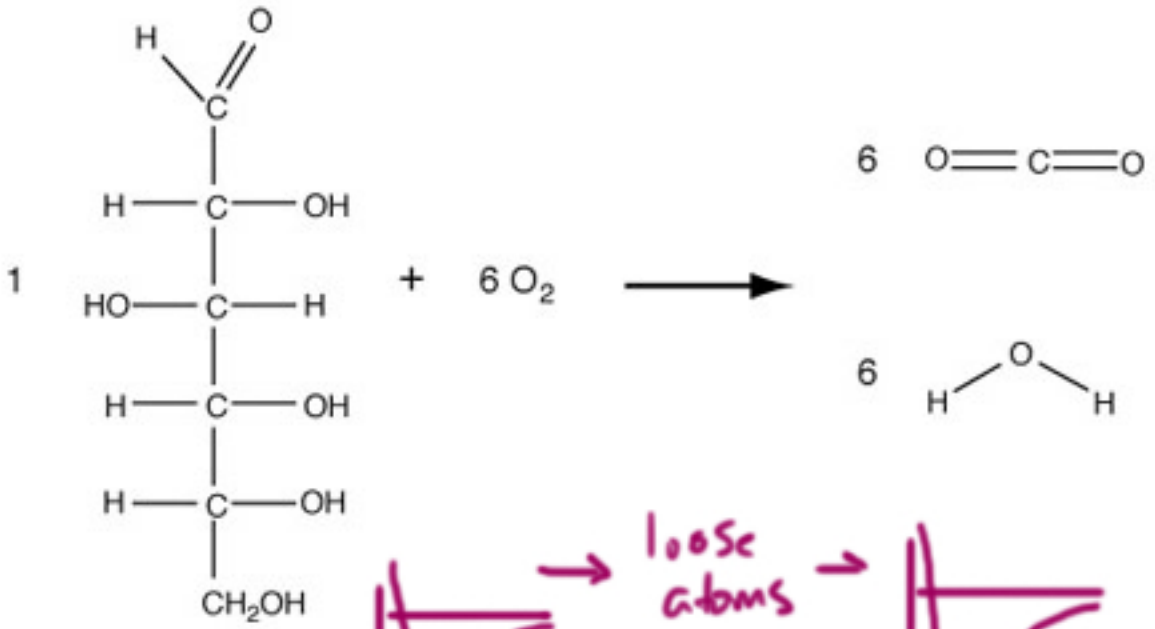
$\Delta U = Q - W$

Is the volume changing?

Combustion of Glucose



$\Delta H \sim -3000$ kJ



loose atoms

H C O

$+\Delta H$

$-\Delta H$

Bond	Bond Energy KJ/mole
H–C	411
C–C	346
H–O	459
C–O	359
C=O	799
O=O	494

Sum it all up

$\Delta H \sim -3000$ kJ

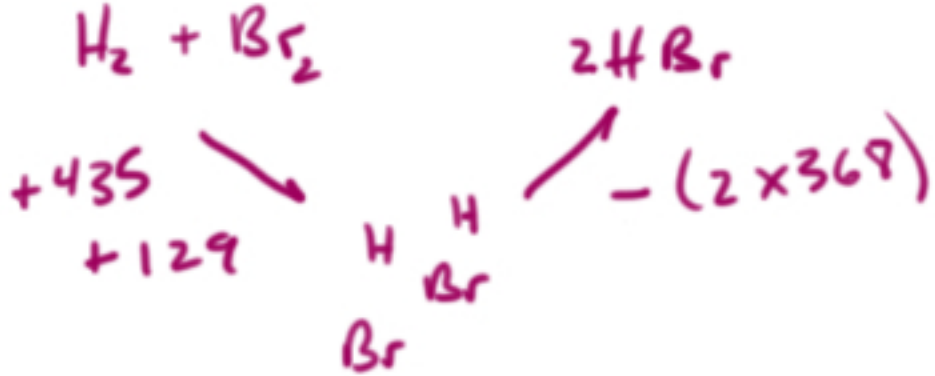
Given these bond energies:

H–H	(435 kJ/mol)
Br–Br	(192 kJ/mol)
H–Br	(368 kJ/mol)

Which is following would be the best estimate of the enthalpy change of the following reaction?

$$H_2\,(g) + Br_2\,(g) \longrightarrow 2HBr\,(g)$$

A. -26 kJ
B. -109 kJ
C. 259 kJ
D. 109 kJ



$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ mol}^{-1}$$

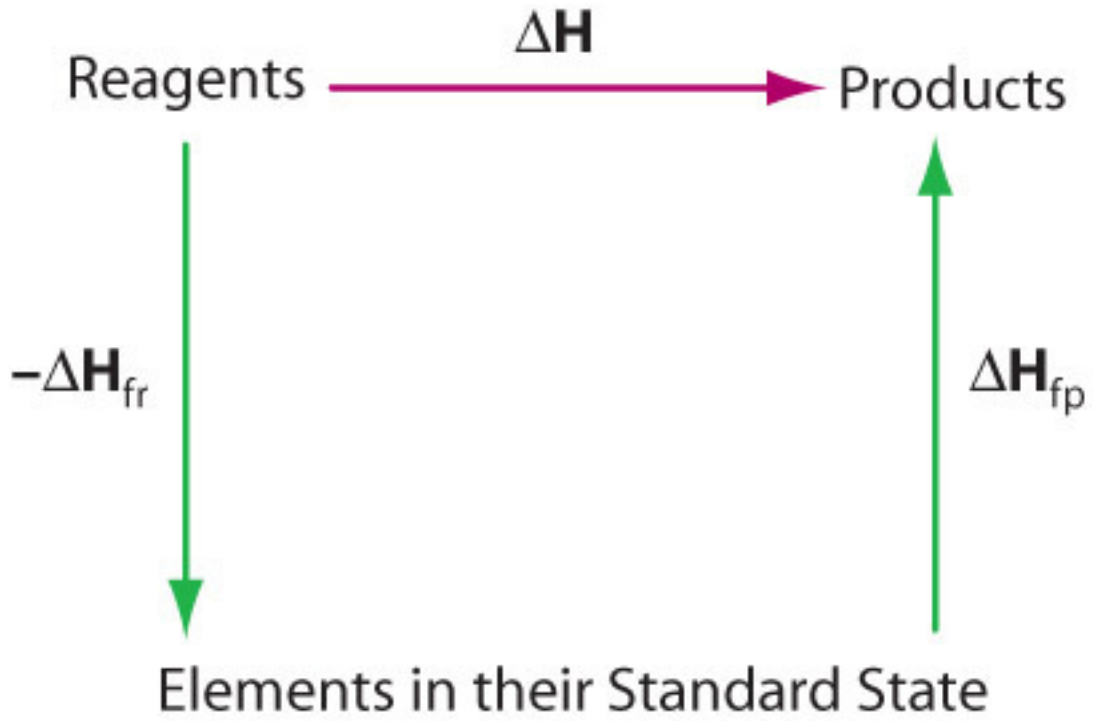
$$6\,C(\text{graphite}) + 6\,H_2(g) + 3\,O_2(g) \longrightarrow C_6H_{12}O_6(l) \qquad \Delta H^\circ = -1250 \text{ kJ mol}^{-1}$$

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$\Delta H = \Delta H^\circ_{f\,\text{products}} - \Delta H^\circ_{f\,\text{reagents}}$$

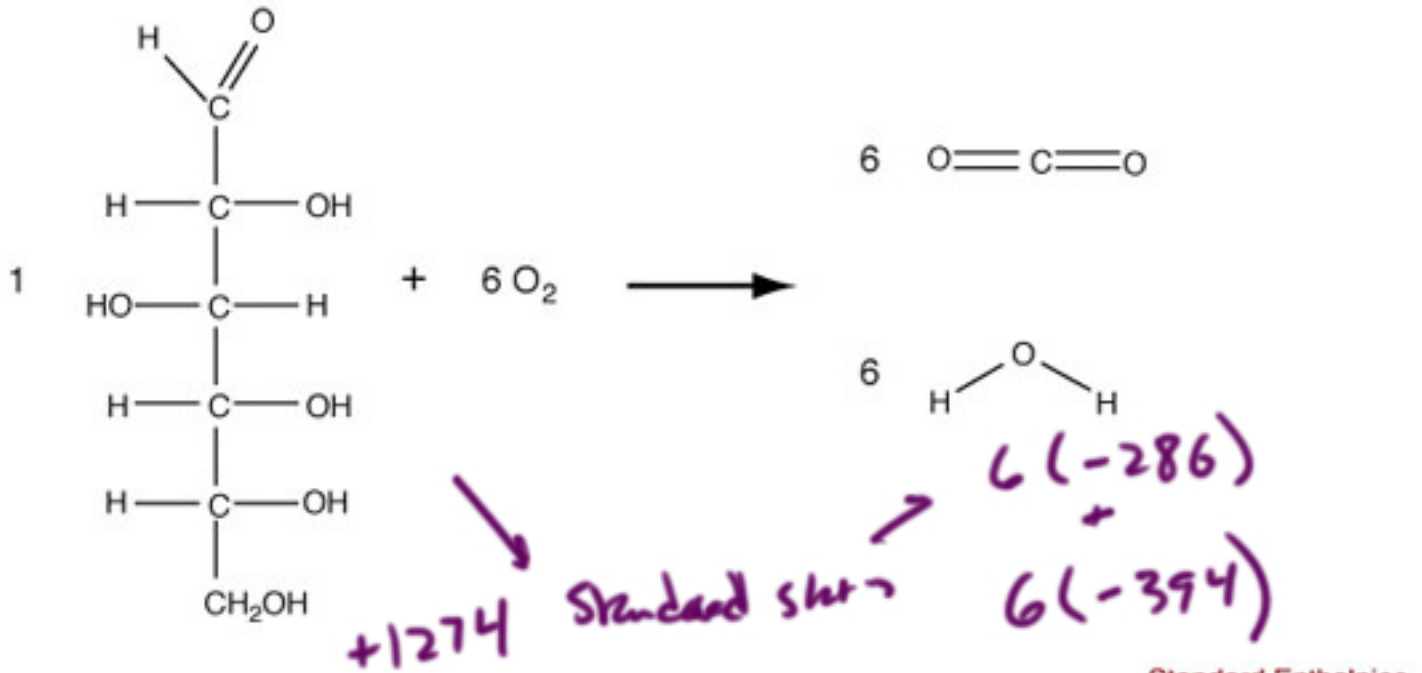
Standard enthalpies of formation

Chemical Compound	Phase (matter)	Chemical formula	ΔH_f^0 in kJ/mol
Ammonia (Ammonium Hydroxide)	aq	NH_3 (NH_4OH)	-80.8
Ammonia	g	NH_3	-46.1
Copper (II) sulfate	aq	$CuSO_4$	-769.98
Sodium carbonate	s	Na_2CO_3	-1131
Sodium chloride (table salt)	s	NaCl	-411.12
Sodium hydroxide	aq	NaOH	-469.6
Sodium hydroxide	s	NaOH	-426.7
Sodium nitrate	s	$NaNO_3$	-424.8
Sulfur dioxide	g	SO_2	-297
Sulfuric acid	l	H_2SO_4	-814
Silica	s	SiO_2	-911


ΔH
Reagents
Products
−ΔH_fr
ΔH_fp
Elements in their Standard State

$$\Delta H = H_{products} - H_{reactants}$$

$$\Delta H = \Sigma \Delta H_f^{\circ}{}_{products} - \Sigma \Delta H_f^{\circ}{}_{reactants}$$



Standard Enthalpies
KJ/mole

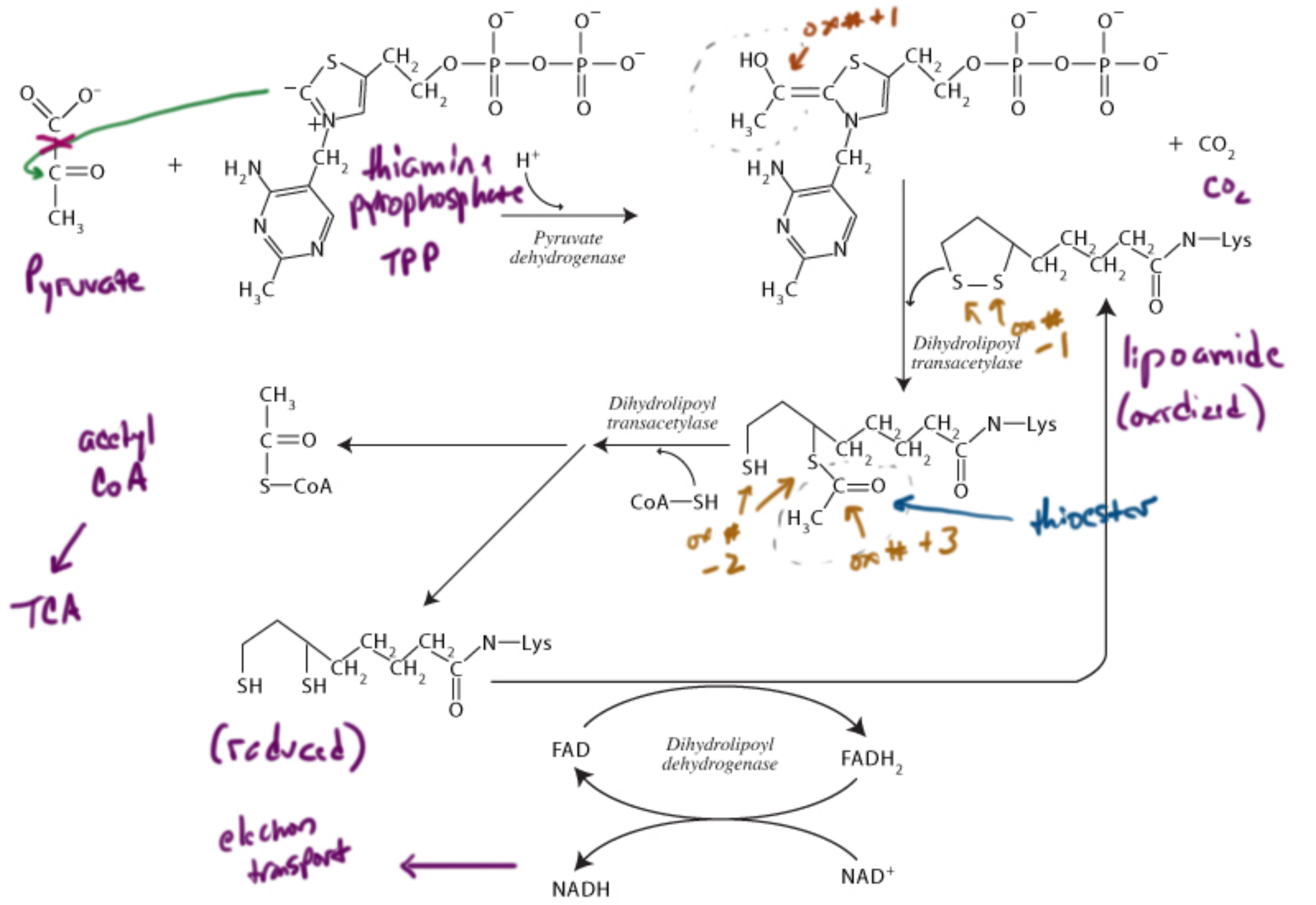
Glucose	-1274
O_2	0
CO_2	-286
H_2O	-394

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

coupled with

$$36\ ADP + 36\ P_i \longrightarrow 36\ ATP$$

- glycolysis
- pyruvate dihydrogenase complex
- TCA
- electron transport system

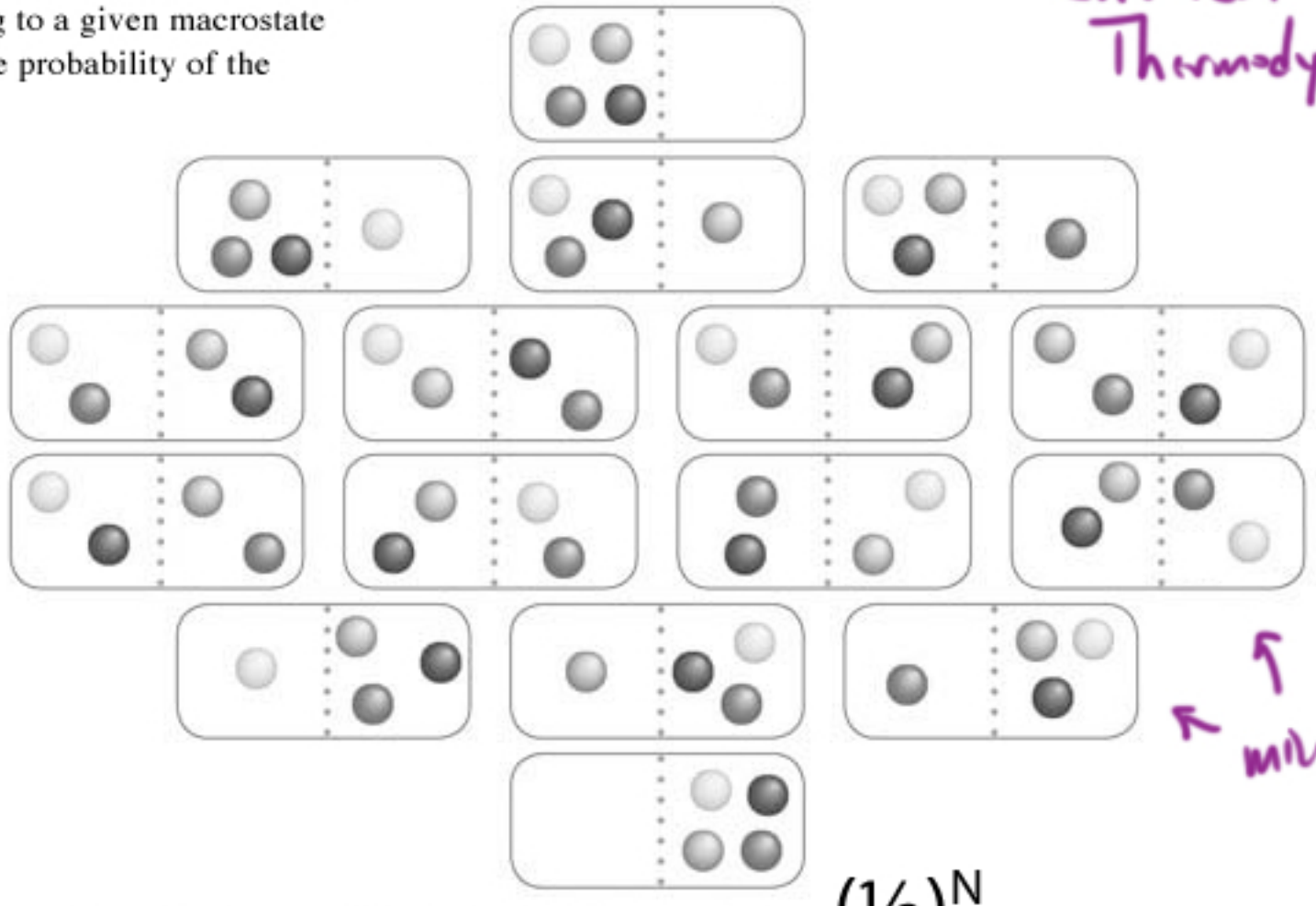

Pyruvate
thiamin pyrophosphate
TPP
Pyruvate dehydrogenase
+ CO2
Dihydrolipoyl transacetylase
lipoamide (oxidized)
Dihydrolipoyl transacetylase
acetyl CoA
TCA
CoA—SH
thioester
(reduced)
FAD
Dihydrolipoyl dehydrogenase
FADH2
NADH
NAD+
electron transport

The entropy of the world only increases.

It never decreases.

The greater the number of microstates corresponding to a given macrostate the greater the probability of the macrostate.

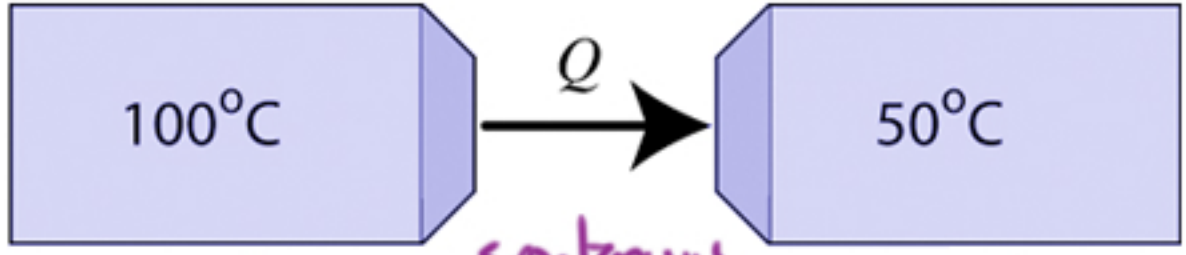
Chemical Thermodynamics



microstates

probability of all particles being in half the container $(\frac{1}{2})^N$

(simplified)



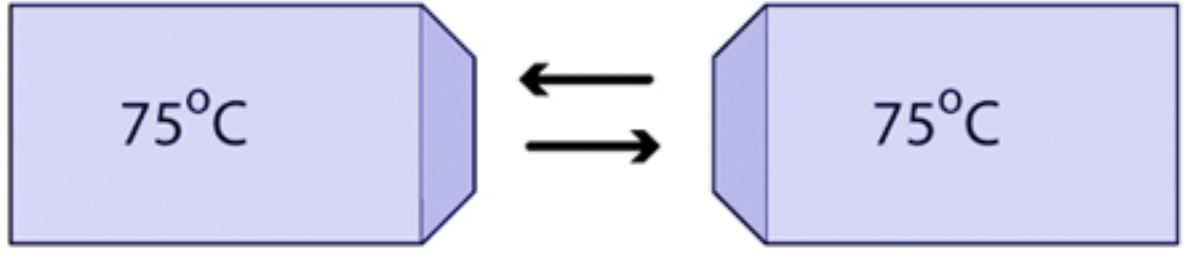
spontaneous

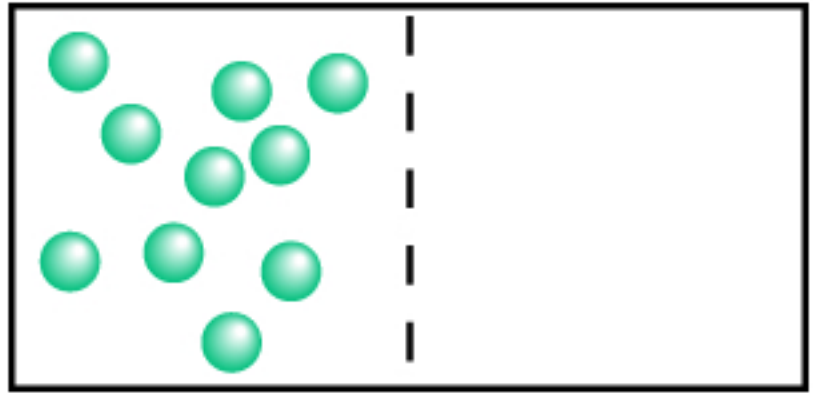
$\Delta S = \frac{Q}{T}$

$\Delta S_H = \frac{Q}{T_H}$

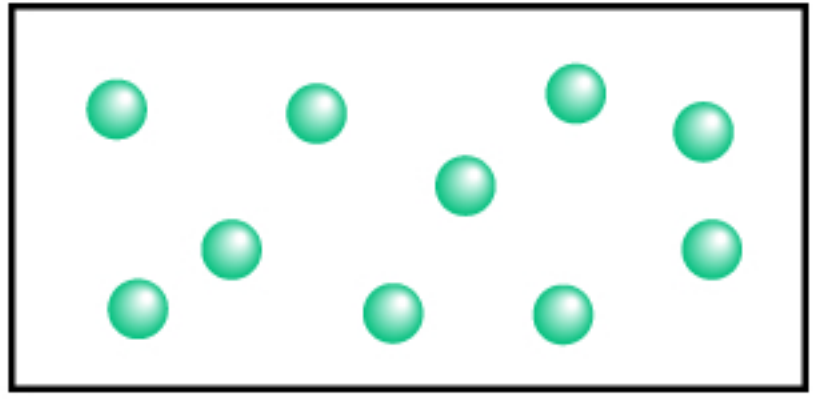
$\Delta S_C = \frac{Q}{T_C}$

$\Delta S_{universe} \oplus$

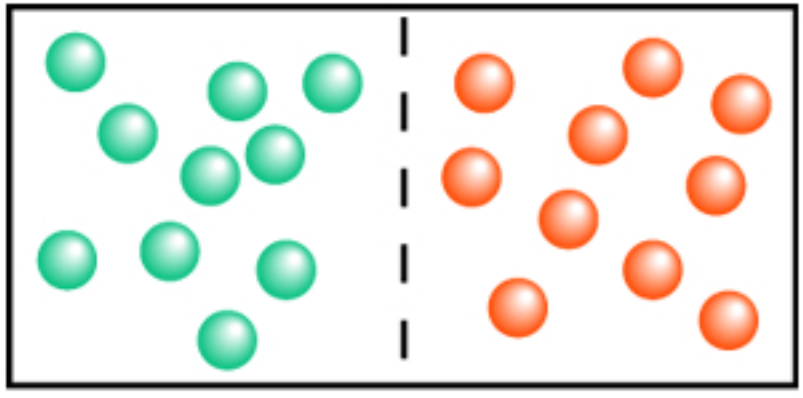




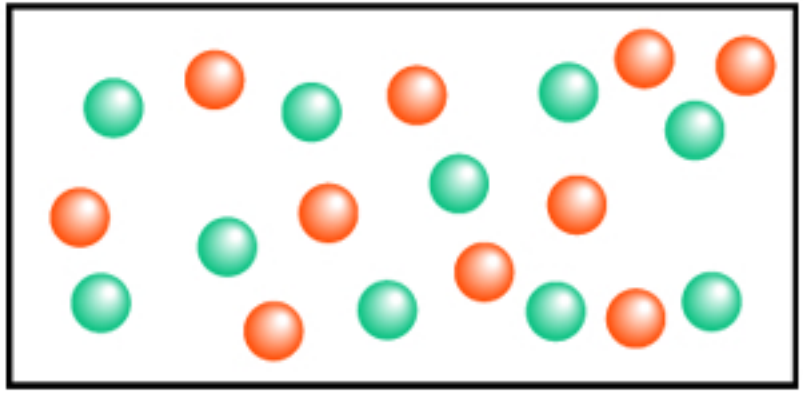
ΔS_{system} is +



$\Delta S_{universe}$ is also +

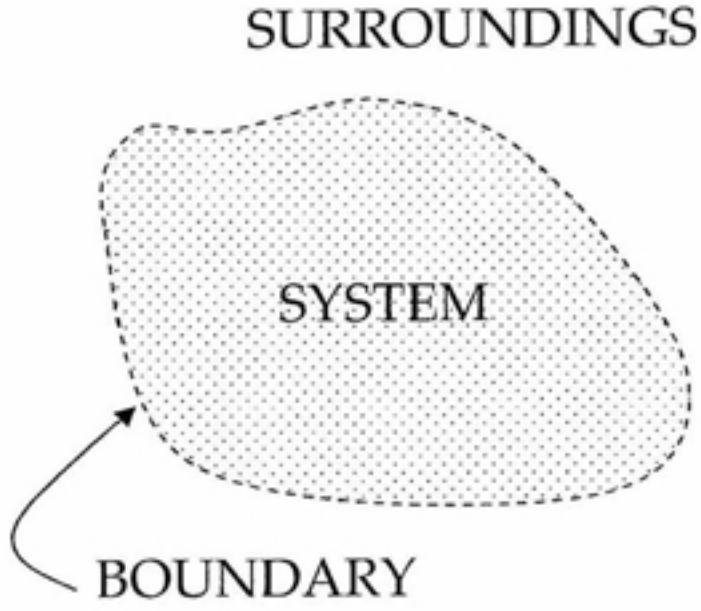


entropy of mixture



ΔS_{syst} ⊕

$$\Delta S_{\text{world}} = \Delta S_{\text{system}} + \Delta S_{\text{environment}}$$



$$\Delta S_{\text{environment}} = \frac{Q_{\text{environment}}}{T}$$

$\Delta S_{\text{surroundings}}$ is because of heat flow

Universe = system + surroundings

$$G = H - TS$$

← entropy of the system

A state function that when it changes means the entropy of the universe changed.

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

$$\frac{-\Delta G}{T} = \frac{-\Delta H}{T} + \Delta S$$

↗ $\Delta S_{universe}$

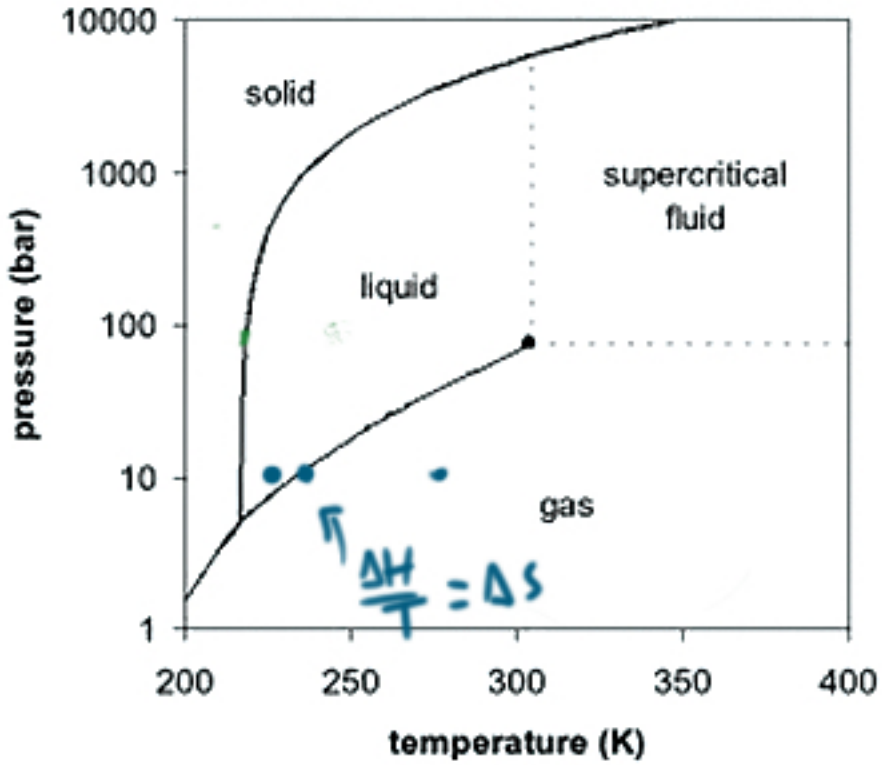
↑ $\Delta S_{surroundings}$

↖ ΔS_{system}

when $\Delta G = 0$

$$\frac{\Delta H}{T} = \Delta S_{system}$$

1



$\frac{\Delta H}{T} = \Delta S$

10 bar 225 K

gas → liquid

$G_{gas} > G_{liquid}$

10 bar 275 K

liquid → gas

$G_{liquid} > G_{gas}$

$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S_{gas}$

↑ favors liquid

↑ favors gas

! $Q = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

standard free energy change

ΔG° describes $[A] = [B]$ 1M

$3\ H_2\ (g) + N_2\ (g) \longrightarrow 2\ NH_3\ (g) \qquad \Delta G^\circ = -16.4\ kJ \text{ at } 298K$

with all $[NH_3]$ and no $[H_2][N]$

$[A] \rightleftharpoons [B]$

$Q = \frac{[B]}{[A]}$

$\Delta G = \Delta G^\circ + RT \ln Q$ $\quad \Delta G = \Delta G^\circ + 2.3RT \log Q$

$Q \to K$ as $\Delta G \to 0$

$\Delta G^\circ = -RT \ln K_{eq}$ $\quad \Delta G^\circ = -2.3RT \log K$

$K_{eq} = e^{\left(\frac{-\Delta G^\circ}{RT}\right)}$

$K = e^{-\Delta G^\circ / RT}$

If ΔG° is ⊖ K is a big #

If ΔG° is ⊕ K is a fraction

Which of the following statements about the relationship between ΔG^0, the standard free energy change, and K, the thermodynamic equilibrium constant, is untrue?

A. If ΔG_0 is large and positive, K is very small.
B. If ΔG_0 is large and negative, K is very large.
C. If ΔG_0 is zero, K = 1.
D. All of the above are true.

Which of the following is the proper expression of K_c for the following reaction?

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_20(g)$$

A. $\dfrac{[NH_3]\,[O_2]}{[NO]\,[H_2O]}$

B. $\dfrac{4[NO]\,6[H_2O]}{4[NH_3]\,5[O_2]}$

C. $\dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^5}$

D. $\dfrac{[NH_3]^4\,[O_2]^5}{[NO]^4\,[H_2O]^6}$

The equilibrium constant under standard conditions for the reaction of SO_2 with O_2 to form SO_3, $K_c = 1.5 \times 10^{-1}$

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

If 0.01 mol of each of the three gases are present along with argon in a 1 liter container at STP, which of the following is occuring?

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$= \frac{(.01)^2}{(.01)^2(.01)}$$

$Q = 100$

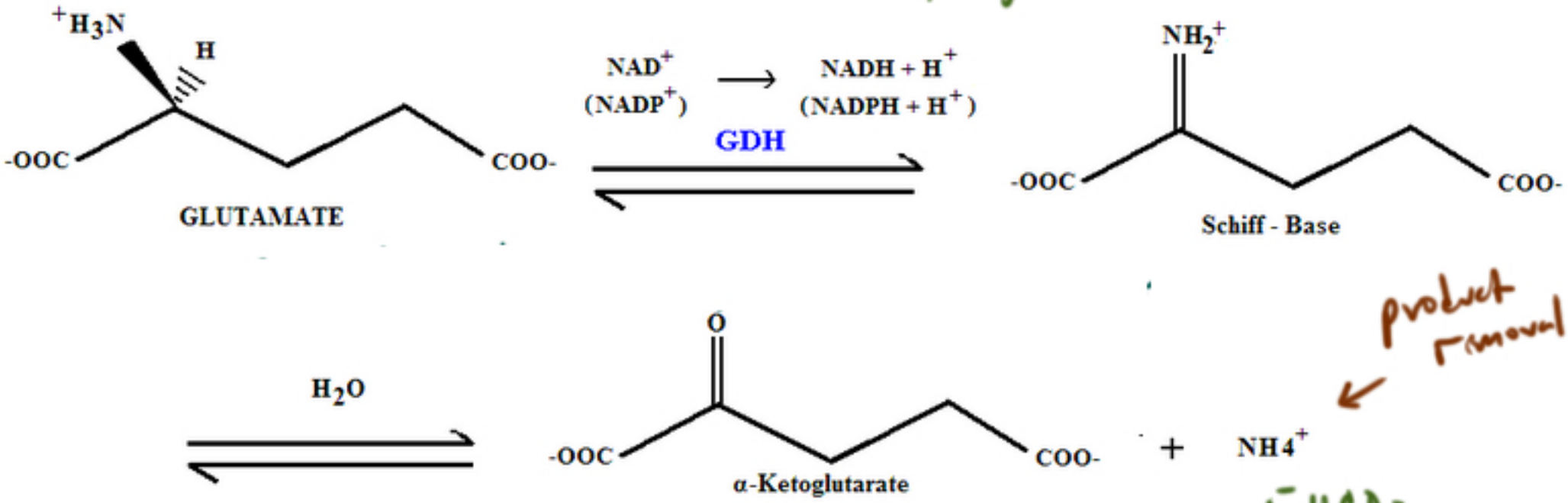
A. The forward reaction occurs at a higher rate than the reverse reaction.

B. The reverse reaction occurs at a higher rate than the forward reaction.

C. The reaction is at equilibrium.

D. Pressure is increasing in the container.

Glutamate Dehydrogenase



product removal

HCO_3^- + 2ATP

Carbamoyl phosphate

ornithine

citrulline

urea cycle

ΔG° is somewhat (+)

However $[NH_4^+]$ is kept very low.

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

(−) (+) (−)

storage of glucose

Glycogen Phosphorylase

product removal

$$\text{glycogen}_{(n\ \text{residues})} + P_i \rightleftharpoons \text{glycogen}_{(n-1\ \text{residues})} + \text{glucose-1-phosphate}$$

in liver and muscle

phosphoglucomutase

glucose-6-phosphate

glucose-6-phosphatase

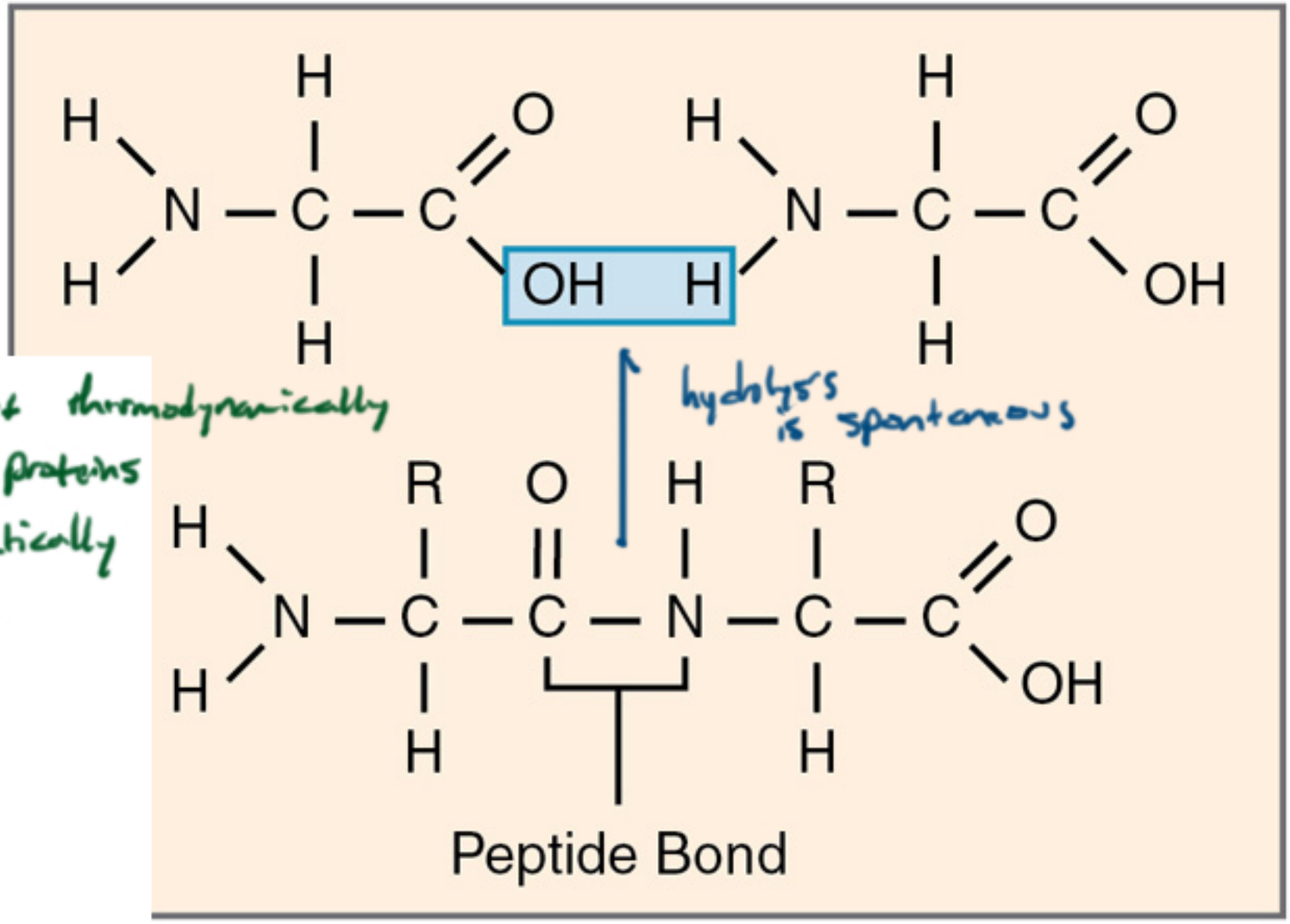
glucose

ΔG° is actually $\oplus$

However in physiology $\frac{[G1P]}{[P_i]} \sim \frac{1}{1000}$

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

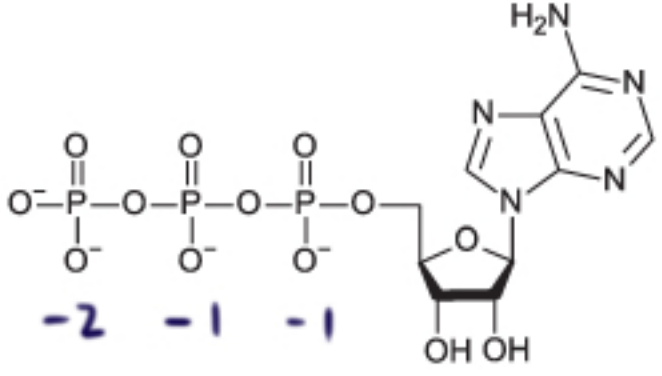
$\ominus$ $\quad$ $\oplus$ $\quad$ $\ominus$



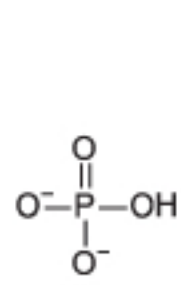
While not thermodynamically stable, proteins are kinetically stable.

Hydrolysis of ATP

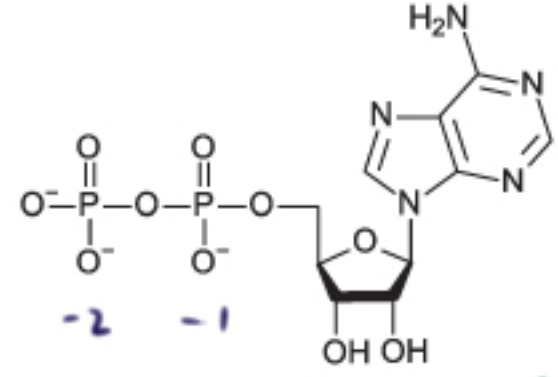
$\Delta G^\circ \sim -30\ kJ$



+ H_2O



+



+ H^+

$U_e = \frac{kq_1q_2}{r}$

ΔU is ⊖

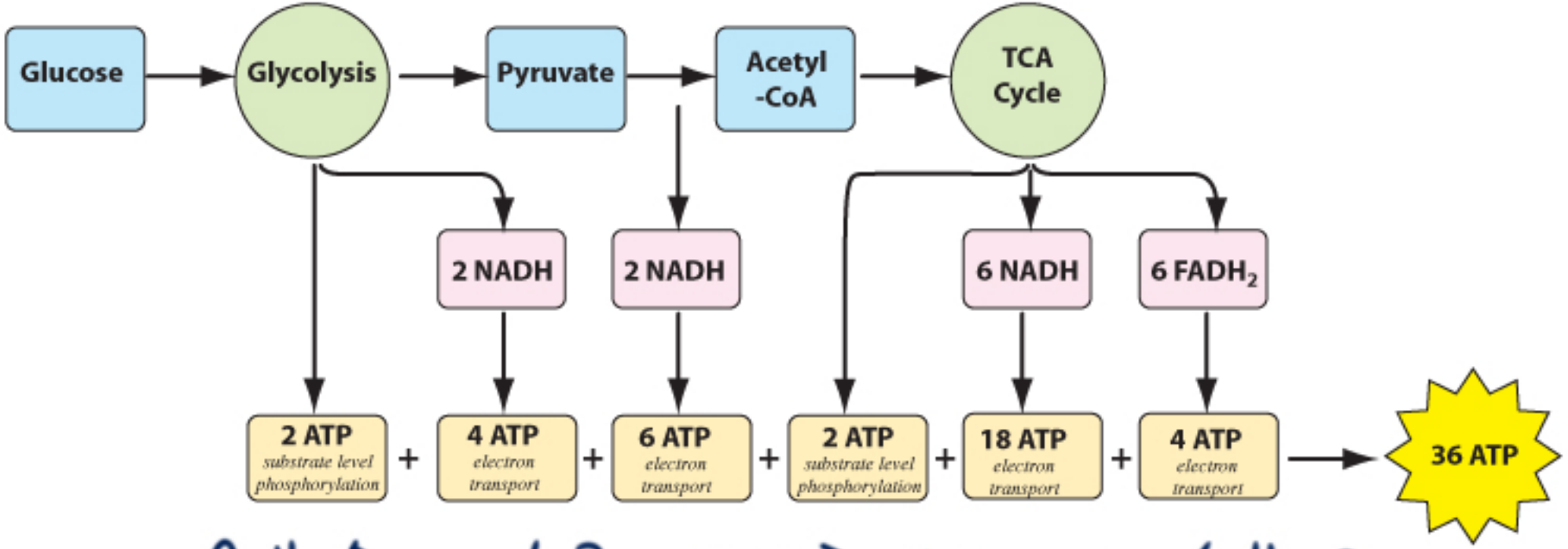
ΔH is ⊖

ΔG is ⊖

$K = e^{-\Delta G^\circ / RT}$

with ATP

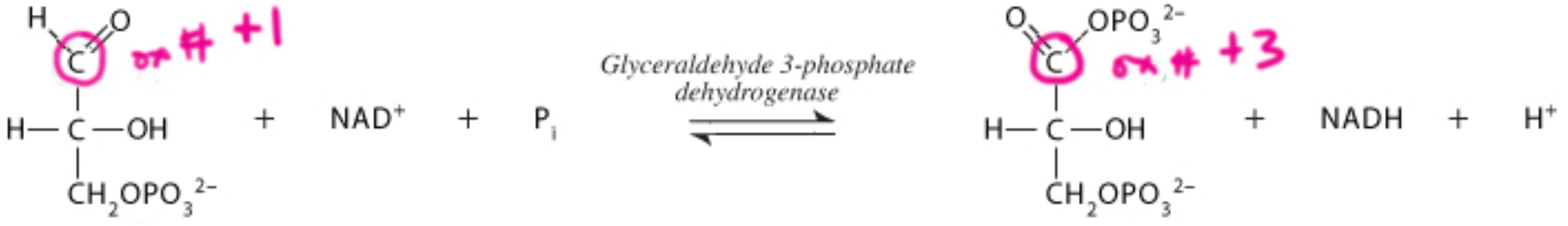
$K = e^{(-\Delta G^\circ_A + \Delta G^\circ)/RT}$



$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

$\Delta G^\circ \sim -3000\ kJ$

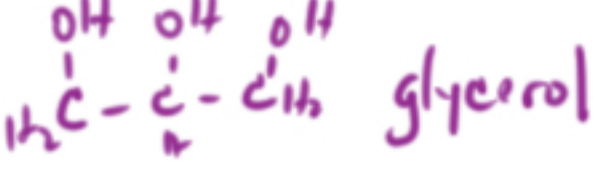
$36\ ADP + 36\ P_i \longrightarrow 36\ ATP \qquad \Delta G^\circ \sim 1100\ kJ$

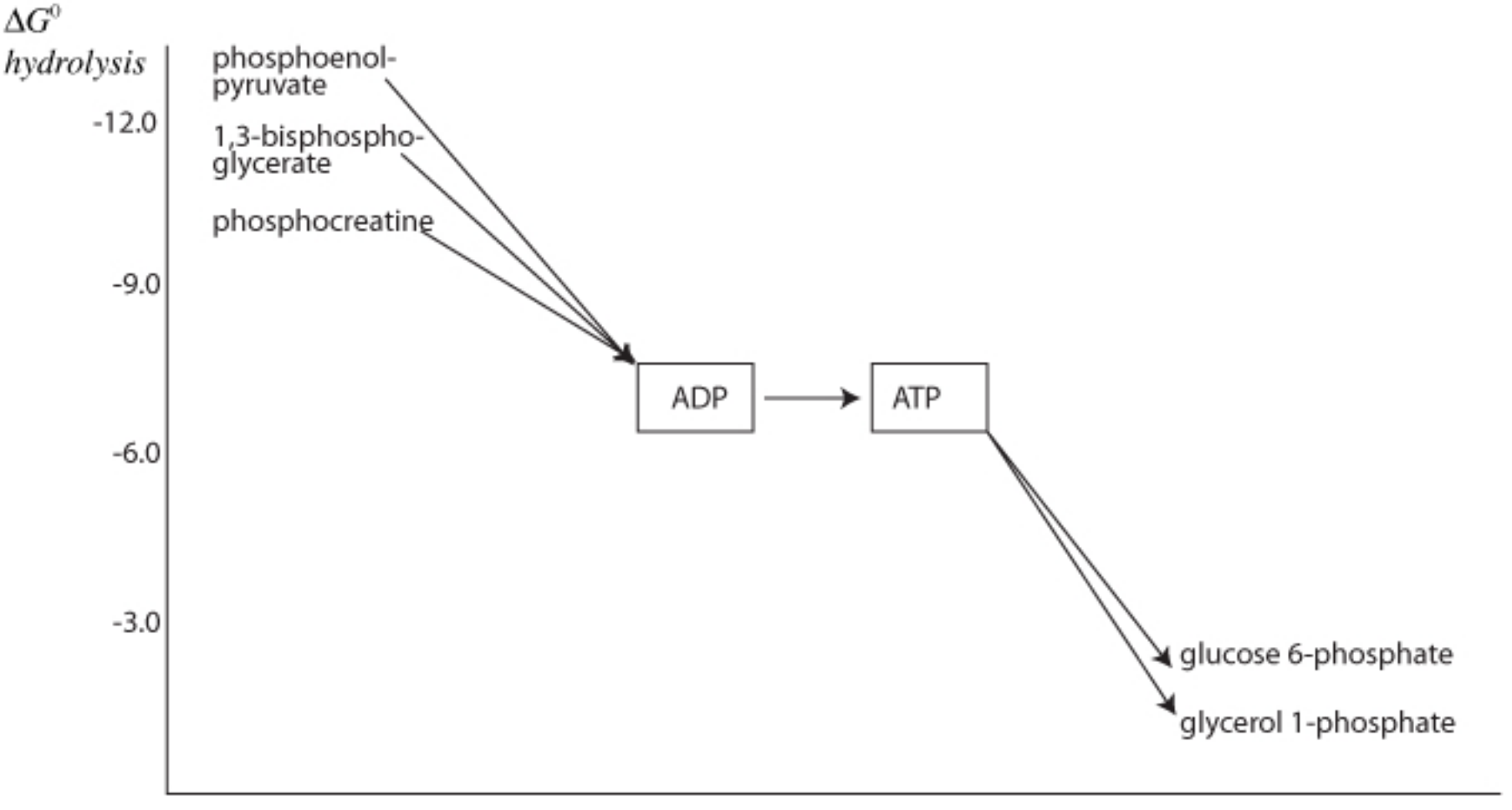


G3P

1,3 BPG

$\Delta G \sim 0$




ΔG^0
hydrolysis
-12.0
-9.0
-6.0
-3.0
phosphoenol-
pyruvate
1,3-bisphospho-
glycerate
phosphocreatine
ADP
ATP
glucose 6-phosphate
glycerol 1-phosphate

$3\,H_2\,(g) + N_2\,(g) \longrightarrow 2\,NH_3\,(g)$

$\Delta H^o = -46.2\ kJ\ mol^{-1}$

$\Delta S^o = -389\ J\ K^{-1}\ mol^{-1}$

$\Delta G^o = -16.4\ kJ$ at 298K

exothermic reaction

increasing T favors endothermic direction

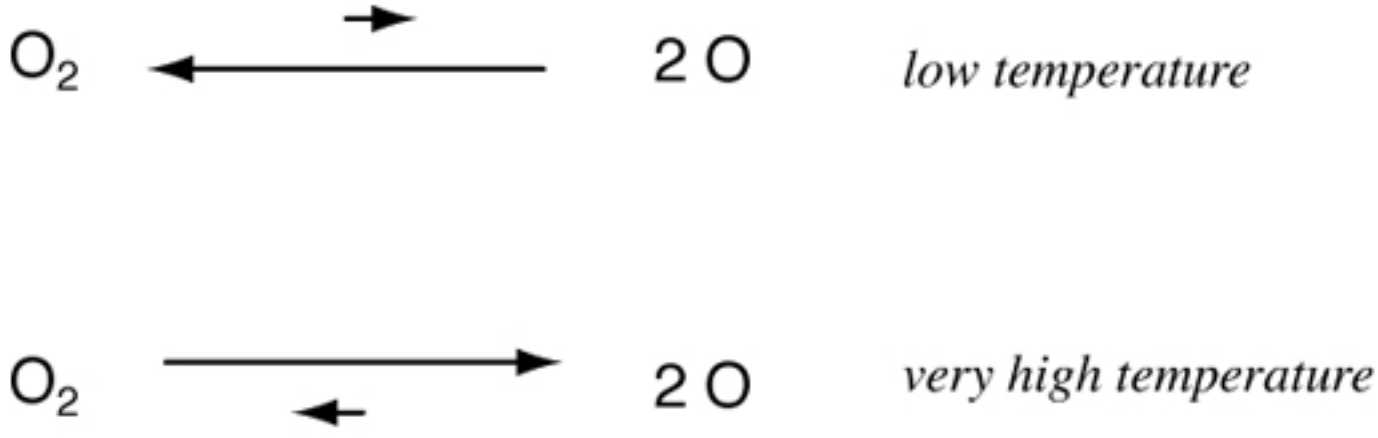
if exothermic this would be +

if $T_2 > T_1$

$$\ln \frac{K_1}{K_2} = \left(-\frac{\Delta H^o}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

then this will be +

then $K_1 > K_2$ reaction should favor reagents


O_2
2 O
low temperature
O_2
2 O
very high temperature

Le Chatelier

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counter-act the imposed change.

- Concentration - adding reagent or removing product drives a reaction forward
- Temperature - Increasing T favors the endothermic direction.

$$\text{heat} + A \rightleftharpoons B$$

- Pressure - Increasing P favors the smaller volume (fewer moles of gas)

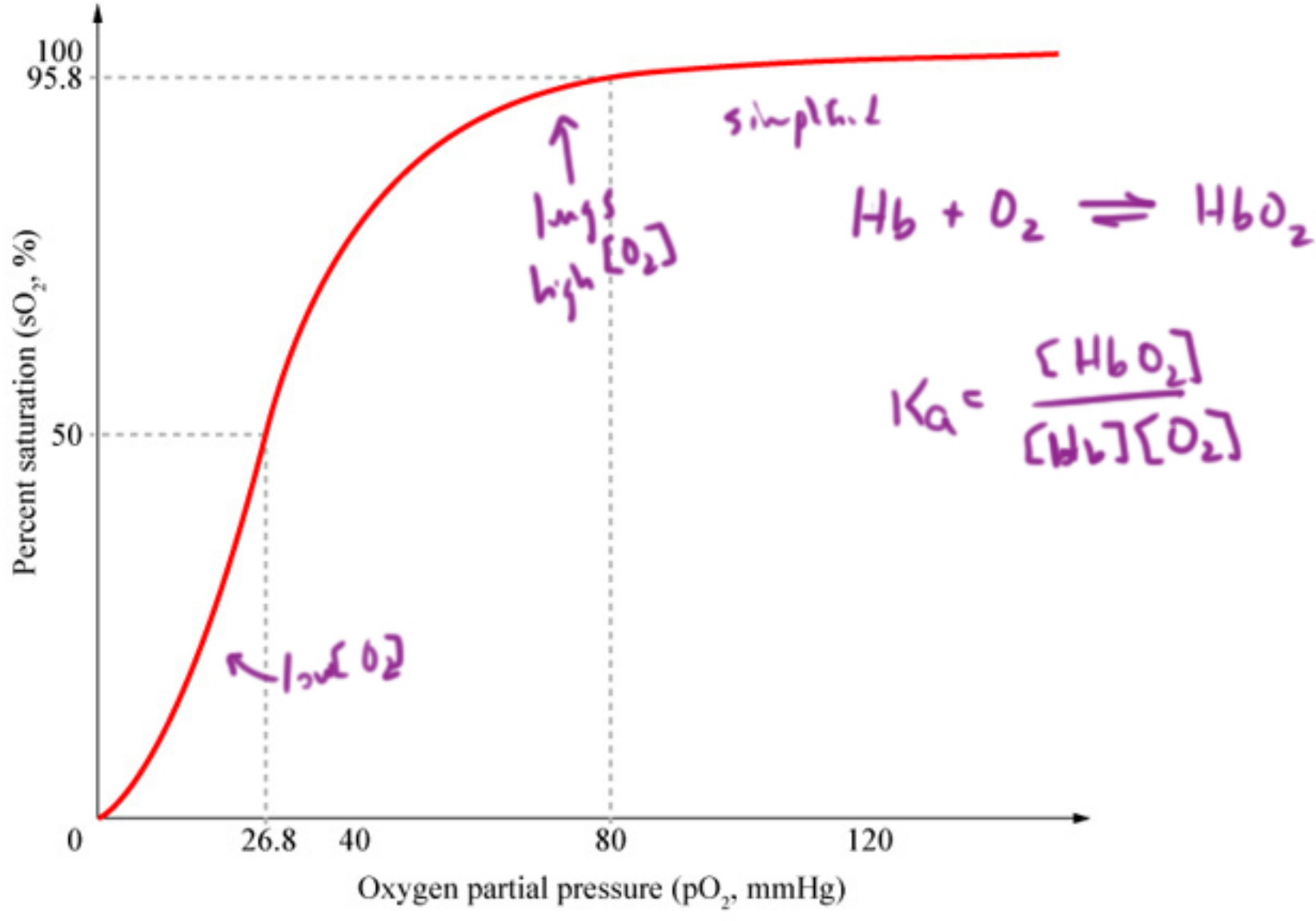
The reaction of sulfur dioxide with oxygen is as follows:

$$3SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \quad + \text{heat}$$
$$\Delta H = -197.8 \text{ KJ mol-1}$$

At 1000°C and 0.3 atm, the equilibrium constant, K_p, is equal to 3.42. Which of the following strategies would increase the yield of sulfur trioxide?

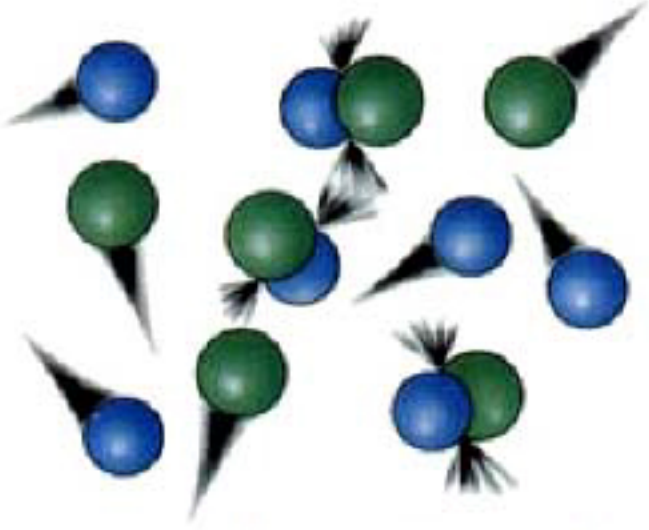
I. Increasing the pressure of the reaction vessel
II. Introducing a catalyst
III. Heating the reaction vessel further

A. I
B. I and III
C. II and III
D. I, II and III

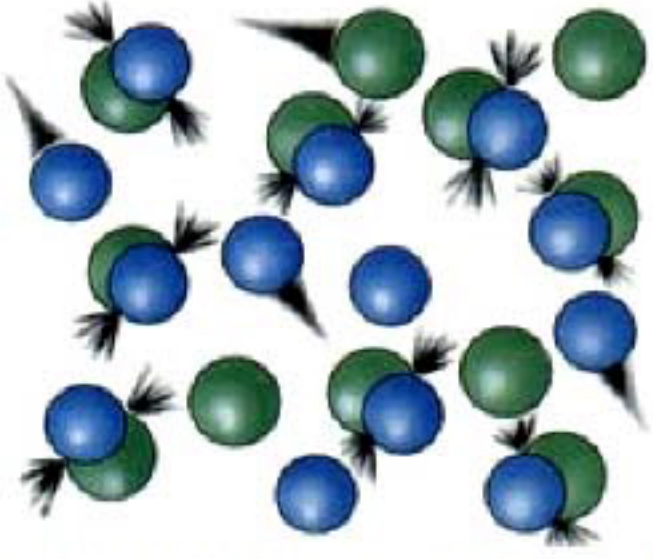

100
95.8
50
0
26.8
40
80
120
Percent saturation (sO_2, %)
Oxygen partial pressure (pO_2, mmHg)
simple
high $[O_2]$
low $[O_2]$
$Hb + O_2 \rightleftharpoons HbO_2$
$K_a = \frac{[HbO_2]}{[Hb][O_2]}$

Chemical Kinetics

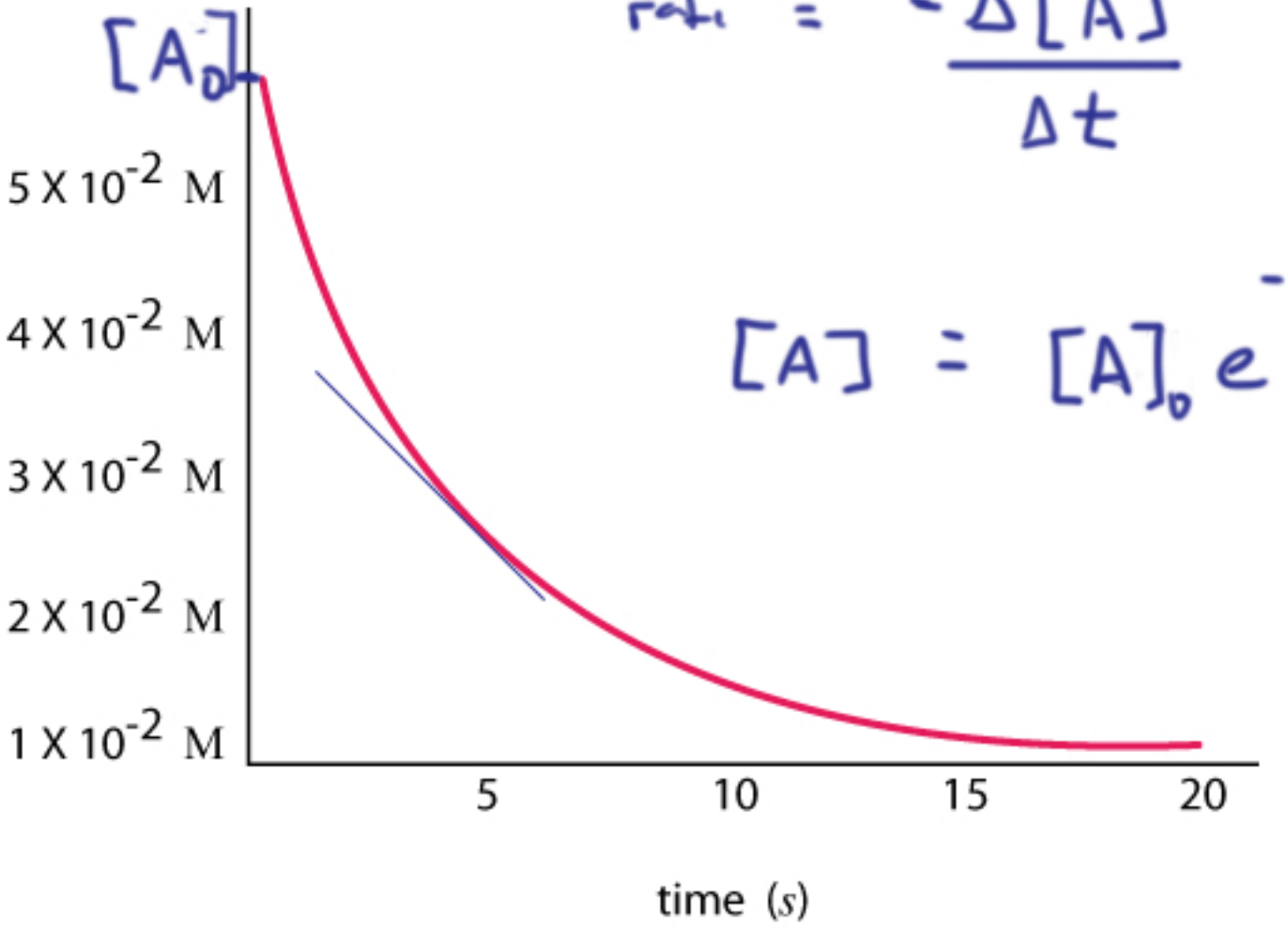
Collision Theory



Low concentration = Few collisions



High concentration = More collisions



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$[A] = [A]_0 e^{-kt}$$

$$n_a\,A \quad + \quad n_b\,B \longrightarrow n_p\,P \quad + \quad n_q\,Q$$

$$Rate = \frac{concentration\ change}{time\ interval}$$

normalize the rate

$$v = \frac{-1}{n_a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_b}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_p}\frac{\Delta[P]}{\Delta t} = \frac{1}{n_q}\frac{\Delta[Q]}{\Delta t}$$

$$v = \frac{-1}{n_a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_b}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_p}\frac{\Delta[P]}{\Delta t} = \frac{1}{n_q}\frac{\Delta[Q]}{\Delta t}$$

$$v = k\, f([A], [B], \ldots)$$

only from experiment (or if you know the actual mechanism)

$$v = k\,[A]^a[B]^b$$

a rate expression

rate constant

$$2\ HI\ (g) \longrightarrow H_2\ (g) + I_2\ (g)$$

$$\frac{\Delta[I_2]}{\Delta t} = k\,[HI]^2$$

← 2nd order rate expression (sum of the exponents)

Choose the correct rate expression for the reaction below

$$2MgO + Si \longrightarrow 2Mg + SiO_2$$

A. rate = k [MgO] [Si]
B. rate = k $[MgO]^2$ [Si]
C. rate = 2k [MgO][Si]
D. impossible to detemine from given information

If the reaction rate is quadrupled by doubling the concentration of a reactant, the order of the reaction with respect to that reactant is

A. 1
B. 2
C. 4
D. cannot be determined except by experiment

$\text{rate} = k[A]^2[B]^1$

3rd order reaction that is 2nd order with respect to A.

SN2

Rate = k [CH_3CH_2Br] [$NaOCH_3$]

Total order: 2

SN1

Rate = k [$CH_3CHBrCH_3$]

Total order: 1

$$A + 3B + C \longrightarrow$$

practice!

rate expression?

$$\text{rate} = k[A]^x[B]^y[C]^z$$

Experiment	1	2	3	4
[A]	0.5 M	1.0 M	1.0 M	0.5 M
[B]	0.5 M	0.5 M	1.0 M	0.5 M
[C]	0.5 M	0.5 M	0.5 M	1.0 M
rate	0.2 M/s	1.6 M/s	1.6 M/s	0.4 M/s

$x = 3$

$y = 0$

$z = 1$

some number N here is N^3 what about $(2N)^3 = 8N^3$

rate = k [A]

1st Order

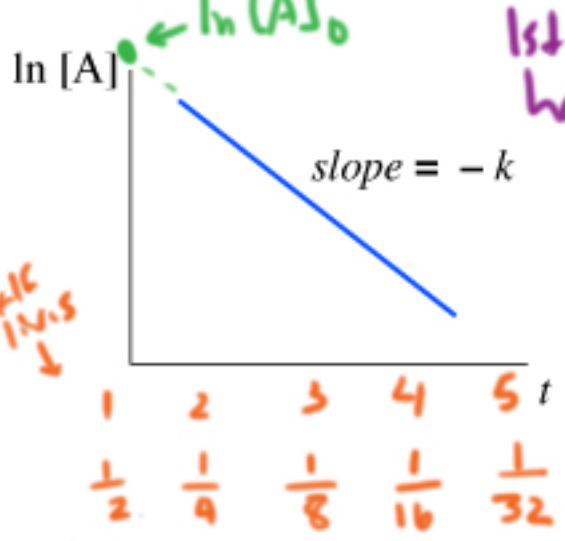
$$-\frac{\Delta[A]}{\Delta t} = k\,[A]$$

exponential decay →

$$[A] = [A]_o\, e^{(-k\,t)}$$

$$\ln [A] = \ln[A]_o - k\,t$$

$y = b + mx$



1st order reactions have a half life

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

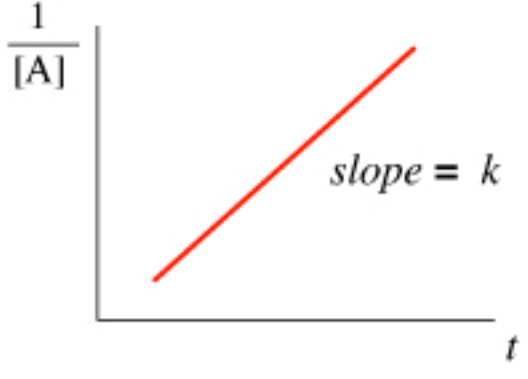
$\ln(2) = .69$

$$t_{\frac{1}{2}} = \frac{0.69}{k}$$

2nd Order

$$-\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k\,t$$



$$t_{\frac{1}{2}} = \frac{1}{k\,[A]_o}$$

The decomposition of N_2O_5 in carbon tetrachloride can be represented

$$N_2O_5 \longrightarrow 4NO_2 + O_2$$

The reaction rate equation was found to be

$$\text{rate} = (6.9 \times 10^{-4}\ \text{M s}^{-1})\ [N_2O_5]$$

If we begin with 30 g of N_2O_5 in solution, approximately how much time elapses before only 1 g remains?

A. 5.0×10^3 s
B. 4.0×10^4 s
C. 2.0×10^4 s
D. 1.4×10^4 s

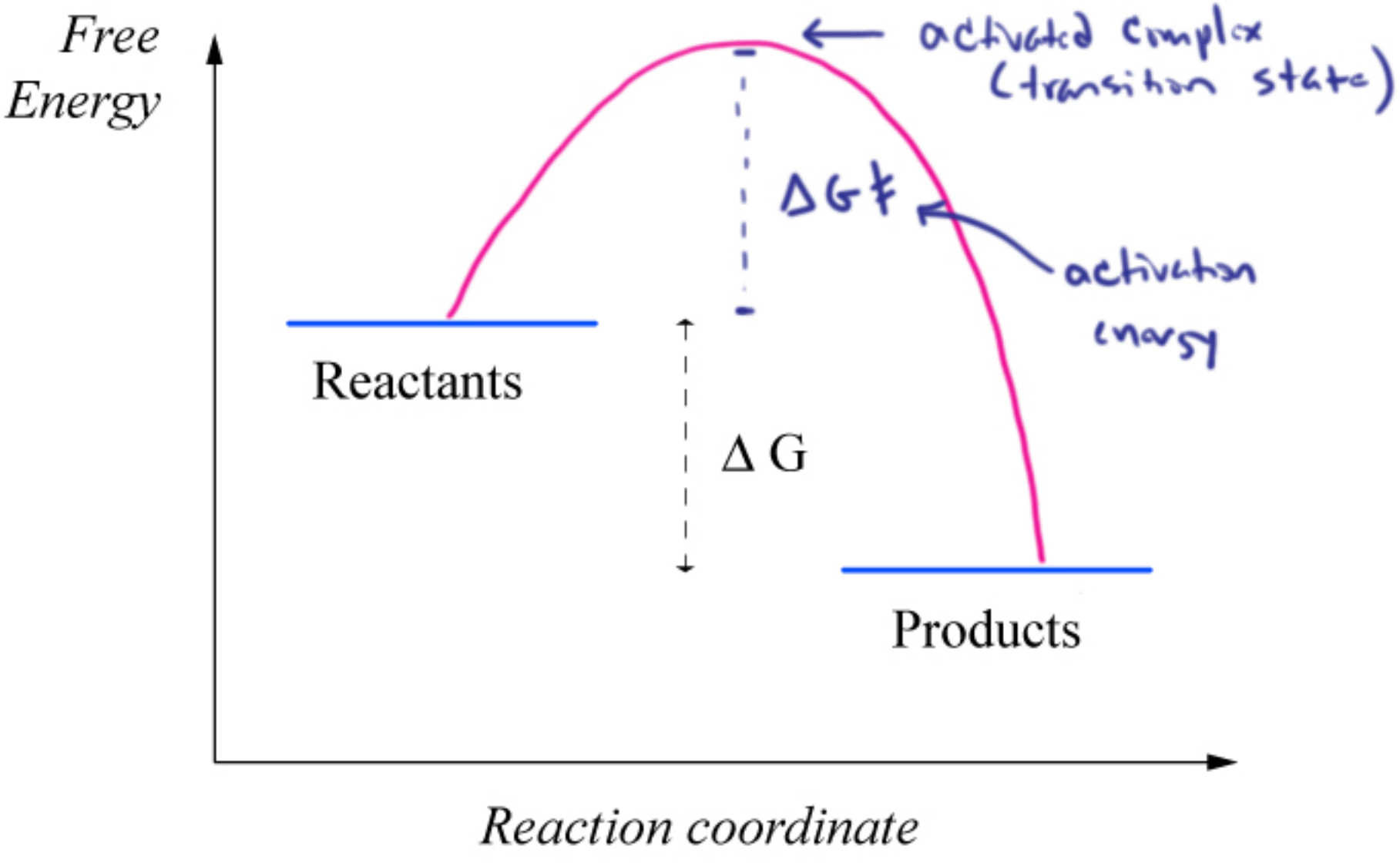
$t_{\frac{1}{2}} = \frac{0.69}{k}$

$t_{\frac{1}{2}} = \frac{6.9 \times 10^{-1}}{6.9 \times 10^{-4}}$

$= 1 \times 10^3$

1 2 3 4 5

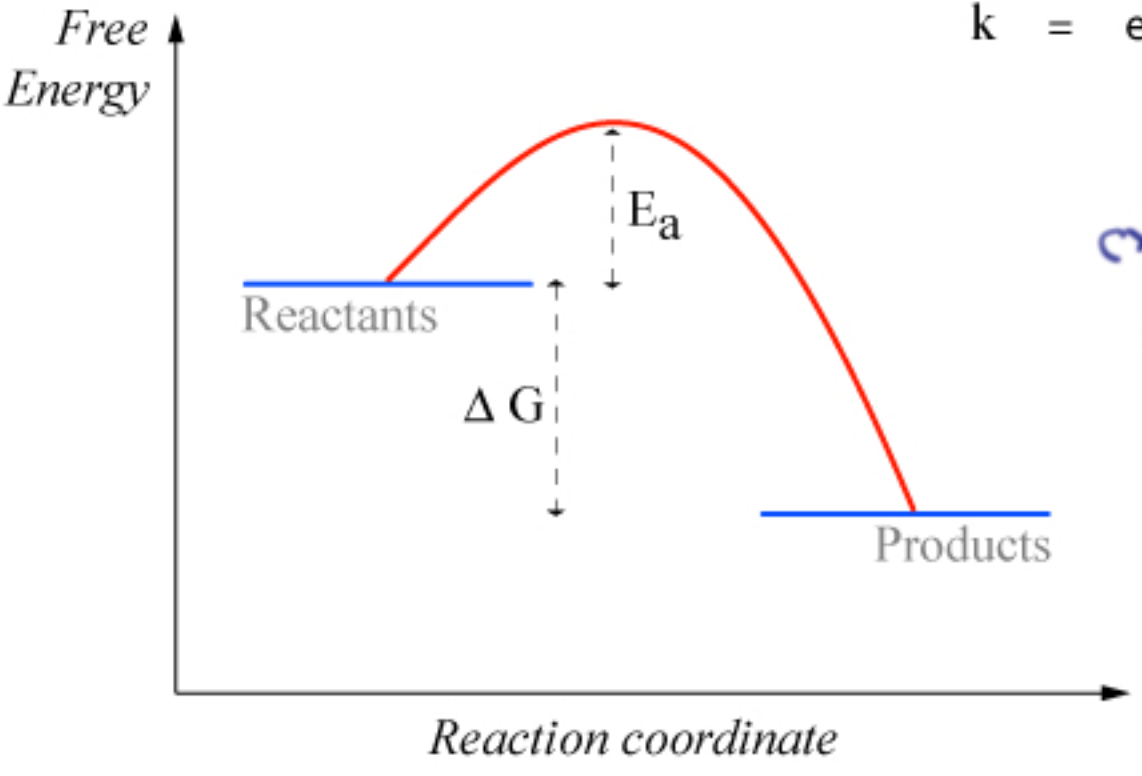
$\frac{1}{2}$ $\frac{1}{4}$ $\frac{1}{8}$ $\frac{1}{16}$ $\frac{1}{32}$

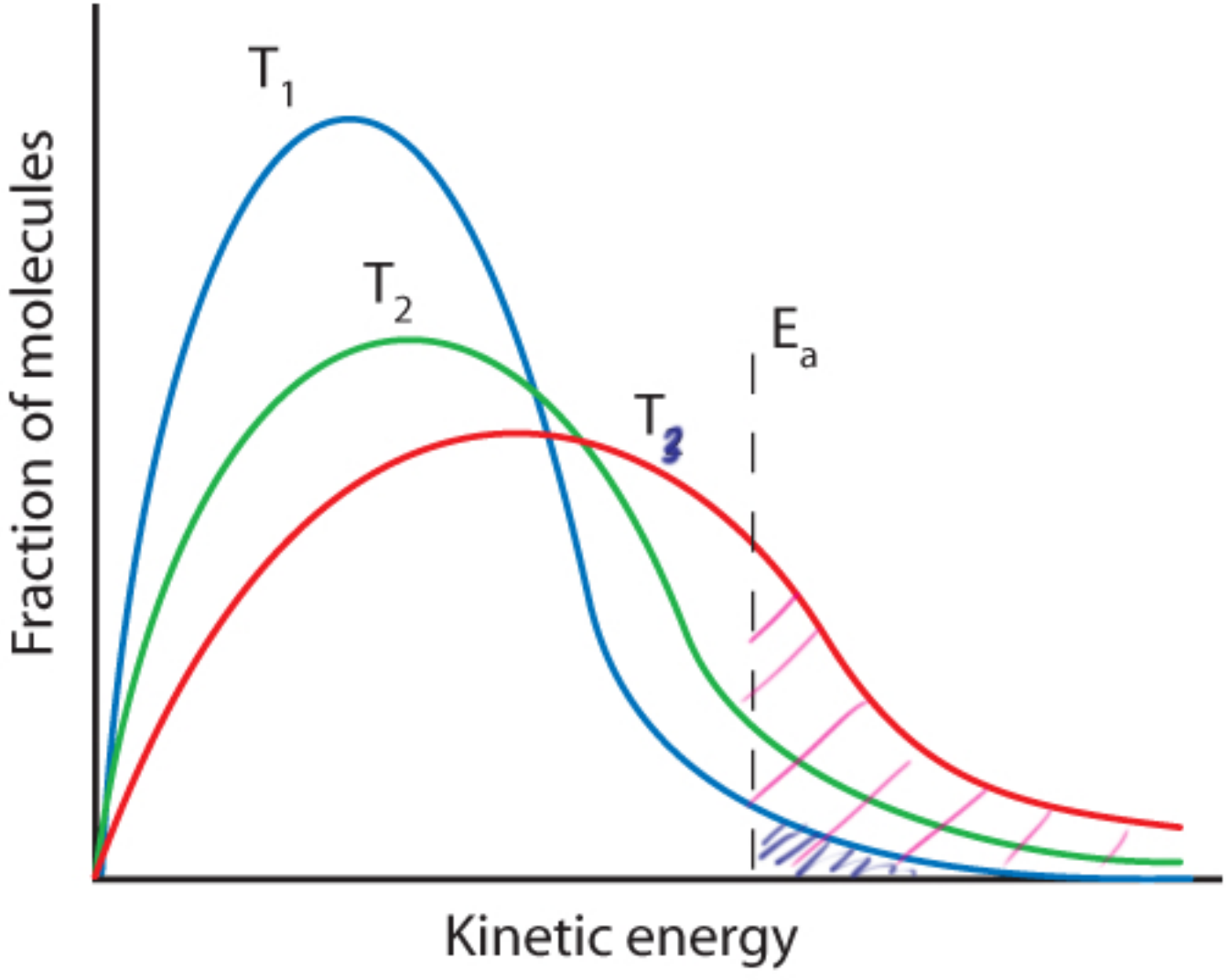

Free Energy
activated complex (transition state)
ΔG‡
activation energy
Reactants
ΔG
Products
Reaction coordinate

$$v = k\,[A]^a[B]^b$$

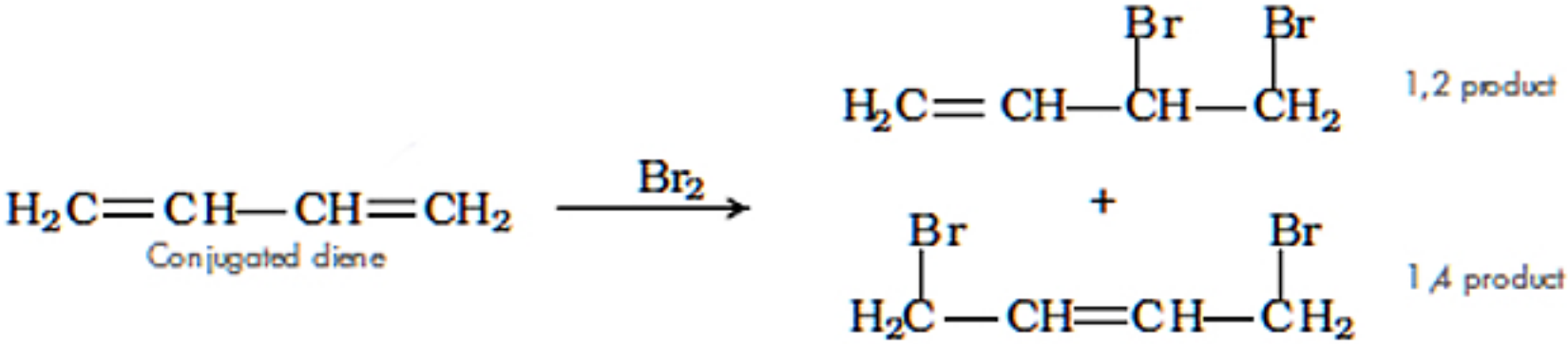
$$k = e^{\left(\frac{-E_a}{RT}\right)}$$ ← Arrhenius equation

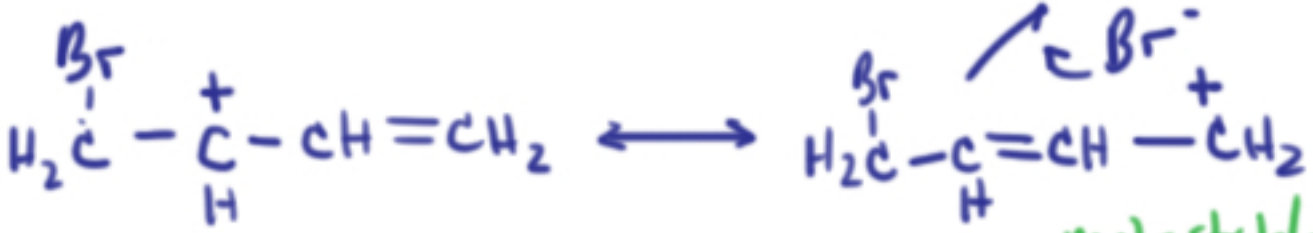
↑ rate increases exponentially with temperature




Fraction of molecules
T1
T2
T3
Ea
Kinetic energy

Kinetic vs Thermodynamic Control

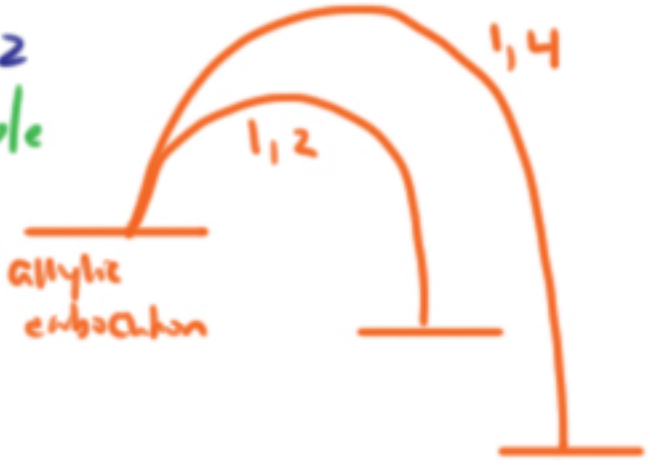


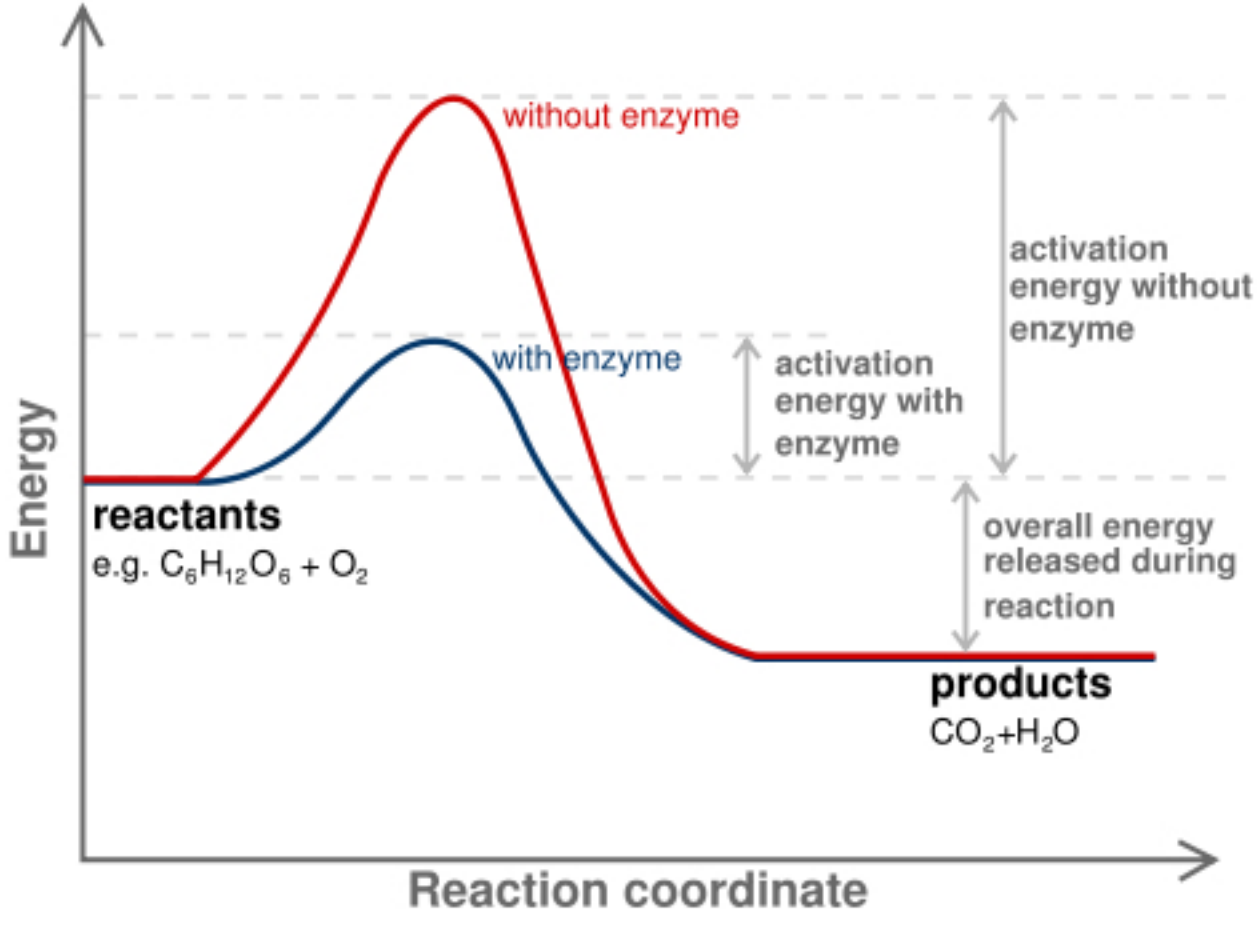


metastable

1,2 ⇒ kinetic product
favored at low T

1,4 ⇒ thermodynamic product
favored at high T





Catalysts

- lowers activation energy

In the presence of a catalyst

I. Effective collisions among reactant molecules become more likely to occur.
II. Chemical equilibrium will shift toward the products.
III. The activation energy for the reaction is lowered.

A. I
B. I and III
C. II and III
D. I, II, and III

Solvent	Solute
gas	gas
liquid	gas
liquid	liquid
liquid	solid
solid	solid

Solutions
- homogeneous

vs

suspensions, emulsions,
colloids, gels, sols

- heterogeneous phase spaces

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solvent or solution}}$$

gaseous solutions

Mole fraction:

partial pressure = mole fraction

$$X_A = \frac{n_A}{n_A + n_B + \ldots}$$

Raoult's Law

$P_{vap} = \chi P_{vap}^{\circ}$

Percent by mass and volume:

$$\text{mass \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{vol \%} = \frac{\text{vol of solute}}{\text{vol of solution}} \times 100\%$$

Practical measurement

lab protocols

Molarity

reaction quotients
equilibrium constants
rate expressions

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

400mL of 0.2 M NaOH solution
How many moles?

$(0.2 \frac{\text{mol}}{\text{L}})(.4\text{L}) = 0.08 \text{ mol}$

6.0 g NaCl (MW 58.4) in water
makes 250mL of solution. Molarity?

58.4 g/mol

Molality

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

$(\frac{1 \text{mol}}{58.4 \text{g}})(6\text{g}) = 0.1 \text{ mol}$

Colligative properties
- BP elevation
- FP depression

$\frac{0.1 \text{mol}}{.25 \text{L}} = 0.4 \text{ M}$

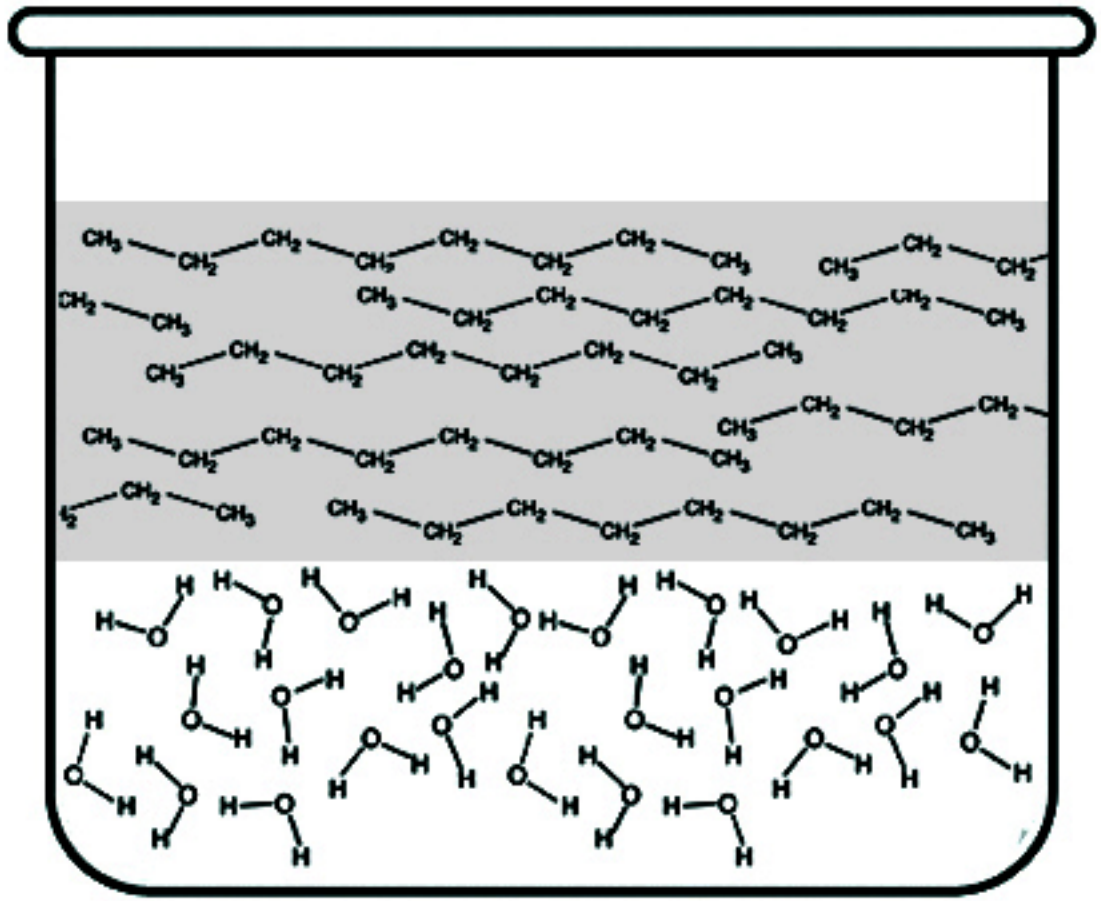
undissolved ⇌ dissolved

Like Dissolves Like

$+\Delta G$

$+\Delta H$

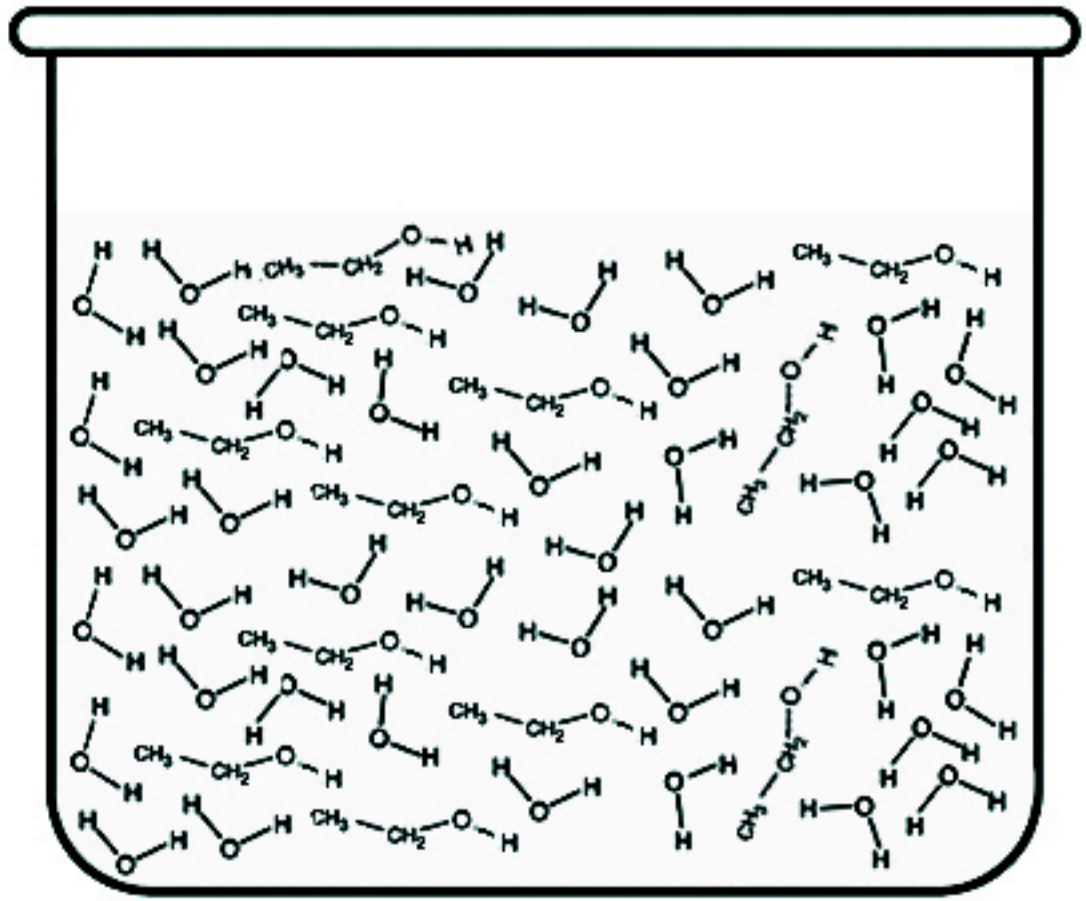
$+\Delta U$

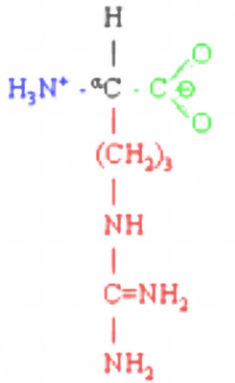


Solubility in Water

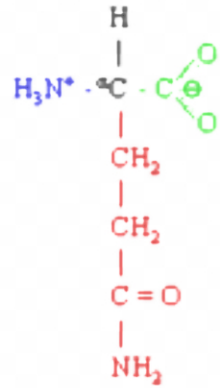
Methanol	infinite
Ethanol	infinite
Propanol	infinite
Butanol	90g/kg
Pentanol	2.7g/kg

Note at about 5:1 hydrocarbon to polar group it becomes insoluble.

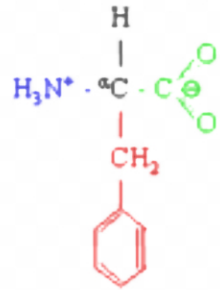




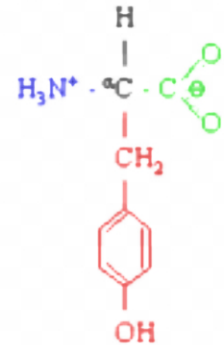
Arginine
(Arg / R)



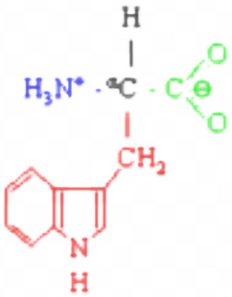
Glutamine
(Gln / Q)



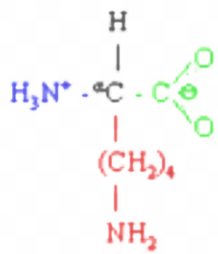
Phenylalanine
(Phe / F)



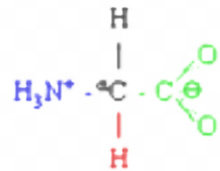
Tyrosine
(Tyr / Y)



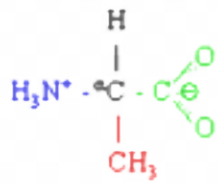
Tryptophan
(Trp, W)



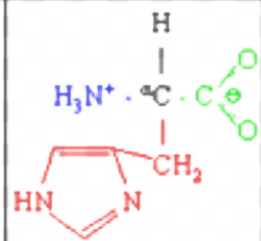
Lysine
(Lys / K)



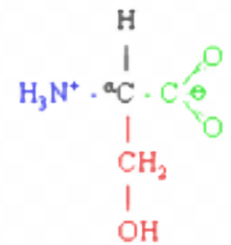
Glycine
(Gly / G)



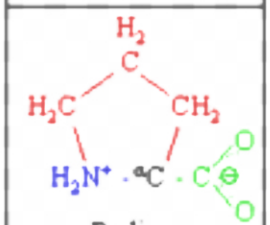
Alanine
(Ala / A)



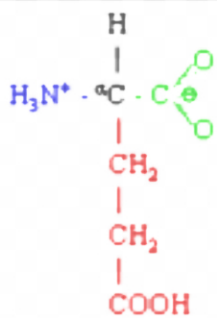
Histidine
(His / H)



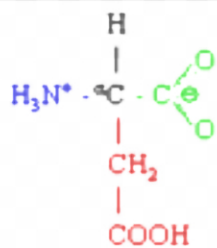
Serine
(Ser / S)



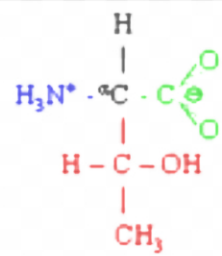
Proline
(Pro / P)



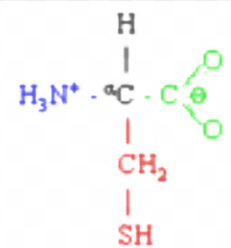
Glutamic Acid
(Glu / E)



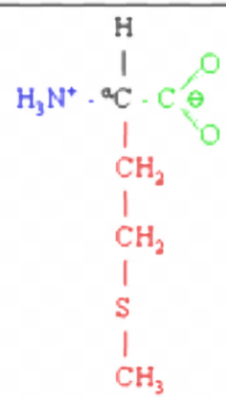
Aspartic Acid
(Asp / D)



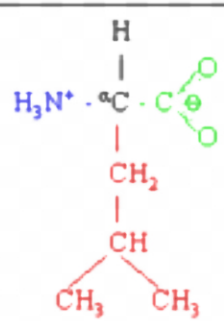
Threonine
(Thr / T)



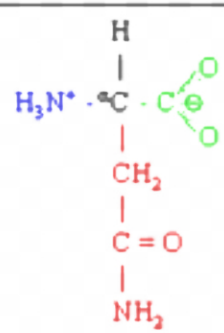
Cysteine
(Cys / C)



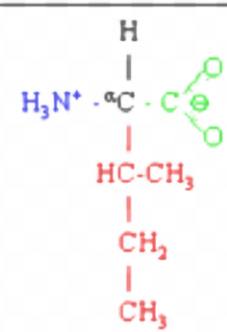
Methionine
(Met / M)



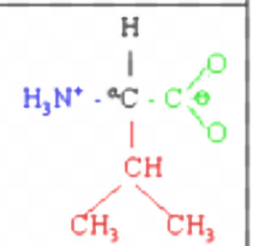
Leucine
(Leu / L)



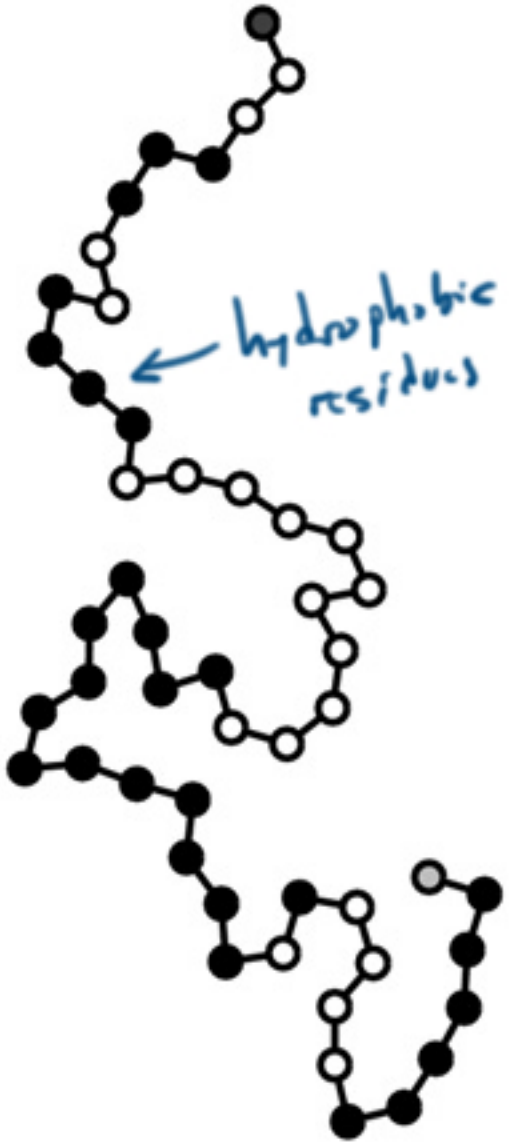
Asparagine
(Asn / N)



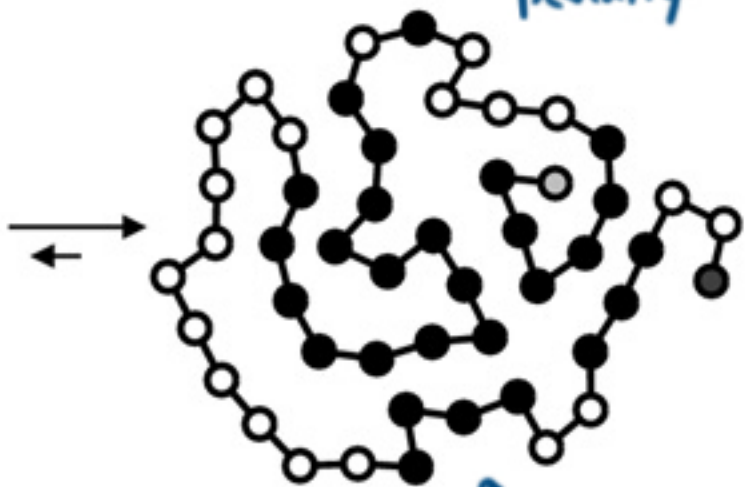
Isoleucine
(Ile / I)



Valine
(Val / V)

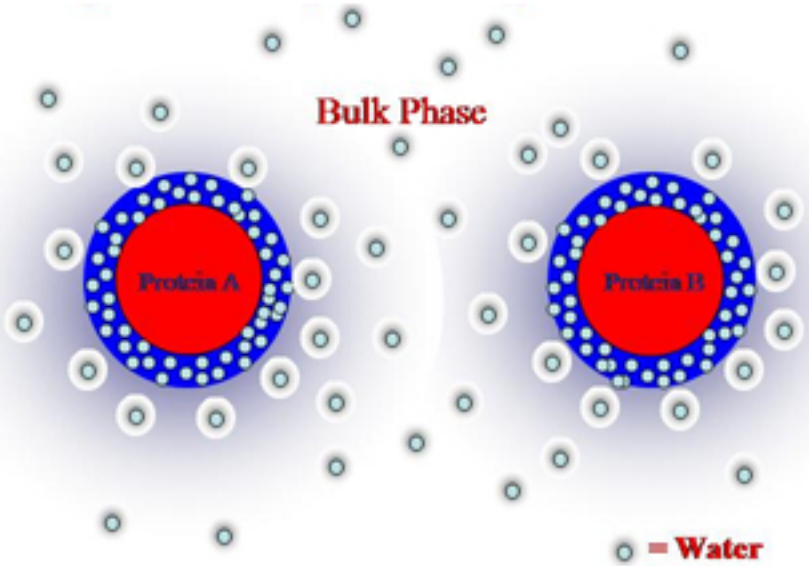


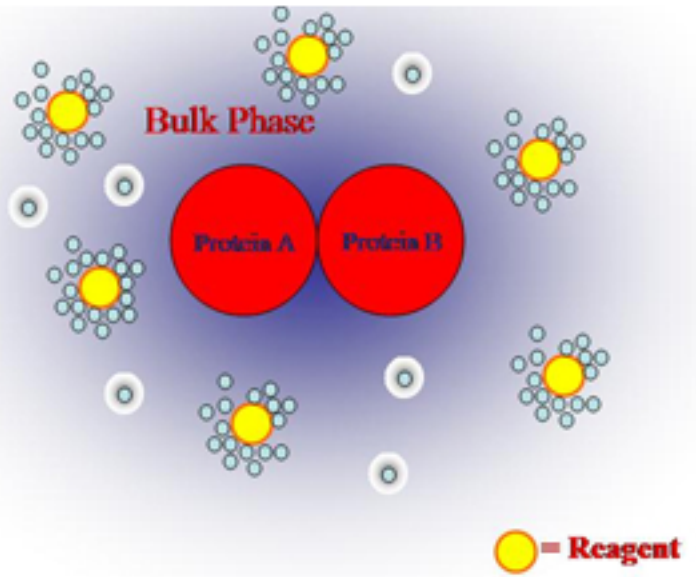
hydrophobic residues



- Driven by enthalpy in self association of water
- also driven by entropic penalty

might form a dimer at this interface





Hofmeister Series

$$F^- \approx SO_4^{2-} > HPO_4^{2-} > \text{acetate} > Cl^- > NO_3^- > Br^- > ClO_3^- > I^- > ClO_4^- > SCN^-$$

$$NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+} > \text{guanidinium}$$

Electrolytes

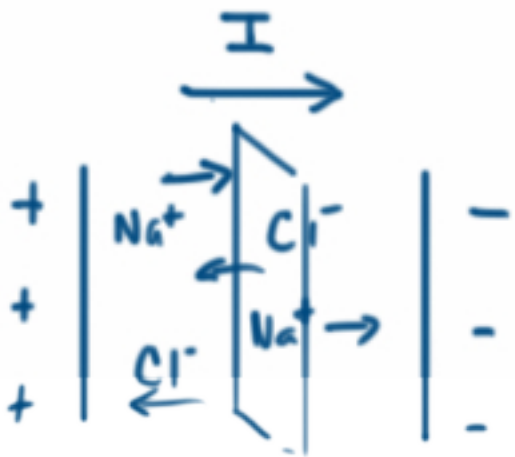
Strong

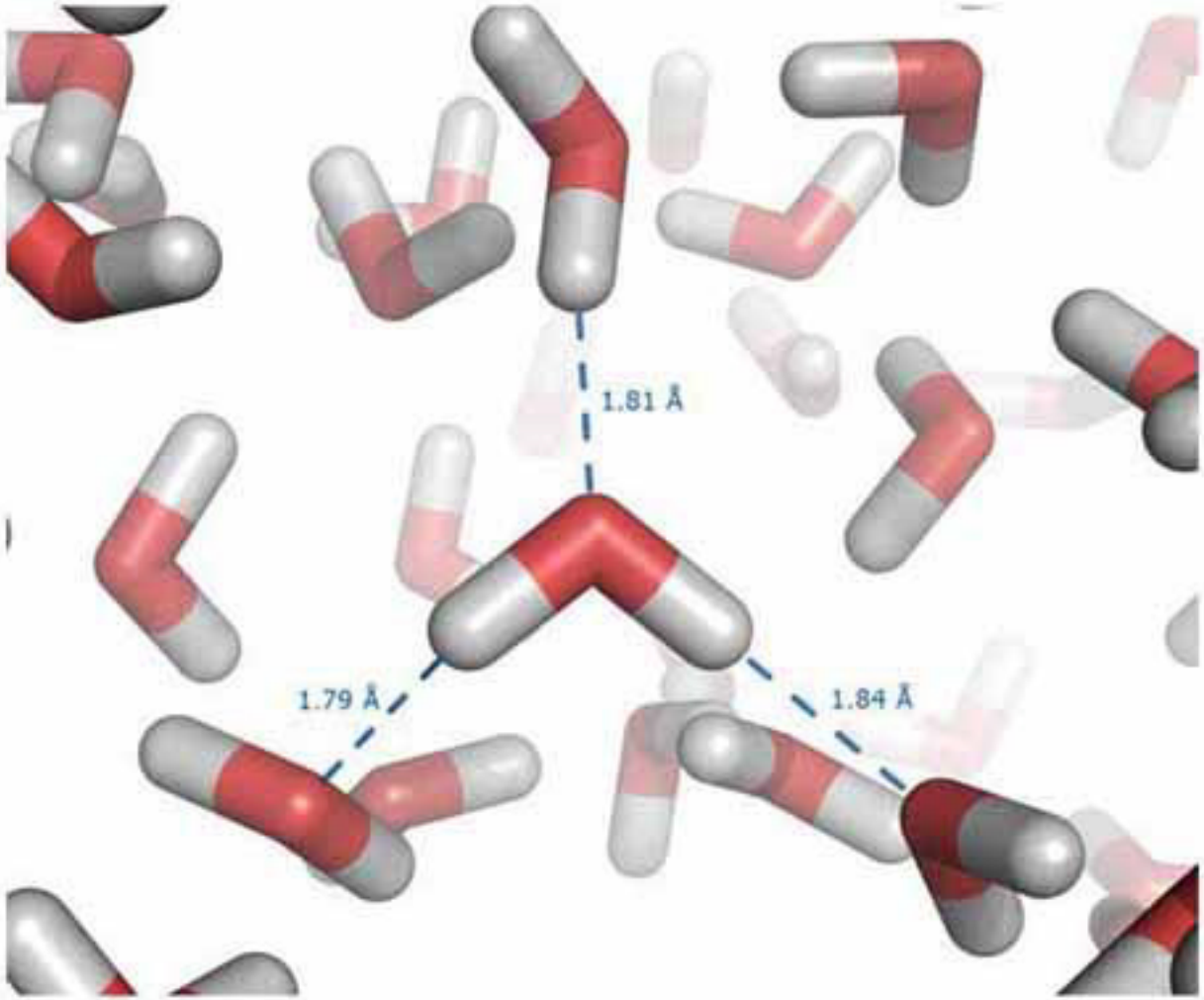
$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$

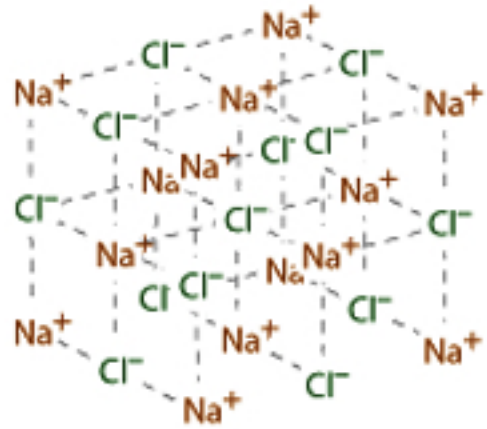
Weak ← sparingly soluble "insoluble"

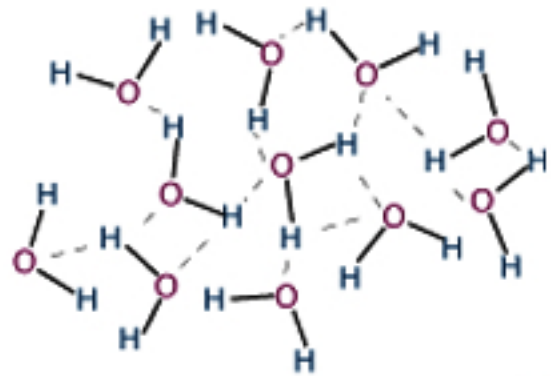
$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

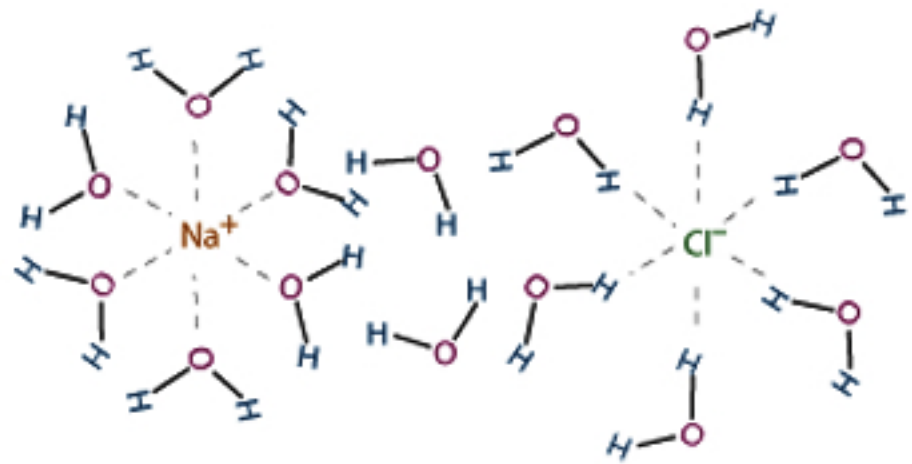
Heterogeneous Solution Equilibria (K_{sp})




1.81 Å
1.79 Å
1.84 Å







enthalpy change ΔH

- for NaCl - increasing T increases solubility
- solution process is endothermic

ΔH consists of

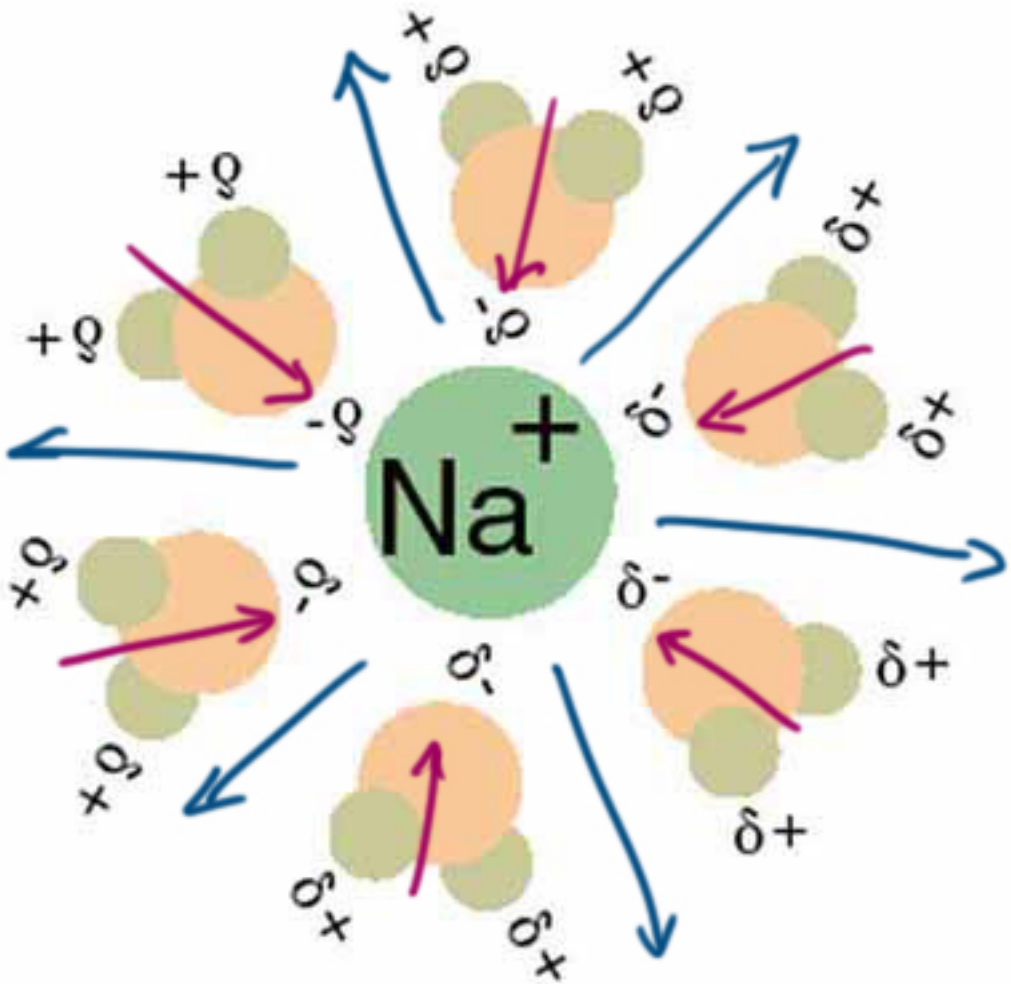
lattice energy
$\oplus \Delta H$

enthalpy of hydration
$\ominus \Delta H$

also entropic penalty

$$F = \frac{k q_1 q_2}{r^2 d_{H_2O}}$$

d_{H_2O} ← dielectric constant ~ 80



Cl⁻

Endothermic solution process - positive ΔH

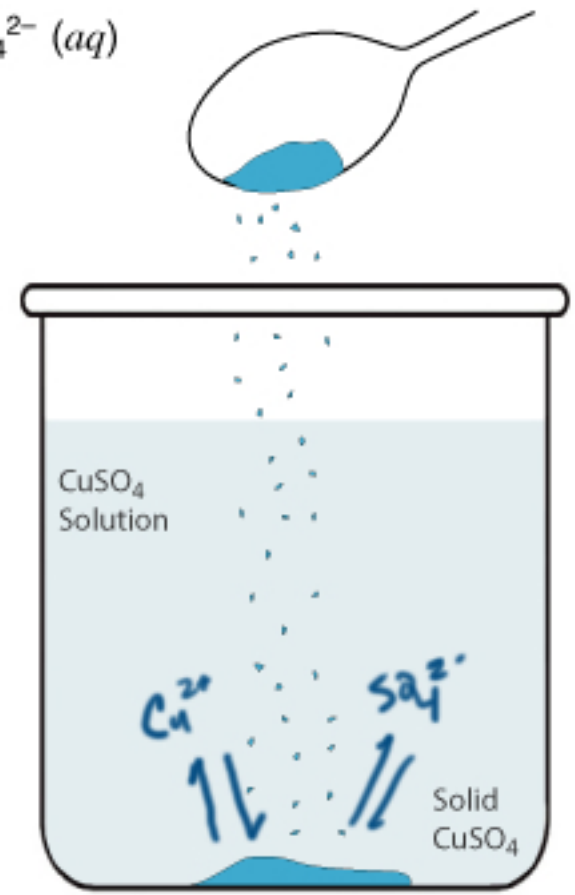
heat + solvent + solute ⇌ solution

Exothermic solution process - negative ΔH

solvent + solute ⇌ solution + **heat**

$CuSO_4\,(s) \longrightarrow Cu^{2+}\,(aq) + SO_4^{2-}\,(aq)$

$CuSO_4\,(s) \rightleftharpoons Cu^{2+}\,(aq) + SO_4^{2-}\,(aq)$



In solution chemistry the equilibrium state is the saturated solution.

SOLUBLE

Na^+, K^+, NH_4^+

NO_3^-

F^- tend to be insoluble

Cl^-, Br^-, I^-
(except with Pb^{2+}, Hg_2^{2+}, Ag^+ & Cu^+)

SO_4^{2-}
(except with Ba^{2+}, Sr^{2+}, Pb^{2+}, Hg_2^{2+}, Ca^{2+} & Ag_2^{2+})

INSOLUBLE

S_2^-
(except with Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+})

O_2^-
(except with Na^+, K^+, Ba^{2+}, Sr^{2+})

OH^- ★
(except with Na^+, K^+, Ca^{2+}, Ba^{2+}, Sr^{2+})

CrO_4^{2-}
(except with Na^+, K^+, Mg^{2+}, NH_4^+)

★ **PO_4^{3-} & CO_3^{2-}** ★
(except with Na^+, K^+, NH_4^+)

Don't worry about all the nitty gritty details.

Testing an Aqueous Solution for the Presence of Flouride

$$CaCl_2\,(s) \longrightarrow Ca^{2+}\,(aq) + 2\,Cl^-\,(aq)$$

Common ion

$$Ca^{2+}\,(aq) + 2\,F^-\,(aq) \longrightarrow CaF_2\,(s)$$

$CaCl_2$ ← soluble

CaF_2 ← insoluble

$$PbSO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

$$K = \frac{[Pb^{2+}]\,[SO_4^{2-}]}{[PbSO_4]}$$

$$K_{sp} = [Pb^{2+}]\,[SO_4^{2-}]$$ ← solubility product

$$= 2.53 \times 10^{-8}$$

Q_{sp} → ion product

If $Q_{sp} < K_{sp}$ more can dissolve

If $Q_{sp} > K_{sp}$ precipitation

If $Q_{sp} = K_{sp}$ saturated

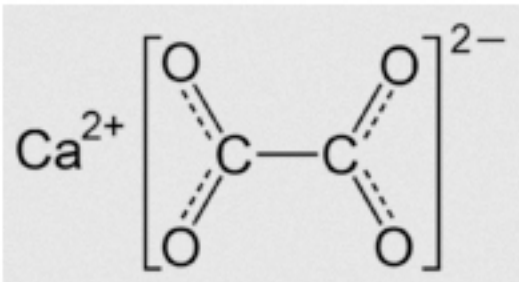
$$A_pB_q\,(s) \rightleftharpoons P\,A^{x+}\,(aq) + Q\,B^{y-}\,(aq)$$

$$K_{sp} = [A^{x+}]^P\,[B^{y-}]^Q$$

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

		K_{sp}
Calcium oxalate	CaC_2O_4	2.7×10^{-9}

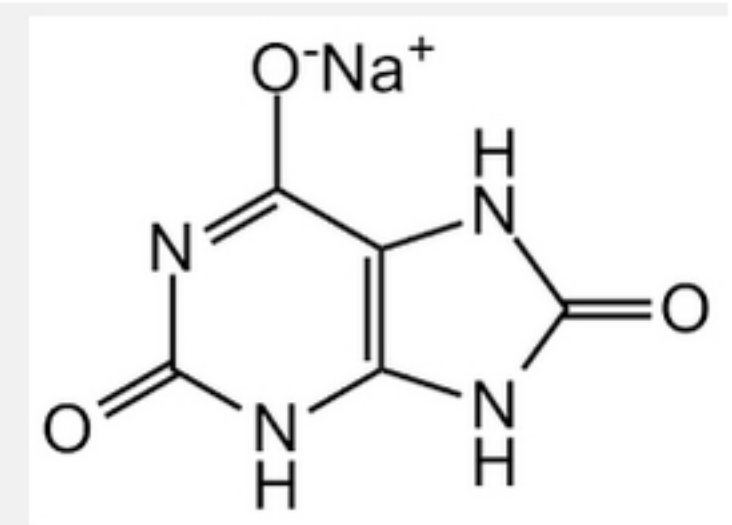


Most common type of kidney stone

Gout is associated with the appearance of crystals of monosodium urate monohydrate (hereafter called sodium urate) in the synovial fluid, causing an inflammatory reaction. There is a good correlation between the incidence of gout and raised serum uric acid concentrations. In particular the occurrence of gout increases rapidly with concentration above the saturation solubility of sodium urate in physiological saline, about 0·4 mmol/l (7 mg/100 ml). Apparently we can view the development of gout as stemming simply from the process of precipitation from a supersaturated solution.

What is the K_{sp} of sodium urate?

(Concentration of physiological saline: 150mM NaCl)



$K_{sp} = [Na^+][urate]$

$= (1.5 \times 10^{-1})(4 \times 10^{-4})$

$= 6 \times 10^{-5}$

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = 2.53 \times 10^{-8}$

x^2 type

What is the molar solubility of $PbSO_4$?

at saturation $[Pb^{2+}][SO_4^{2-}] = 2.5 \times 10^{-8}$

in pure H_2O $[Pb^{2+}] = [SO_4^{2-}]$

call $[Pb^{2+}] = x$

$x^2 = 2.5 \times 10^{-8}$

$x = 1.6 \times 10^{-4}$

1.6×10^{-4} M

What is the molar solubility of $PbSO_4$ in a 0.1 M solution of Na_2SO_4?

or solution $[SO_4^{2-}] \sim 0.1$

$[Pb^{2+}][0.1] = 2.5 \times 10^{-8}$

$[Pb^{2+}] = 2.5 \times 10^{-7}$ M

2.5×10^{-7} M

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

1 liter of saturated CaF_2 solution was evaporated at room temperature, leaving 0.017 g (2.2×10^{-4} mol) which was collected as a residue. Calculate the K_{sp} of CaF_2 at room temperature.

at saturation $[Ca^{2+}] = 2.2 \times 10^{-4}$ m.l/L

$[F^-] = 4.4 \times 10^{-4}$ m.l/L

$K_{sp} = [Ca^{2+}][F^-]^2$

$(2.2 \times 10^{-4})(4.4 \times 10^{-4})^2$

$\downarrow$

20×10^{-8}

$\downarrow$

$(2 \times 10^{-4})(2 \times 10^{-7}) = 4 \times 10^{-11}$

$4x^3$ type

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

The solubility product of CaF_2 is 3.5×10^{-11}, calculate the molar solubility of CaF_2 at room temperature.

$K_{sp} = [Ca^{2+}][F^-]^2 = 3.5 \times 10^{-11}$

call $[Ca^{2+}] = x$

$[F^-] = 2x$

$4x^3 = 3.5 \times 10^{-11}$

$x^3 = 0.9 \times 10^{-11}$

$x^3 = 9 \times 10^{-12}$

$x = 2.1 \times 10^{-4}$

Which is more soluble in water?

Tricky!

$CaCO_3$	$K_{sp} =$	4.8×10^{-9}
✓ Ag_2CO_3	$K_{sp} =$	4.8×10^{-12}

$x^2 = 4.8 \times 10^{-9}$

$x = 7 \times 10^{-5}$

$4x^3 < 4.8 \times 10^{-12}$

$< 1 \times 10^{-4}$

Which precipitates first when concentrated Na_2CO_3 is added to a solution 0.1M for both Ca^{2+} and Ag^{+}?

✓

$(0.1)[CO_3^{2-}] = 4.8 \times 10^{-9}$

$[CO_3^{2-}] = 4.8 \times 10^{-8}$

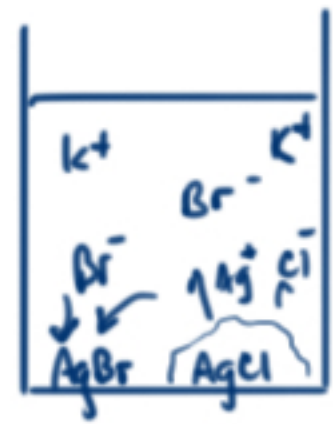
$(0.1)^2[CO_3^{2-}] = 4.8 \times 10^{-12}$

$[CO_3^{2-}] = 4.8 \times 10^{-10}$

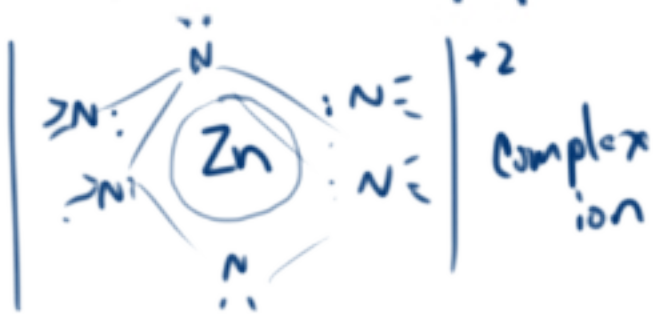
MCAT like

The solubility product constants of AgCl, AgBr, and AgI are, respectively, 1.7×10^{-10}, 4.1×10^{-13}, and 1.5×10^{-16}. If a concentrated solution containing KBr is stirred with solid AgCl

A. silver will be oxidized
B. AgCl will dissolve and solid AgBr will precipitate
C. no reaction will occur
D. silver will be reduced



Add ammonia (imagine the pellet had Zn^{2+}) the $ZnBr_2$ all dissolves and the solution turned purple



$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$Ag^+ + Br^- \rightleftharpoons AgBr$$

$$AgCl + Br^- \longrightarrow AgBr + Cl^-$$

Metathesis reaction toward the least soluble

The K_{sp} of FeS is 8 X 10^{-19}. The K_{sp} of PbS is 3 X 10^{-28}. In a solution containing 0.1 mM concentrations of both Fe^{2+} and Pb^{2+}, which will precipitate first upon dropwise addition of 0.01mM Na_2S?

What is the lowest concentration of Pb^{2+} obtainable before FeS begins to precipitate?

When the anion is a weak base. !

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$$

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$$

How will lowering pH affect the solubility of MgF_2?

Often the problem involves carbonate

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ ← bicarbonate

$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$ ← carbonic acid

remember $H_2CO_3 \rightleftharpoons H_2O + CO_2$

Many hydroxide salts are insoluble.

What effect will ~~changing~~ lowering pH have on Lead(II) solubility ?

$Pb(OH)_2 \quad K_{sp} = 1.4 \times 10^{-20}$

More could dissolve.

$H^+ + OH^- \rightleftharpoons H_2O$

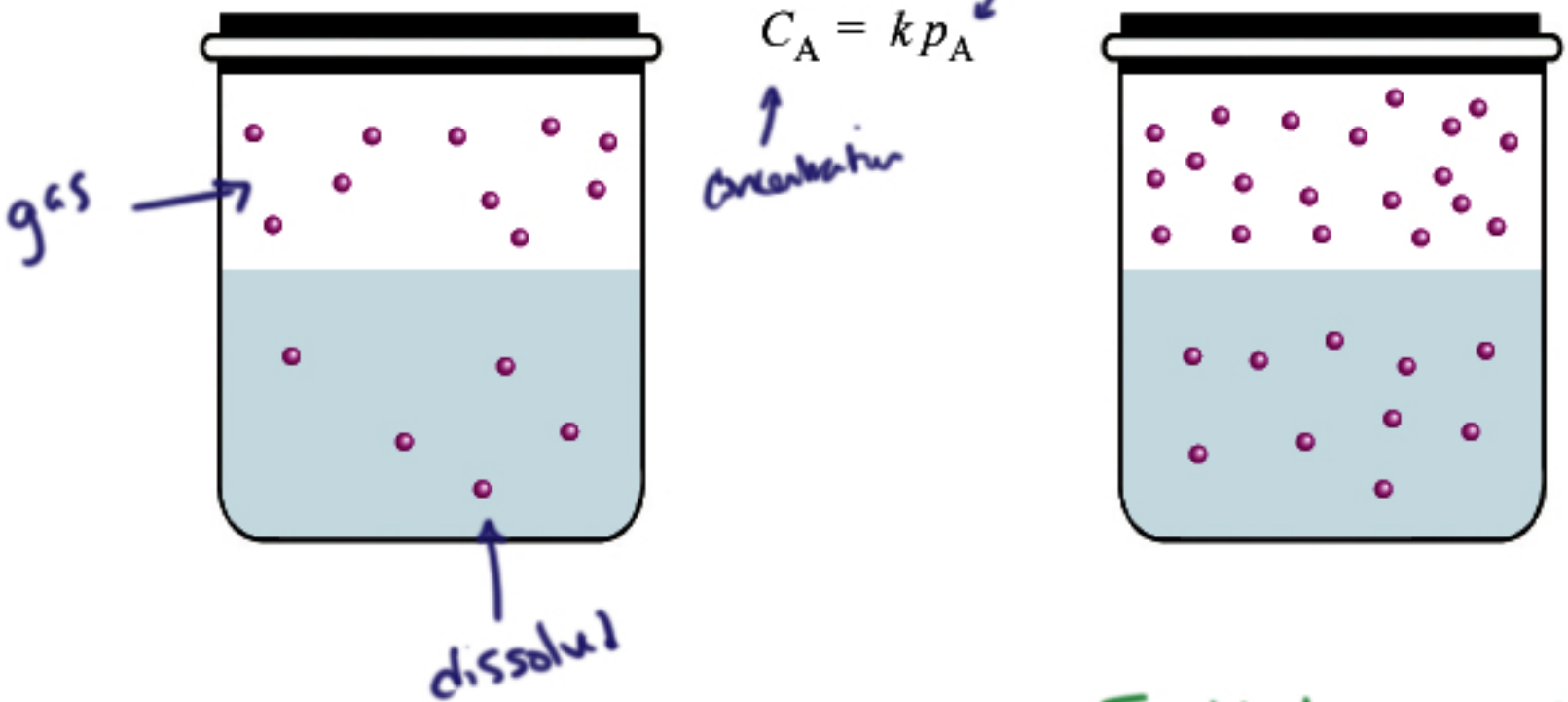
↑ lowering OH^-

Henry's Law

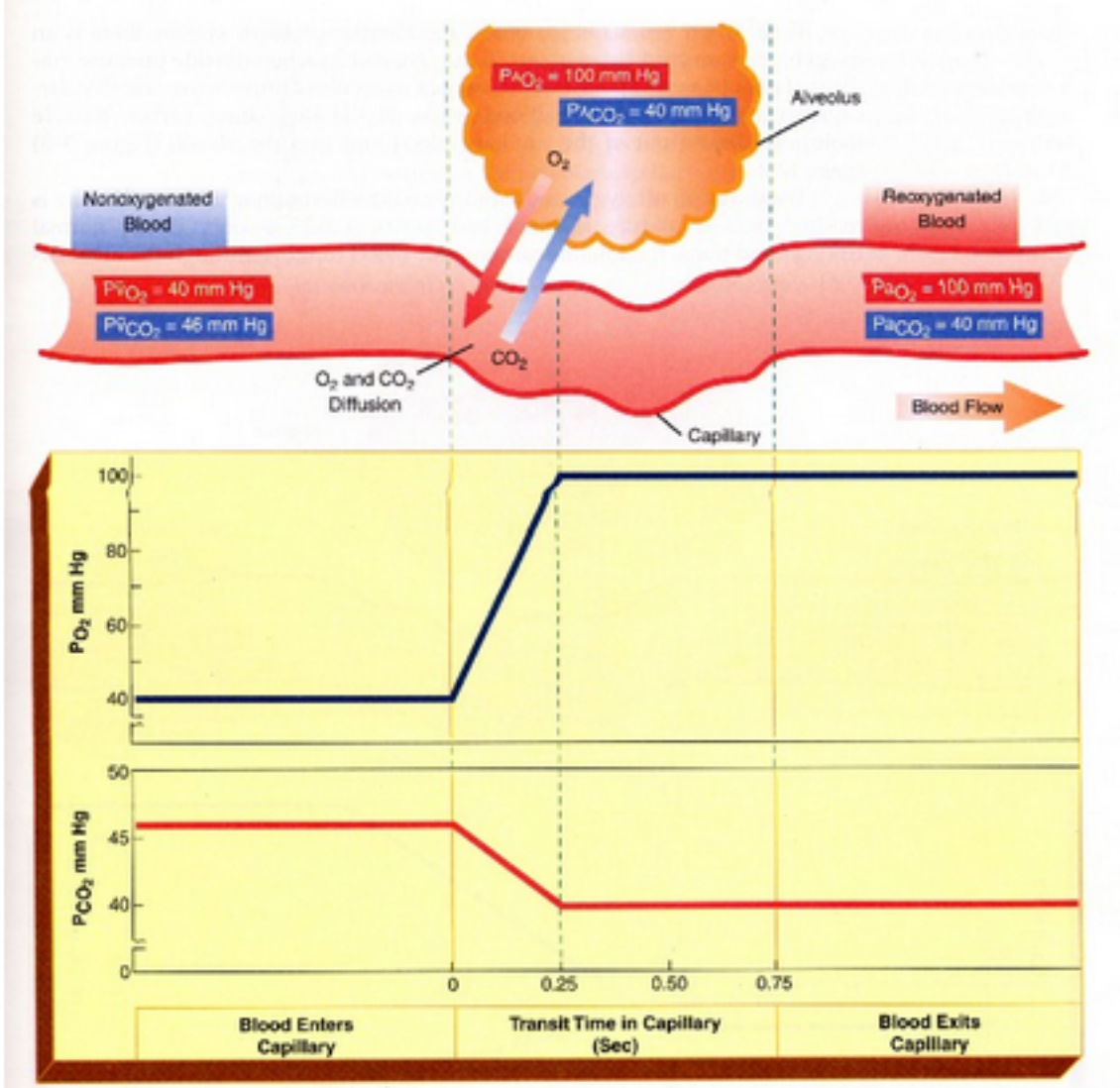
$$C_A = k p_A$$

C_A: concentration

p_A: partial pressure of gas



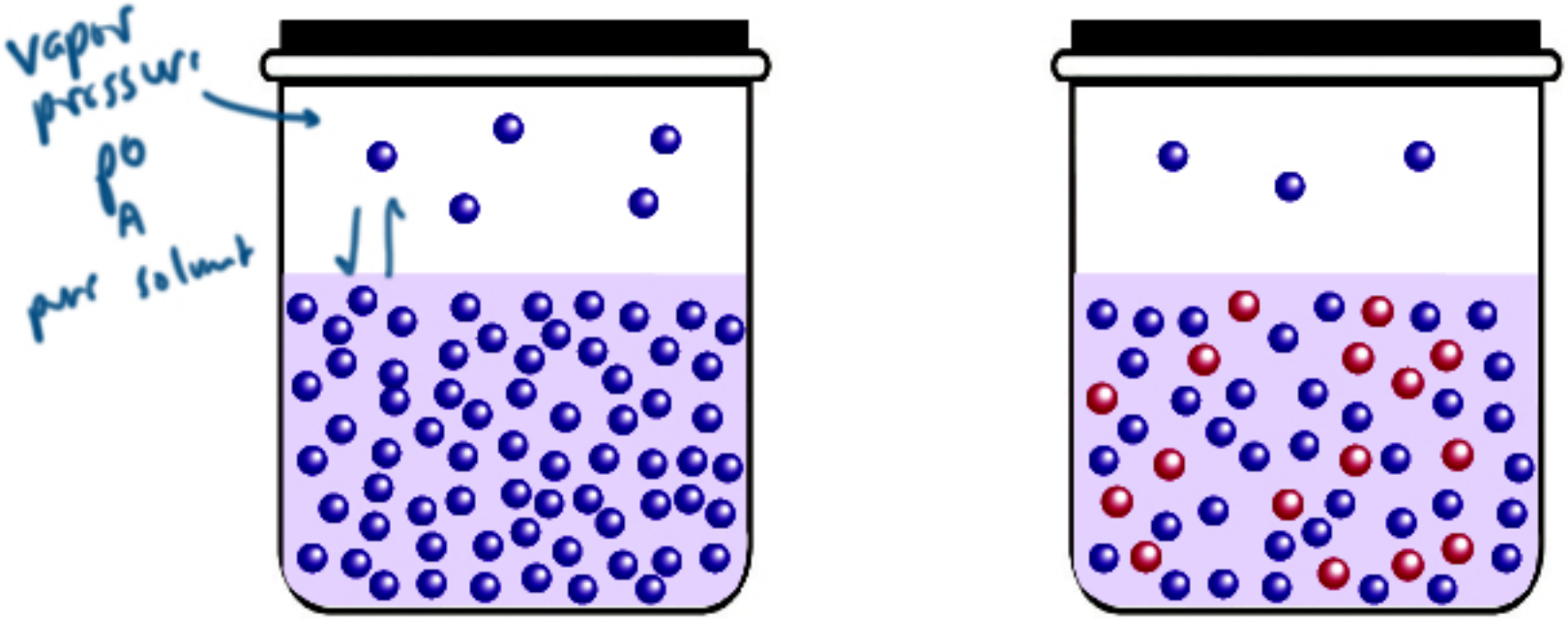
In blood - concentrations of O_2 and CO_2 are influenced by Henry's Law equilibrium pressure.


$P_{A_{O_2}}$ = 100 mm Hg
$P_{A_{CO_2}}$ = 40 mm Hg
Alveolus
O_2
Nonoxygenated Blood
Reoxygenated Blood
$P_{\bar{v}_{O_2}}$ = 40 mm Hg
$P_{\bar{v}_{CO_2}}$ = 46 mm Hg
$P_{a_{O_2}}$ = 100 mm Hg
$P_{a_{CO_2}}$ = 40 mm Hg
CO_2
O_2 and CO_2 Diffusion
Capillary
Blood Flow
100
80
60
40
P_{O_2} mm Hg
50
45
40
0
P_{CO_2} mm Hg
0
0.25
0.50
0.75
Blood Enters Capillary
Transit Time in Capillary (Sec)
Blood Exits Capillary

$$p_A = X_A p_A^o$$

Raoult's Law

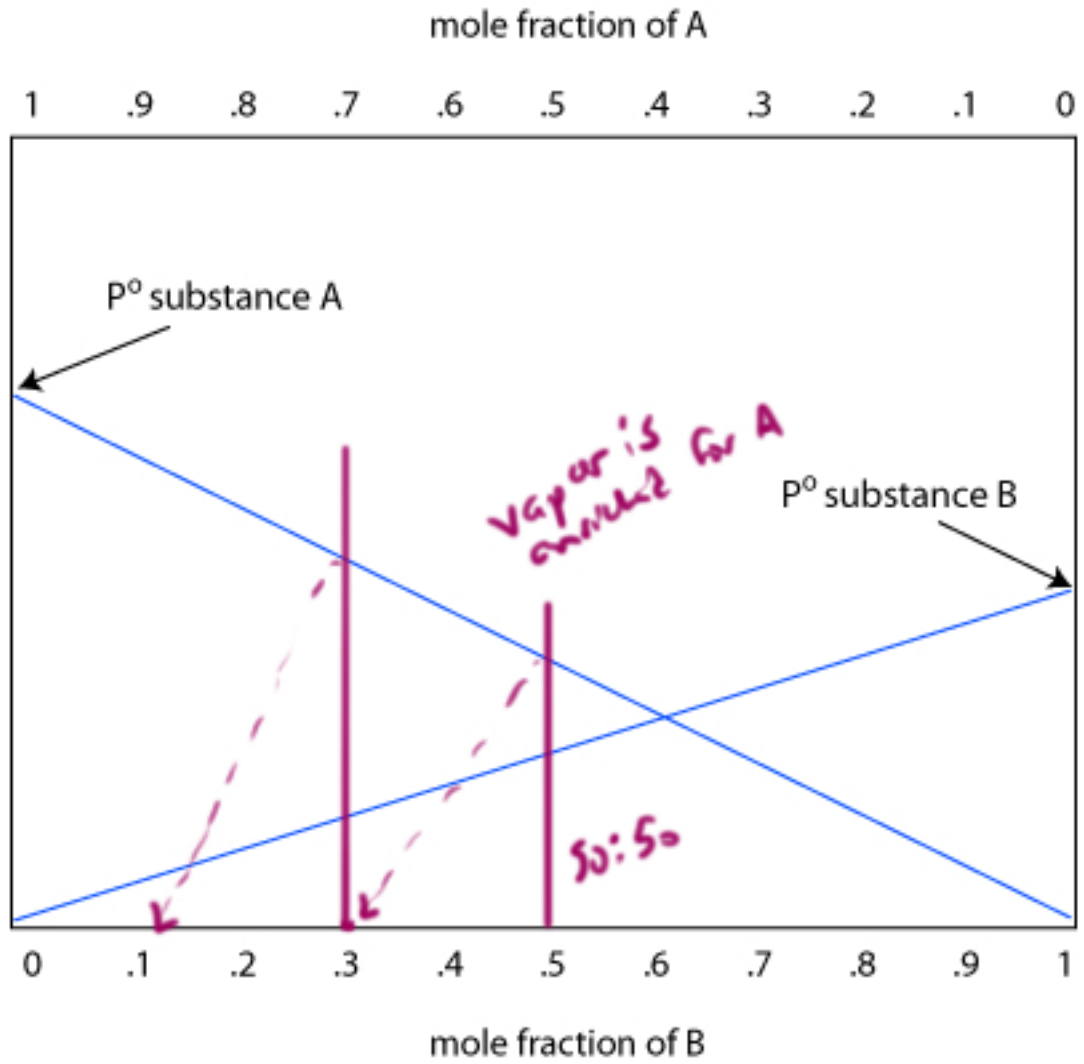
↑ mole fraction of solvent



Ideal solutions obey Raoult's Law.

An ideal solution

Distillation



If the solution is not ideal - may form an azeotrope. (constant boiling mixture)

vapor has the same composition as the mixture.

Colligative Properties

Freezing Point Depression and Boiling Point Elevation

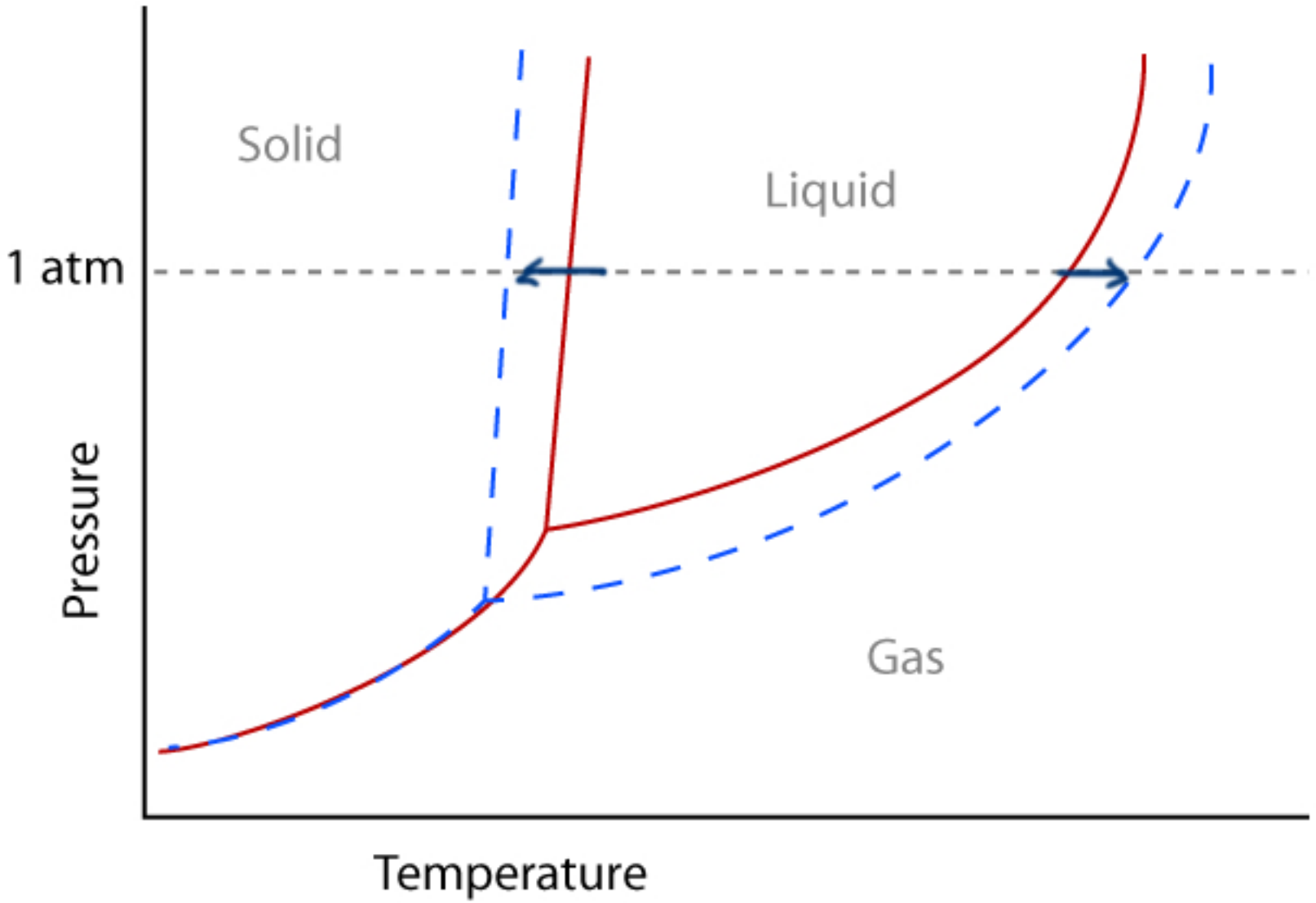
Use 2 for NaCl

FP depression $\Delta T_{FP} = k_f (i)\ m$ ← molality $\frac{\text{mol}}{\text{kg solvent}}$

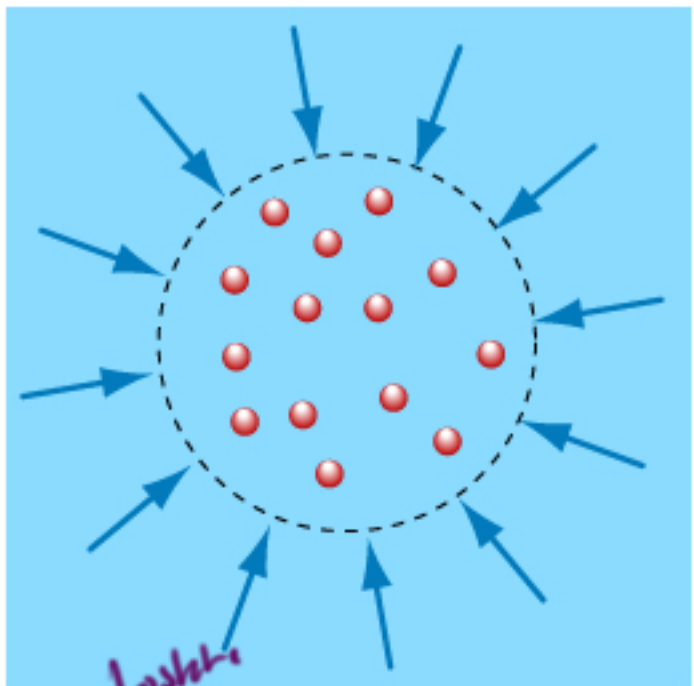
BP elevation $\Delta T_{BP} = k_b (i)\ m$

For water, $k_f = -1.85\ \text{K}\ \text{L}^{-1}\ \text{mol}^{-1}$

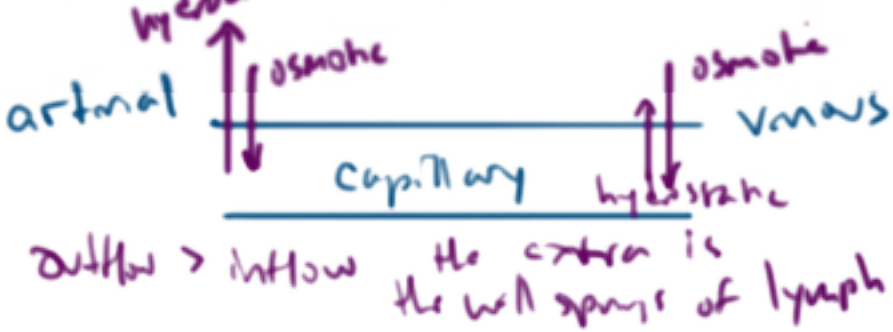
For water, $k_b = 0.51\ \text{K}\ \text{L}^{-1}\ \text{mol}^{-1}$

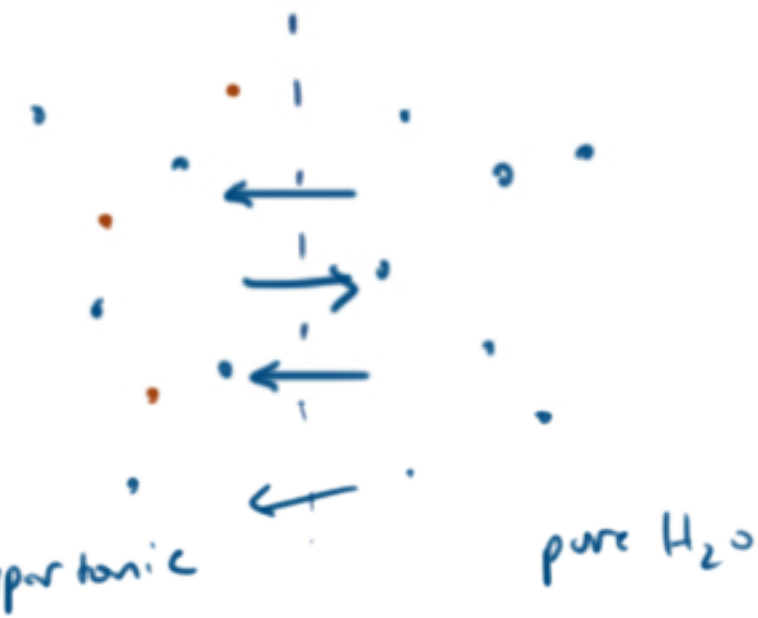

Solid
Liquid
1 atm
Pressure
Gas
Temperature

The osmotic pressure Π in a solution of volume V liters containing n moles of solvent is given by the *van't Hoff* equation:



$$\Pi V = nRT$$





Brønsted–Lowry Acids & Bases

- acid - proton donor
  base - proton receiver

An Brønsted-Lowry acid is a proton (H^+) donor.

$$HCl \longrightarrow H^+ + Cl^-$$

$$H_2O \longrightarrow H^+ + OH^-$$

An Brønsted-Lowry base is a proton (H^+) receiver.

$$NH_3 + H^+ \longrightarrow NH_4^+$$

$$H_2O + H^+ \longrightarrow H_3O^+$$

other systems

Arrhenius -
acid - H^+ donor
base - OH^- donor
acid + base → salt + H_2O

Lewis
acid - electron pair receiver
base - electron pair donor

- Context is aqueous solutions

acid + base ⇌ base + acid

$H_3CCOOH + H_2O \rightleftharpoons H_3CCOO^- + H_3O^+$

acetic acid — acetate

Weak acids and bases - an equilibrium establishes

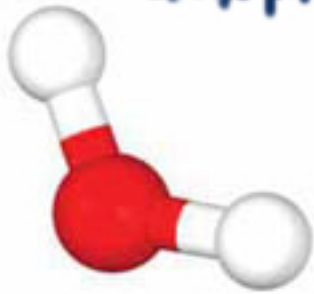
strong acids and bases. completely dissociate or the process to completion

HCl, H_2SO_4, HNO_3

$NaOH$ $NaNH_2$ etc

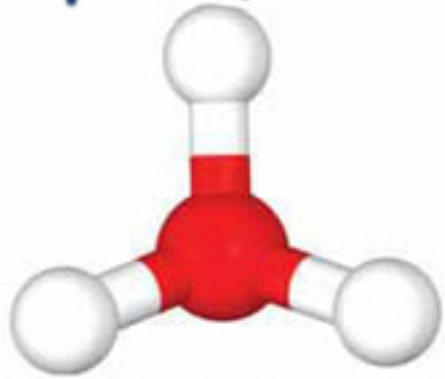
autoprotolysis of H_2O

acid base activity is in coupled equilibrium with autoprotolysis of H_2O



1 Bonded hydrogen ions dissociate from the water molecules ($2H_2O$)

2 Hydroxide ion (OH^-) forms the conjugate base



3 Oxonium ion forms a conjugate acid by accepting H^+ ion

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

$$= 1.00 \times 10^{-14}$$

At 25°C the autoprotolysis of pure water, shown below, attains equilibrium hydronium and hydroxide ion concentrations of about 1×10^{-7} moles per liter for each. The equilibrium concentrations vary somewhat with temperature, however. At 0°C, the concentrations are about 8×10^{-8} moles per liter, and at 100°C the concentrations are about 7×10^{-7} moles per liter. What does this directly imply about the autoprotolysis of water?

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

a. Autoprotolysis of water is a second order reaction.
b. Autoprotolysis of water is an endothermic process.
c. Autoprotolysis of water is spontaneous.
d. Water is a strong electrolyte.

heat + A ⇌ B

endothermic

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.00 \times 10^{-14}$$

If 0.1 mol HCl in a 1L solution what is the pH?

0.1 M HCl solution

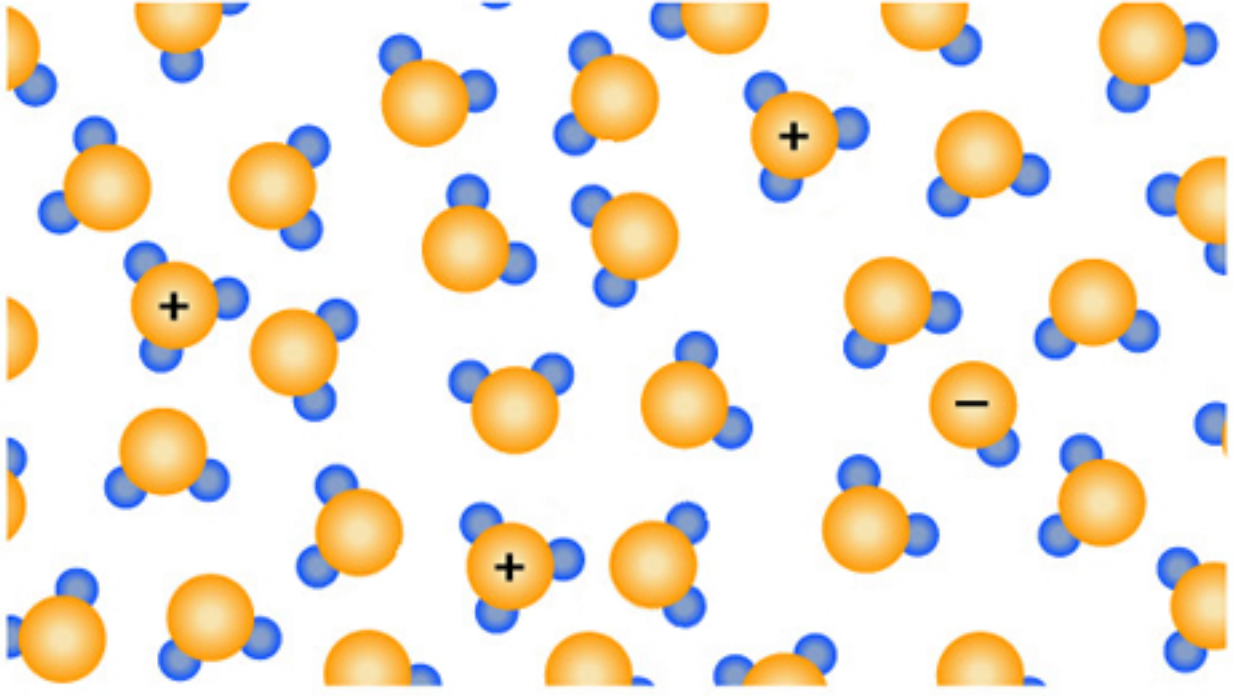
$[H^+] = \frac{1}{10} = 10^{-1}$

$-\log(10^{-1}) = pH = 1$

Acid solutions have a proton pressure

Basic solutions have a proton pull

an acidic solution



$\log(10^a) = a$

$$pH = -\log[H^+]$$

$\log(100) = 2$

$\log(1000) = 3$

$\log(1) = 0$ $\log(10) = 1$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+][OH^-]$$

$$= 1.00 \times 10^{-14}$$

Calculate the pH of a 0.001M solution of NaOH.

$[OH^-] = 10^{-3}$

$[H^+][OH^-] = 10^{-14}$

$[H^+] = 10^{-11}$

$pH = 11$

Use the following relationship to calculate the pH of a 0.001M solution of NaOH

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_{\mathrm{w}} = 14$$

$HA \rightleftharpoons A^- + H^+$

Acids

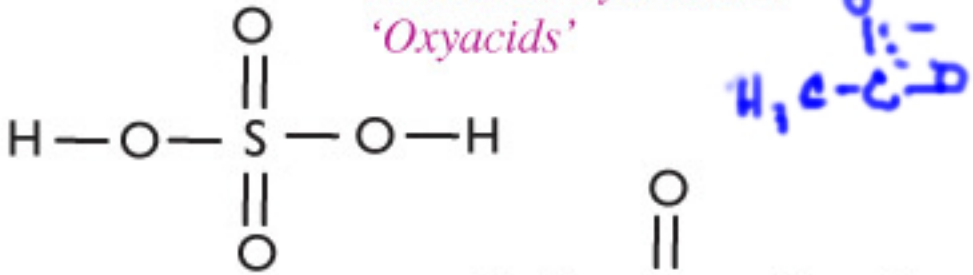
F—H ← weak

Cl—H Br—H

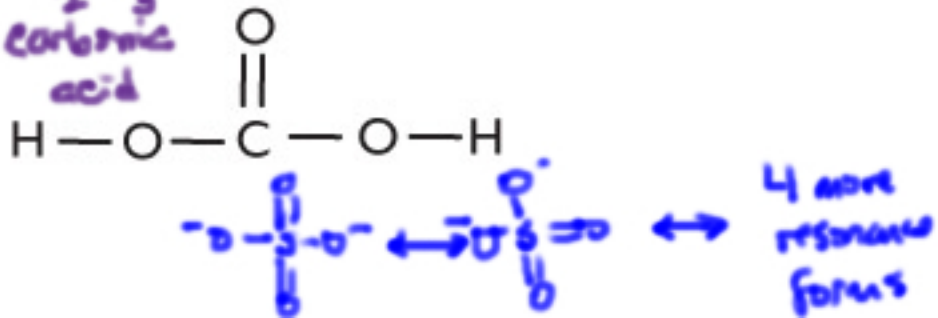
Nonmetal Hydrides

N≡C—H

Nonmetal Hydroxides 'Oxyacids'



H_2CO_3 carbonic acid



Bases

Metal Hydrides

Na—H Li—H

$NaH + H_2O \rightarrow H_2 + OH^- + Na^+$

Metal Oxides

$[Ca^{2+}][O^{2-}]$ $[Na^+]_2[O^{2-}]$

Metal Hydroxides

$[Na^+][OH^-]$

$[K^+][OH^-]$

$[Ca^{2+}][OH^-]_2$

Ammonia & Amines

NH_3 $H_3C—NH_2$

most important organic bases

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log[K_a]$$

EXAMPLE

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

For weak acids, K_a is a number with a negative exponent

The weaker the acid, the higher pKa.

Determine the pK_a:

K_a of HNO_2 : 7 x 10^{-4}

K_a of CH_3CO_2H : 1.8 x 10^{-5} = 4.8

$-\log(7 \times 10^{-4})$

shortcut say $4 - 0.7 = 3.3$

Which is the stronger acid?

$HA \rightleftharpoons A^- + H^+$

CF_3CO_2H	CH_3CO_2H	CH_3CH_2OH
K_a : 5.9×10^{-1}	K_a : 1.8×10^{-5}	K_a : 1.3×10^{-16}

conjugate base

conjugate base $CH_3CH_2O^-$

weakest

$pK_a = 15.9$

$K = e^{-\Delta G^\circ / RT}$

True or false:? The larger the pK_a the weaker the acid.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

$$pK_b = -\log[K_b]$$

EXAMPLE

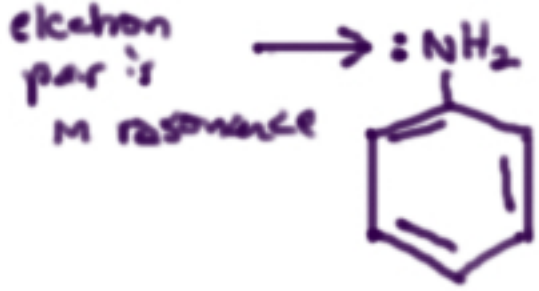
$$\frac{[NH_4^+][OH^-]}{[NH_3]}$$

Determine the pK_b:

K_b of CH_3NH_2 : 4.4×10^{-4} 3.6

K_b of CN^- : 1.6×10^{-5} 4.8

Which is the stronger base?



NH_3	CH_3NH_2	$C_6H_5NH_2$
K_b : 1.8 x 10^{-5}	K_b : 4.4 x 10^{-4}	K_b : 4.3 x 10^{-10}

NH_4^+

$H_3C\,NH_3^+$

↑ electron donating by induction

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_a acetic acid $\approx 10^{-5}$

K_b acetate $\approx 10^{-9}$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \times K_b = \frac{[H^+]\,[A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H^+]\,[OH^-] = K_w$$

$$K_a \times K_b = K_w$$

K_a of an acid

K_b of its conjugate base

The stronger a weak acid the weaker its conjugate base.

$K = e^{-\Delta G^\circ / RT}$

ΔG°

strong

-20

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

0

$H_3O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O$

20

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

40 weak

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$

60

80

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

Acid		pK_a	Base	pK_b
H_2SO_4	sulfuric acid	–3	HSO_4^-	17
HCl	hydrochloric acid	–3	Cl^-	17
HNO_3	nitric acid	–1	NO_3^-	15
H_3O^+	hydronium ion	0	H_2O	14
HSO_4^-	bisulfate	1.8	SO_4^{2-}	12.1
H_3PO_4	phosphoric acid	2.1	$H_2PO_4^-$	11.9
HF	hydrofluoric acid	3.2	F^-	10.8
CH_3COOH	acetic acid	4.7	CH_3COO^-	9.3
H_2CO_3	carbonic acid : $CO_2(aq)$	6.3	HCO_3^-	7.7
$H_2PO_4^-$	dihydrogen phosphate	7.2	HPO_4^{2-}	11.9
HCN	hydrogen cyanide	9.2	CN^-	4.8
NH_4^+	ammonium ion	9.25	NH_3	4.75
HCO_3^-	bicarbonate	10.3	CO_3^{2-}	3.7
HPO_4^{2-}	hydrogen phosphate	12.3	PO_4^{3-}	1.7
H_2O	water	14	OH^-	0
NH_3	ammonia	23	NH_2^-	–9

What is the pH of a 0.1M CH_3CO_2H solution? K_a : 1.8×10^{-5}

$HA \rightleftharpoons A^- + H^+$

$$K_a = \frac{[H^+]\,[CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

$[H^+] \approx [CH_3CO_2^-]$ *so approximate* $[H^+] = [CH_3CO_2^-]$ ← ignoring $[H^+]$ already there

$[CH_3CO_2H] \approx 0.1M$ *so approximate* $[CH_3CO_2H] = 0.1M$ ← assuming not too much dissociated

$$K_a = \frac{[H^+]^2}{0.1} = 1.8 \times 10^{-5}$$

$[H^+]^2 = 1.8 \times 10^{-6}$

$[H^+] = 1.4 \times 10^{-3}$

$\sqrt{10^{2x}} = 10^x$

$(10^x)(10^x) = 10^{x+x}$

⇒ 2 ways to look at it

1) What's the pH of a buffer solution?

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{[HA]}{[A^-]} \times K_a$$

$$\log [H^+] = \log K_a + \log \left(\frac{[HA]}{[A^-]} \right)$$

Suppose a solution:
0.1 M acetic acid
1.0 M acetate

$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$ (effect / cause)

$= 5 + \log\left(\frac{1}{0.1}\right)$

$= 6$

After adding 0.1 mol HCl to 1L

$pH = 5 + \log\left(\frac{0.9}{0.2}\right)$

$= 5.5$

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right)$$

! Henderson-Hasselbach Equation !

2) What is the state of ionization of a solution component?

$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$ (cause / effect)

Asp-$COOH$ ← $pK_a \sim 4$

physiological pH (cytosol 7.4)

$7 = 4 + \log\left(\frac{[A^-]}{[HA]}\right)$

$\log\left(\frac{[A^-]}{[HA]}\right) = 3$

$\frac{[A^-]}{[HA]} = \frac{1000}{1}$

Lys-NH_3^+ ← $pK_a \sim 10.5$

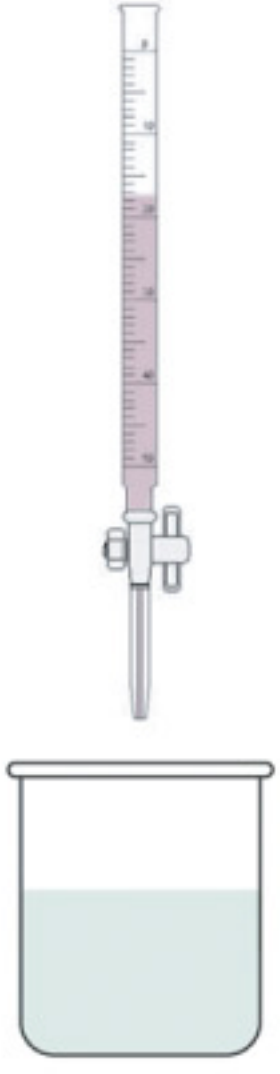
$7 = 10.5 + \log\left(\frac{[A^-]}{[HA]}\right)$

$\frac{[A^-]}{[HA]} = \frac{1}{3000}$

$$\text{pH} = \text{p}K_{\text{ind}} + \log\left(\frac{[A^-]}{[HA]}\right)$$

4 7

$$HA \rightleftharpoons A^- + H^+$$



$$N_a V_a = N_b V_b$$

$N_a(0.1L) = (0.2N)(.025)$

$N_a = .05N$

100 ml of HCl solution was completely neutralized by 25ml of 0.2N NaOH solution. What was the normality of the HCL solution?

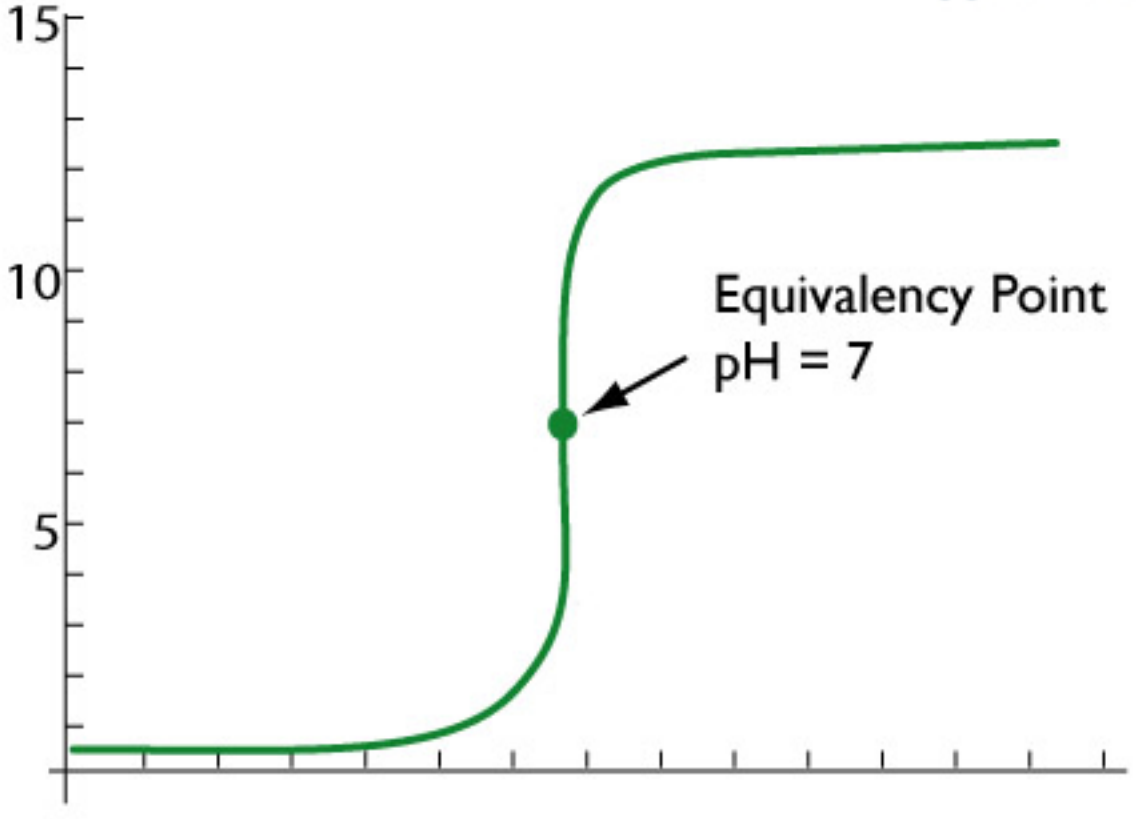
H_2SO_4 $\frac{2\ equiv}{mol} \cdot 1M\left(\frac{mol}{L}\right) = 2N$

HCl $\frac{1\ equiv}{mol} \cdot 1M = 1N$

equivalency point - when you've added exactly as many equivalents of base as acid.

$HCl + NaOH \longrightarrow NaCl + H_2O$

neutral solution



Titration of a Strong Acid with a Strong Base

$H_3CCOOH + NaOH \longrightarrow H_3CCOO^- \; Na^+ + H_2O$

acetic acid

acetate

solution at equivalency is a solution of weak base

15

10

5

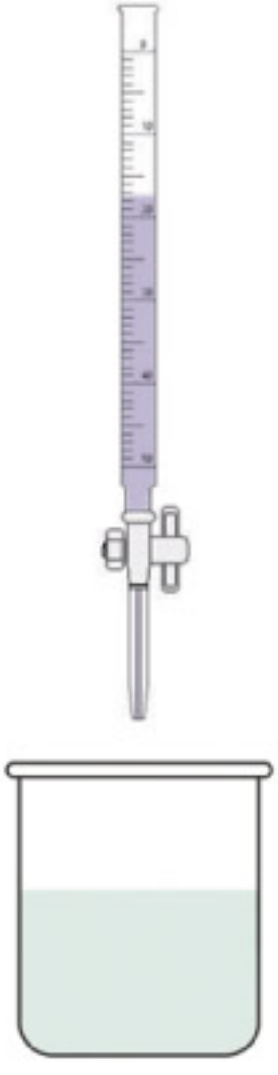
buffer solution $[HA] = [A^-]$

Half Equivalency
pH = pK_a

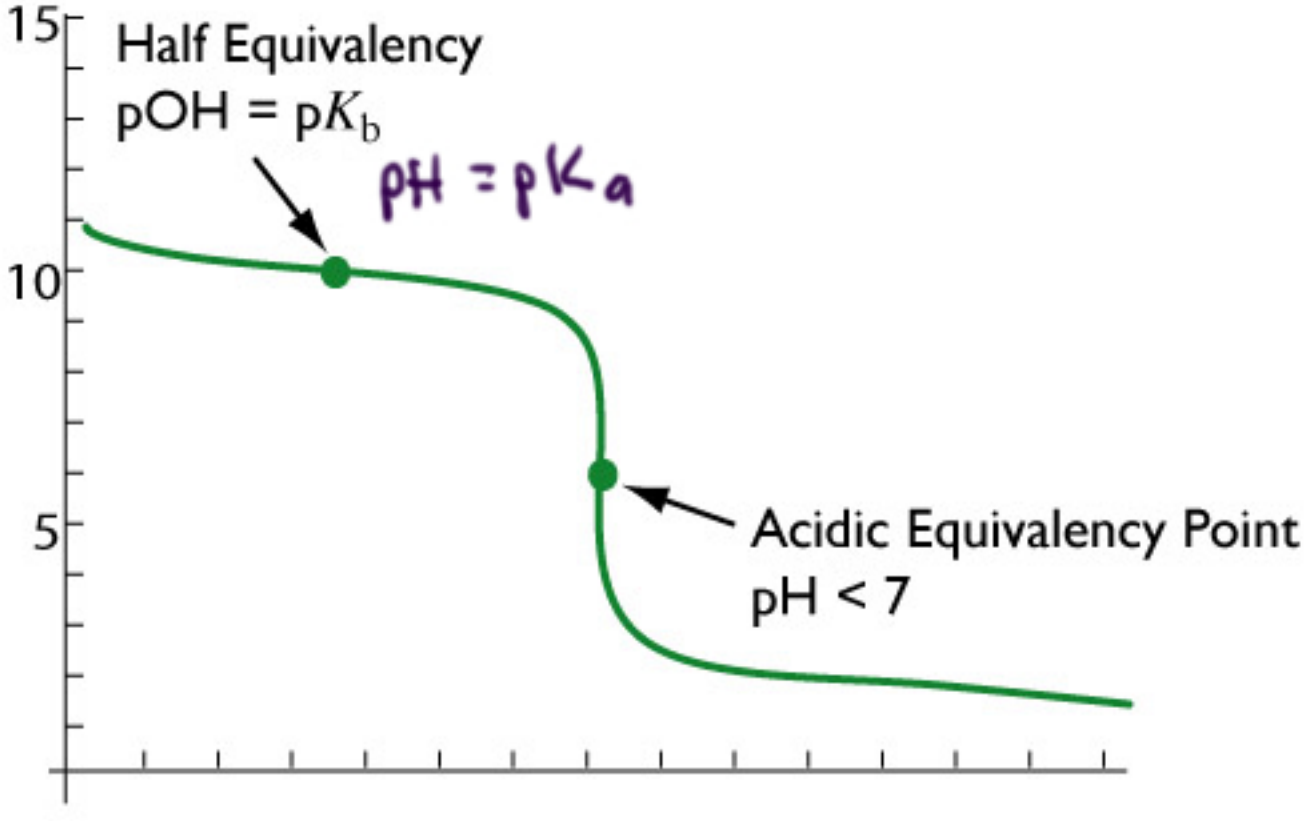
Basic Equivalency Point
pH > 7

half way

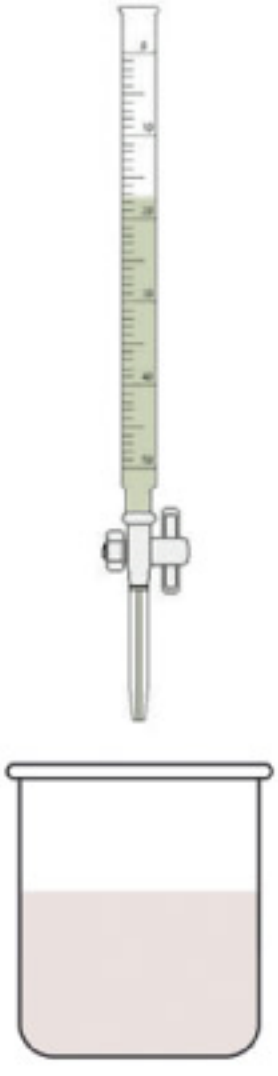
Titration of a Weak Acid with a Strong Base



$$\ddot{N}H_3 + HCl \longrightarrow NH_4^+ Cl^-$$



Titration of a Weak Base with a Strong Acid



$H_2CO_3 + NaOH \longrightarrow -HCO_3 \; Na^+$ bicarbonate

$-HCO_3 + NaOH \longrightarrow 2^-CO_3 \; 2Na^+$

15

10

5

pH = pK_{a2}

pH = pK_{a1}

2^-CO_3 solution

Equivalency Point

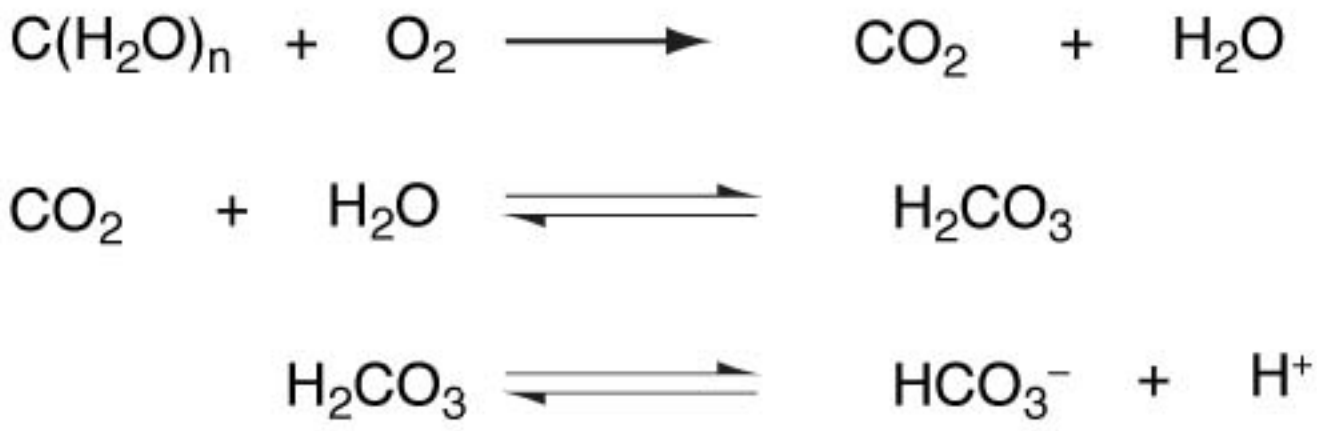
← pKa of bicarbonate

$-HCO_3$ solution

Equivalency Point

↑ pKa of carbonic acid

Titration of a Diprotic Acid with a Strong Base



Maintainance of acid-base balance in physiology

- Exhalation of CO_2
- Excretion of $H_2PO_4^-$ and NH_4^+ by the kidneys
- $NaHCO_3$ buffer system
- Secondary buffer systems including phosphates and proteins

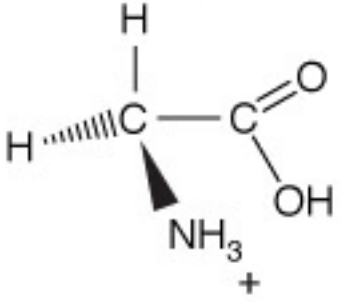
Which results from combining a concentrated solution of HCl with concentrated K_2CO_3?

forms carbonic acid

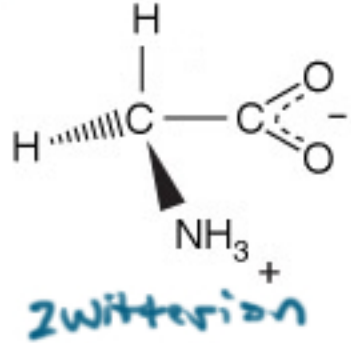
A. formation of a colored complex
B. precipitation
C. liberation of gas
D. a solution of weak base

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

pH < 2.4

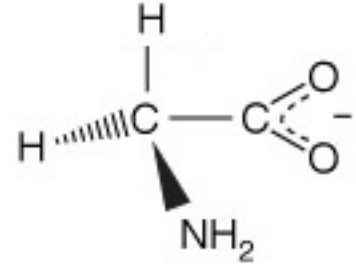


2.4 < pH < 9.8



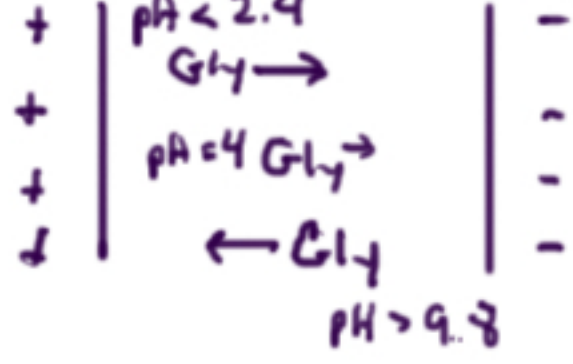
Zwitterion

pH > 9.8



$$K_1 = \frac{[H^+]\,[HGly]}{[H_2Gly^+]} \qquad K_2 = \frac{[H^+]\,[Gly^-]}{[HGly]}$$

$$pK_1 = 2.4 \qquad pK_2 = 9.8$$

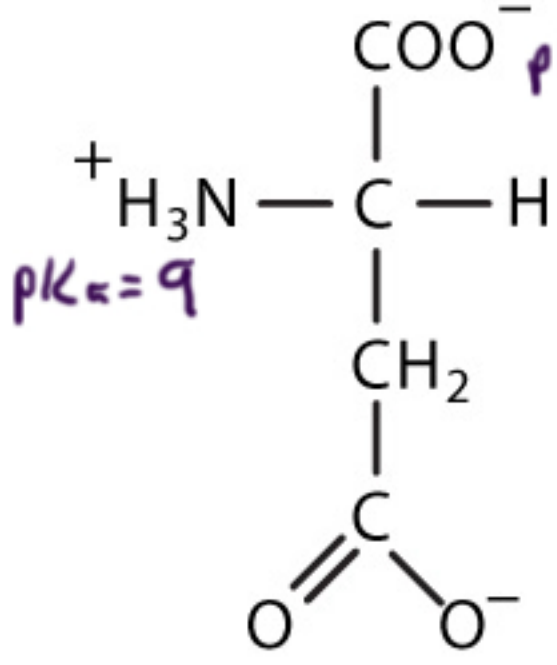


at pI it doesn't migrate

$$\frac{2.4 + 9.8}{2} = 6.1$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Aspartate



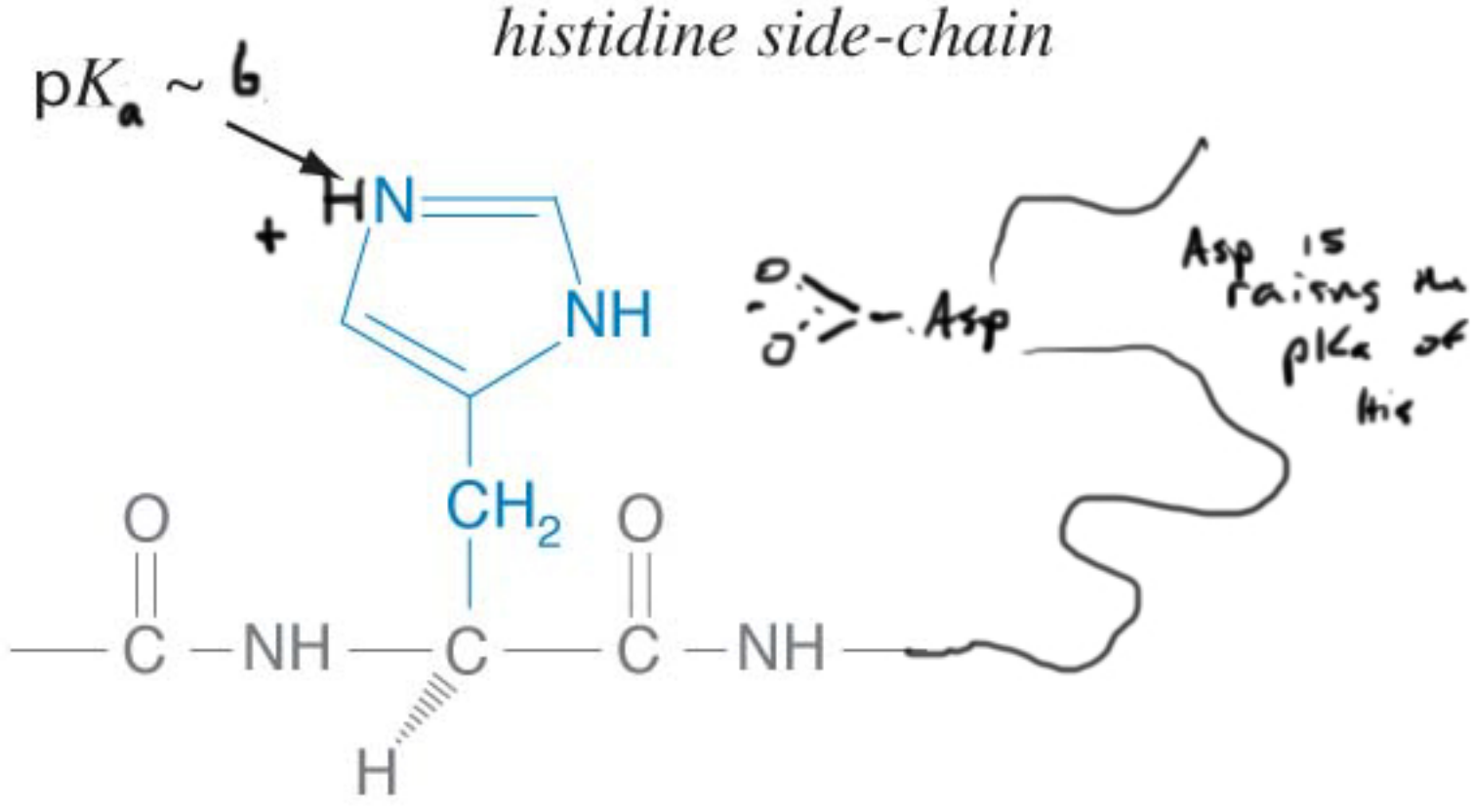
pKa = 4

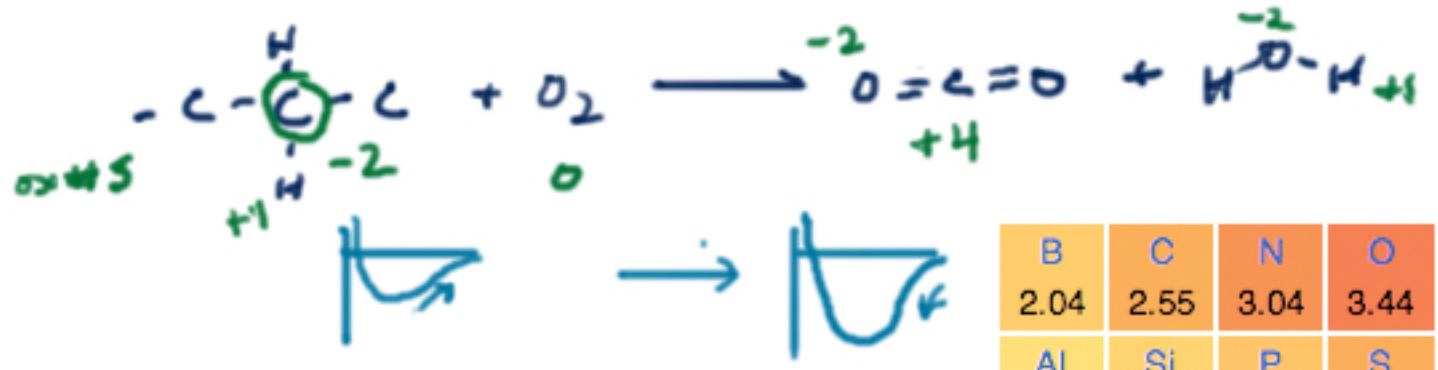
(2 most pKa's)

To find pI

average the like groups.

$$pI = \frac{4+2}{2} = 3$$


histidine side-chain
pKa ~ 6
HN
+
NH
CH2
O
C
NH
C
O
C
NH
H
Asp
Asp is raising the pKa of his



H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

no oxidation #'s change

metathesis reaction

ox #

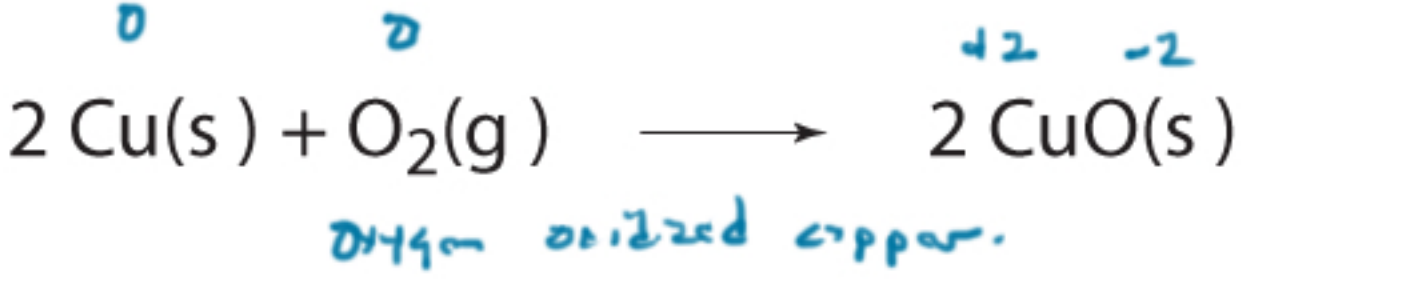
$$\overset{+3\ -2}{Fe_2O_3} + \overset{+2\ -2}{3CO} \longrightarrow \overset{0}{2Fe} + \overset{+4\ -2}{3CO_2}$$

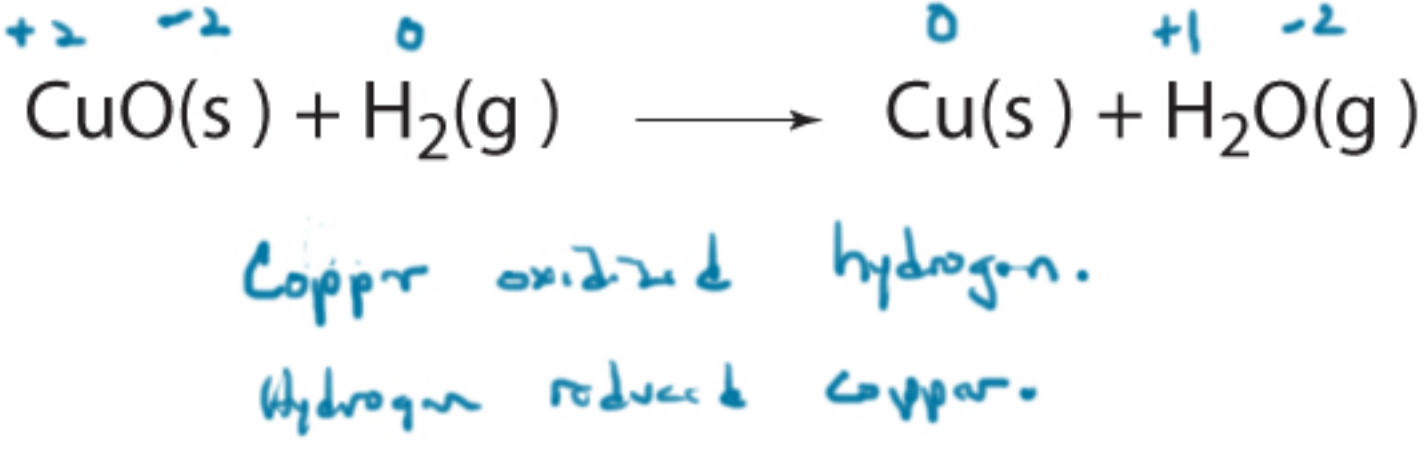
oxidation-reduction reaction

Iron oxidized carbon.

Carbon reduced iron.

ox #s


0
0
+2
-2
2 Cu(s) + O2(g) ⟶ 2 CuO(s)
Oxygen oxidized copper.


+2
-2
0
0
+1
-2
CuO(s) + H2(g) ⟶ Cu(s) + H2O(g)
Copper oxidized hydrogen.
Hydrogen reduced copper.

The oxidation number of an atom is zero in a neutral substance that contains atoms of only one element.

O_2 H_2 C *(graphite)*

The oxidation number of simple ions is equal to the charge on the ion.

Na^{+} Cl^{-} Mg^{2+}

The oxidation number of hydrogen is +1 when it is combined with a nonmetal.

CH_4 NH_3 H_2O

The oxidation number of hydrogen is -1 when combined with a metal.

NaH MgH_2 $LiAlH_4$

Hydride

In compounds the metals in Group IA have an oxidation number of +1.

ox #

KNO_2^{-2}

+1 +3

LiF

Na_2S

In compounds the metals in Group IIA have an oxidation number of +2.

MgH_2 $CaCO_3$ BeO

Oxygen usually has an oxidation number of -2.

H_2O CO_2 MgO

exceptions

O=O

+2
F O F

R-O-O-H
-1
ox #

peroxides

Halogens usually has an oxidation number of -1

AlF_3 HBr $ZnCl_2$

The sum of the oxidation numbers in a neutral compound is zero, and the sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.

SO_4^{-2}

H_2CO_3

+7

$KMnO_4$

+1 -2

ox # 0 0 +3 -1

$$2\,Fe + 3\,Cl_2 \longrightarrow 2\,FeCl_3$$

$$\overset{0}{4\,Al} + \overset{0}{3\,O_2} \longrightarrow \overset{+3}{\overset{-2}{2\,Al_2O_3}}$$

$$2\,Al_2 \;+\; 3\,Zn^{2+} \longrightarrow 2\,Al^{3+} \;+\; 3\,Zn$$

Zinc is oxidizing aluminum.

ox #'s

$$\overset{0}{2\,Al} + \overset{+3\ -2}{Fe_2O_3} \longrightarrow \overset{+3\ -2}{Al_2O_3} + \overset{0}{2\,Fe}$$

Fe - oxidizing agent

Al - reducing agent

Ox #

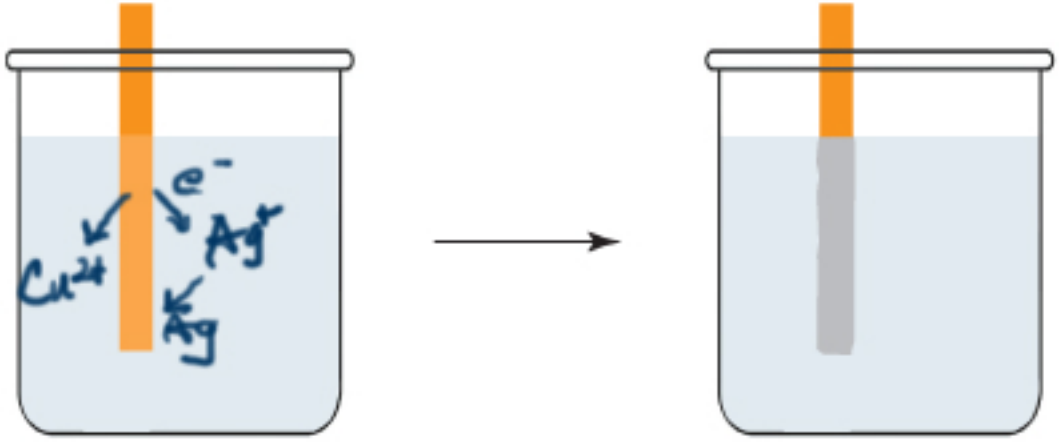
$$\overset{0}{3\,Ag} + 4\,\overset{+1\ +5\ -2}{HNO_3} \longrightarrow 3\,\overset{+1\ +5\ -2}{AgNO_3} + 2\,H_2O + \overset{+2\ -2}{NO}$$

Oxidizing agent - N (one of them)

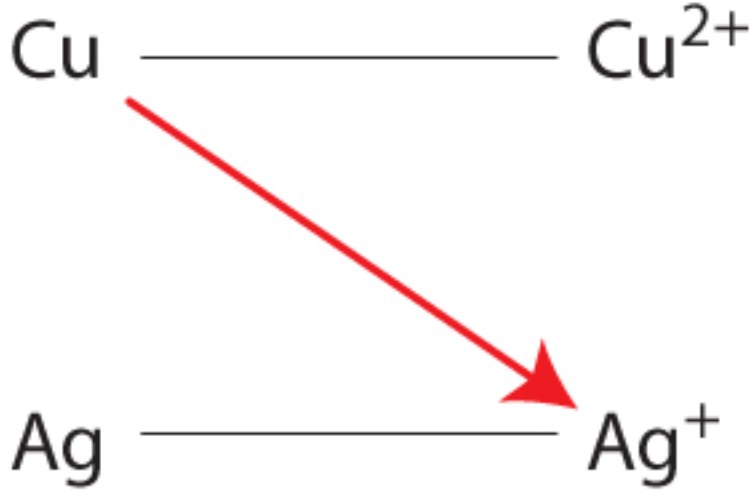
Reducing agent - Ag

$$Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

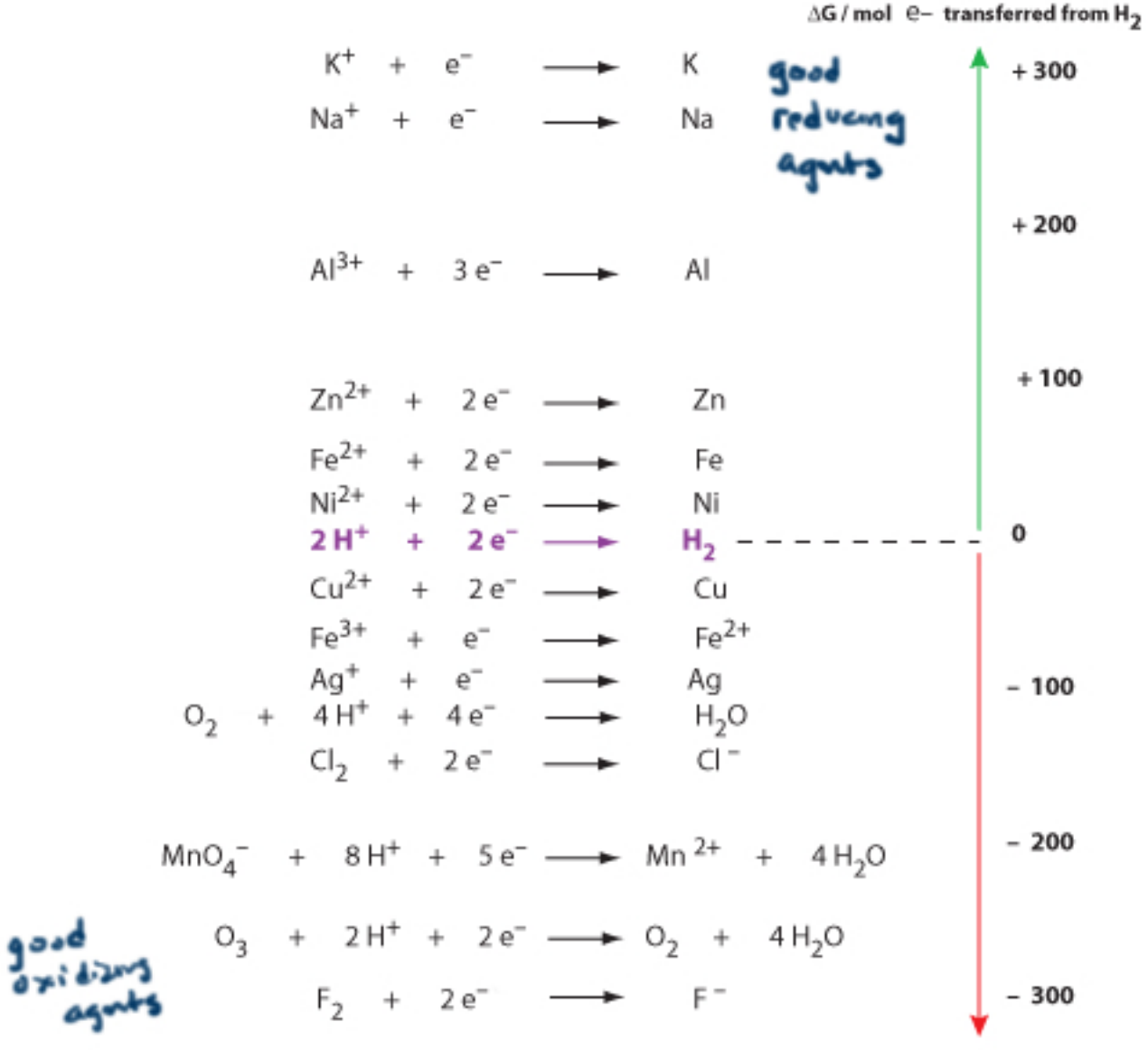
Ag^{+} oxidized Cu



$$Cu(s) + 2\,Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$



the fall of the electron


ΔG / mol e– transferred from H2
K+ + e– → K
Na+ + e– → Na
good reducing agents
Al3+ + 3 e– → Al
Zn2+ + 2 e– → Zn
Fe2+ + 2 e– → Fe
Ni2+ + 2 e– → Ni
2 H+ + 2 e– → H2
Cu2+ + 2 e– → Cu
Fe3+ + e– → Fe2+
Ag+ + e– → Ag
O2 + 4 H+ + 4 e– → H2O
Cl2 + 2 e– → Cl –
MnO4– + 8 H+ + 5 e– → Mn 2+ + 4 H2O
O3 + 2 H+ + 2 e– → O2 + 4 H2O
F2 + 2 e– → F –
good oxidizing agents
+ 300
+ 200
+ 100
0
– 100
– 200
– 300

Reacting potassium metal with pure water produces

a. potassium oxide, K_2O
b. a basic solution
c. an acidic solution
d. oxygen gas

$2K + 2H_2O \longrightarrow H_2 + 2OH^-$

Reducing Agents

$LiAlH_4$
lithium aluminium hydride

$NaHg$
sodium amalgum

$NaBH_4$
sodiuim borohydride

H_2
hydrogen

Metals

Carbon

Hydrocarbons

Oxidizing Agents

O_2 oxygen

O_3 ozone

F_2 fluorine

Cl_2 chlorine

Br_2 bromine

I_2 iodine

OCl^- hypochlorite

ClO_3^- chlorate

HNO_3 nitric acid

CrO_3 chromium trioxide

CrO_4^{2-} chromate

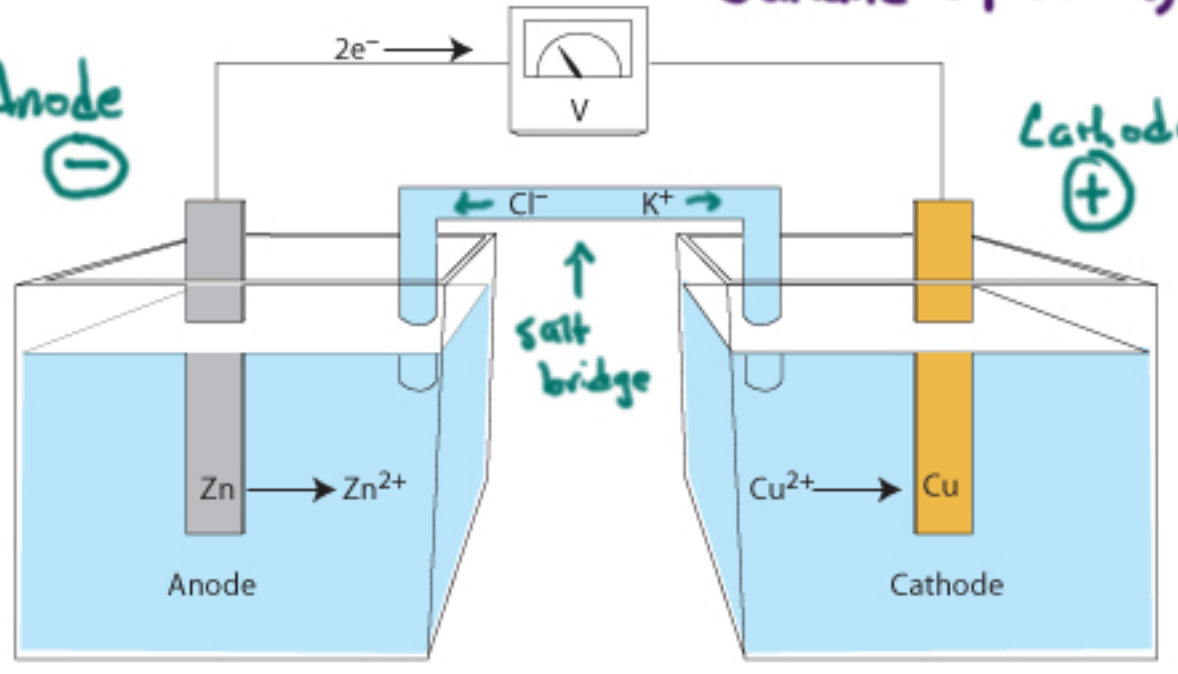
$Cr_2O_7^{2-}$ dichromate

H_2O_2 peroxides

MnO_4^- permanganate

$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$

Galvanic (spontaneous) Electrochemistry



Anode ⊖

Cathode ⊕

galvanic anode is ⊖

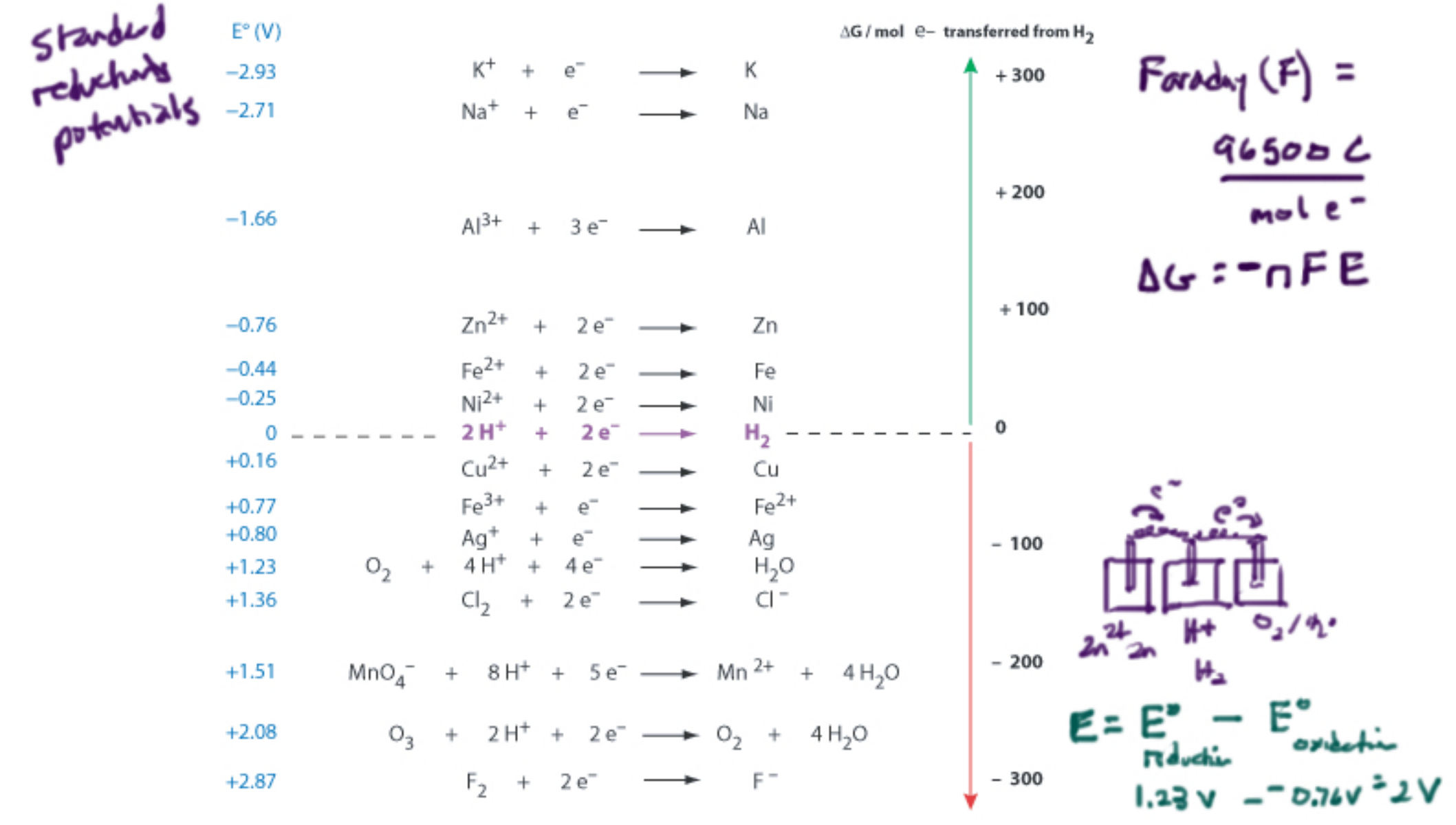
$Zn \longrightarrow Zn^{2+} + 2e^-$ oxidation half reaction

$Cu^{2+} + 2e^- \longrightarrow Cu$ reduction half reaction

$Zn \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu$

Standard reduction potentials

E° (V)					
−2.93	K^+	+	e^-	→	K
−2.71	Na^+	+	e^-	→	Na
−1.66	Al^{3+}	+	$3\,e^-$	→	Al
−0.76	Zn^{2+}	+	$2\,e^-$	→	Zn
−0.44	Fe^{2+}	+	$2\,e^-$	→	Fe
−0.25	Ni^{2+}	+	$2\,e^-$	→	Ni
0	$2\,H^+$	+	$2\,e^-$	→	H_2
+0.16	Cu^{2+}	+	$2\,e^-$	→	Cu
+0.77	Fe^{3+}	+	e^-	→	Fe^{2+}
+0.80	Ag^+	+	e^-	→	Ag
+1.23	O_2 + $4\,H^+$	+	$4\,e^-$	→	H_2O
+1.36	Cl_2	+	$2\,e^-$	→	Cl^-
+1.51	MnO_4^- + $8\,H^+$	+	$5\,e^-$	→	Mn^{2+} + $4\,H_2O$
+2.08	O_3 + $2\,H^+$	+	$2\,e^-$	→	O_2 + $4\,H_2O$
+2.87	F_2	+	$2\,e^-$	→	F^-



Faraday (F) = $\frac{96500\ C}{mol\ e^-}$

$\Delta G = -nFE$

$E = E^\circ_{reduction} - E^\circ_{oxidation}$

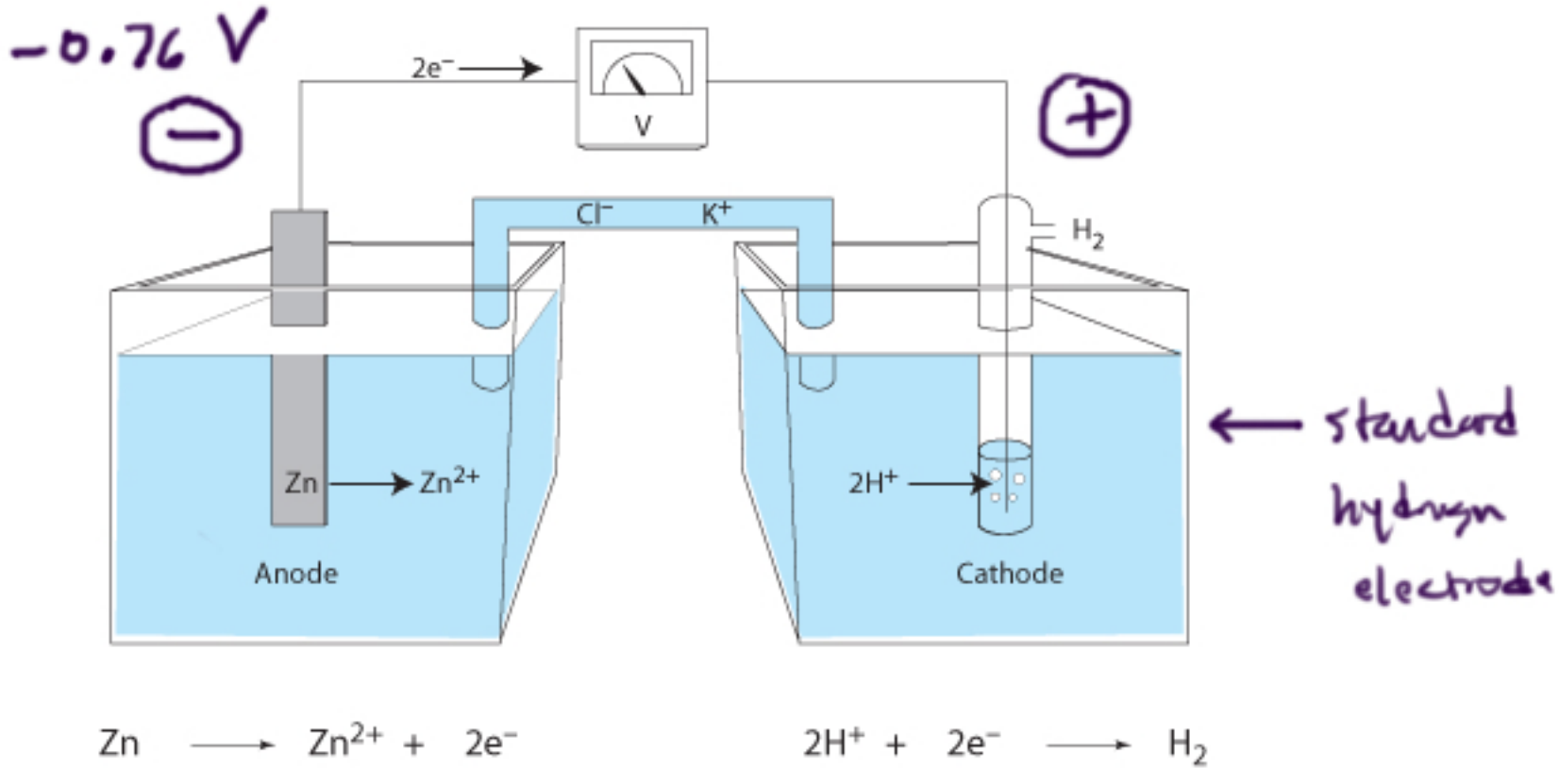
1.23 V − −0.76 V = 2 V

The anode and cathode reactions for the silver oxide battery are respectively as follows:

$$Zn\,(s) + 2OH^-\,(aq) \longrightarrow Zn(OH)_2\,(s) + 2e^-$$
$$Ag_2O\,(s) + H_2O + 2e^- \longrightarrow 2Ag\,(s) + 2OH^-(aq)$$

The standard reduction potential of Zn^{2+} is –0.762, and the standard reduction potential of Ag+ is 0.800 V. What is the approximate emf of the silver oxide battery?

a. 0.04 V
b. 0.8 V
c. 1.6 V
d. 2.4 V



$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_2$$

Stoichiometry in electrochemistry often involves converting to DC current parameters.

Faraday = $\frac{96500\ C}{mol\ e^-}$

Commercial aluminum is formed electrolytically from aluminum oxide (Al_2O_3), which is reduced at the cathode. Approximately how long must a current of 965*A* be applied to form 27 g of aluminum?
(Note that 96500 *C* = 1 mole e^-)

1 mol →

$Al^{3+} + 3e^- \rightarrow Al$

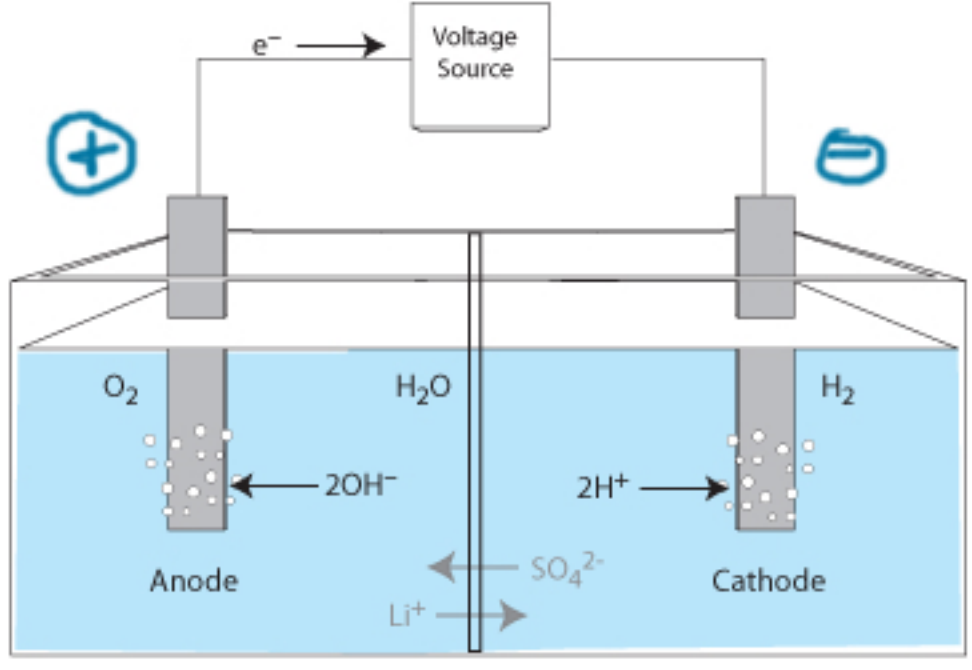
$\frac{1\ mol\ Al}{3\ mole^-}$ $\frac{3\ mole^-}{mol\ Al}$

a. 1 second
b. 1 1/2 minutes
c. 5 minutes
d. 300,000 seconds

$\frac{3\ mol\ e^-}{mol\ Al} \cdot 1\ mol\ Al \cdot \frac{96500\ C}{mole^-} \cdot \frac{1\ s}{965\ C} = 300\ s$

Electrolytic Cell

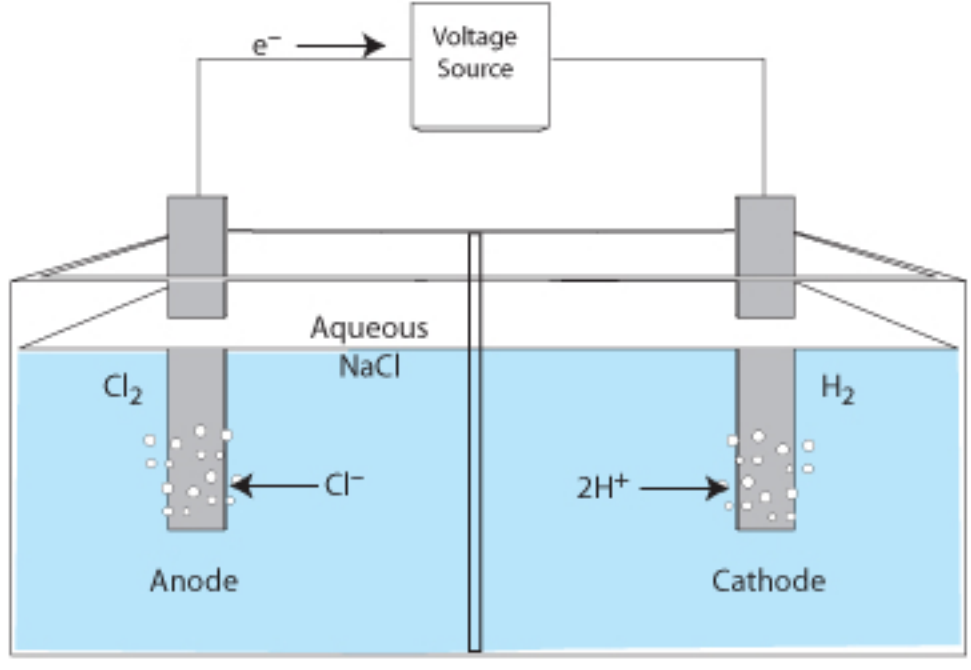
Anode is ⊕ in an electrolytic cell.



$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

$2H^+ + 2e^- \longrightarrow H_2$

Electrolysis of brine (concentrated NaCl)



$2Cl^- \longrightarrow Cl_2 + 2e^-$ $\qquad$ $2H^+ + 2e^- \longrightarrow H_2$

Nernst equation →

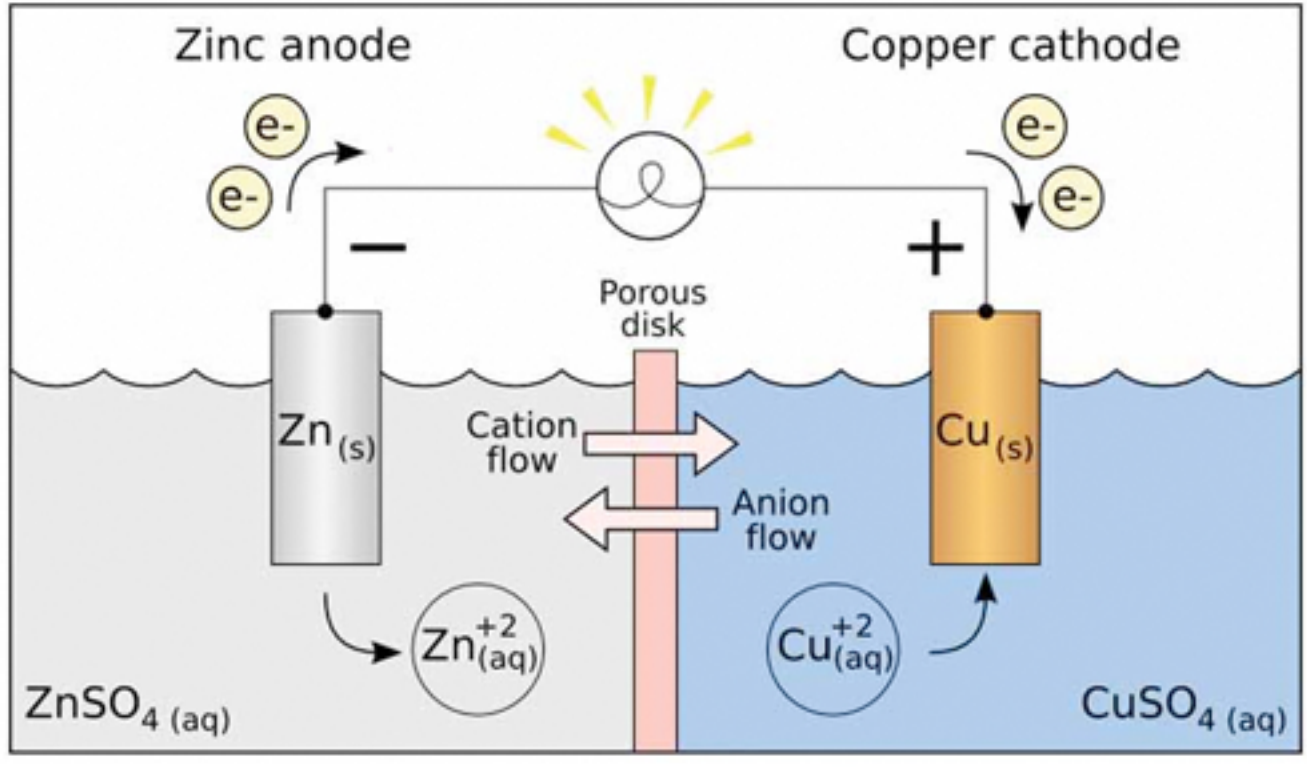
$$\Delta E = \Delta E^{o} - \frac{0.0592\ V}{n} \log Q$$

$\Delta G = \Delta G^{\circ} + 2.3\,RT \log Q$

$Q = \frac{[B]}{[A]}$

as $\Delta G \to 0$

$Q \to K$



$Zn \longrightarrow Zn^{2+} + 2e^{-}$

$Cu^{2+} + 2e^{-} \longrightarrow Cu$