



*“Microbes are remarkable chemists...”*  
- Fenchel et al. (1998)

How do we **know** what bacterial processes dominate under a given set of circumstances?

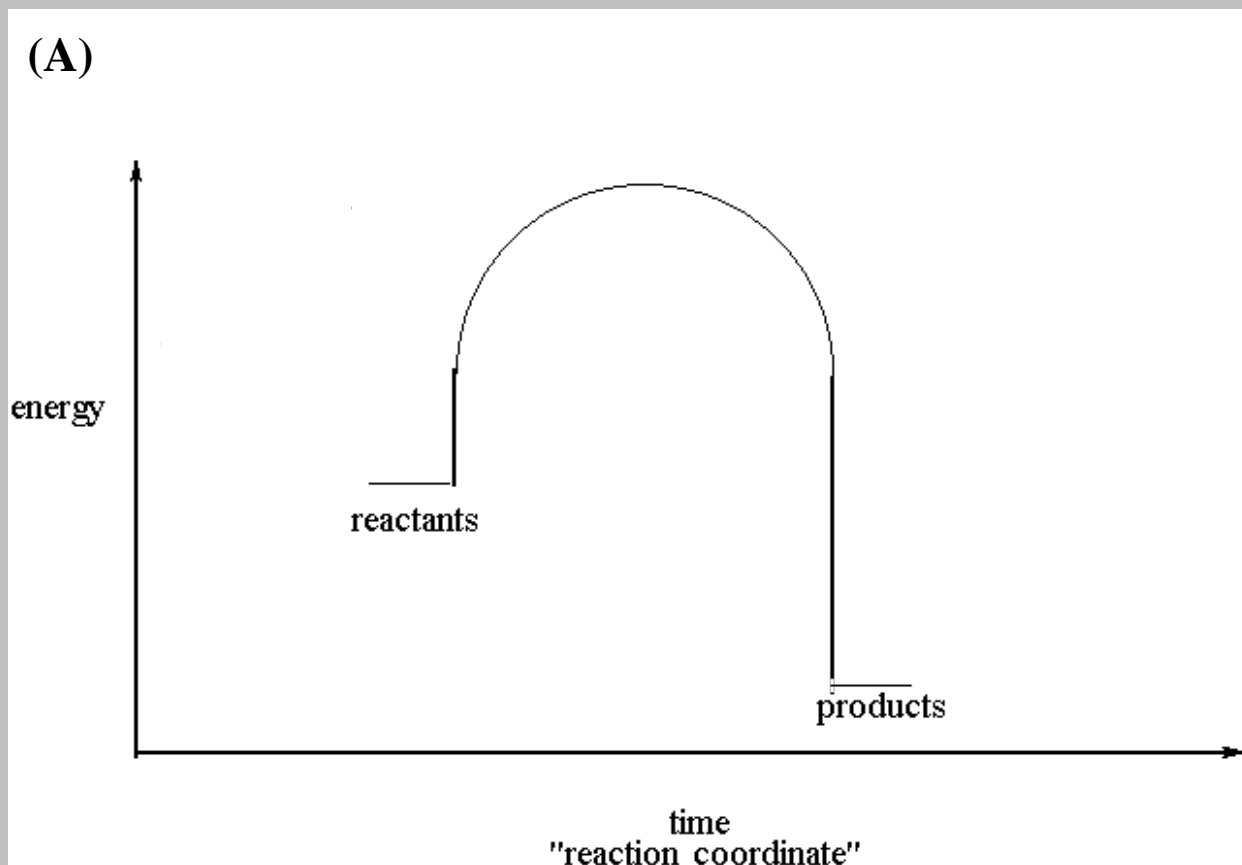
**Kinetics** deals with mechanisms and rates.

**Thermodynamics** provides a framework for:

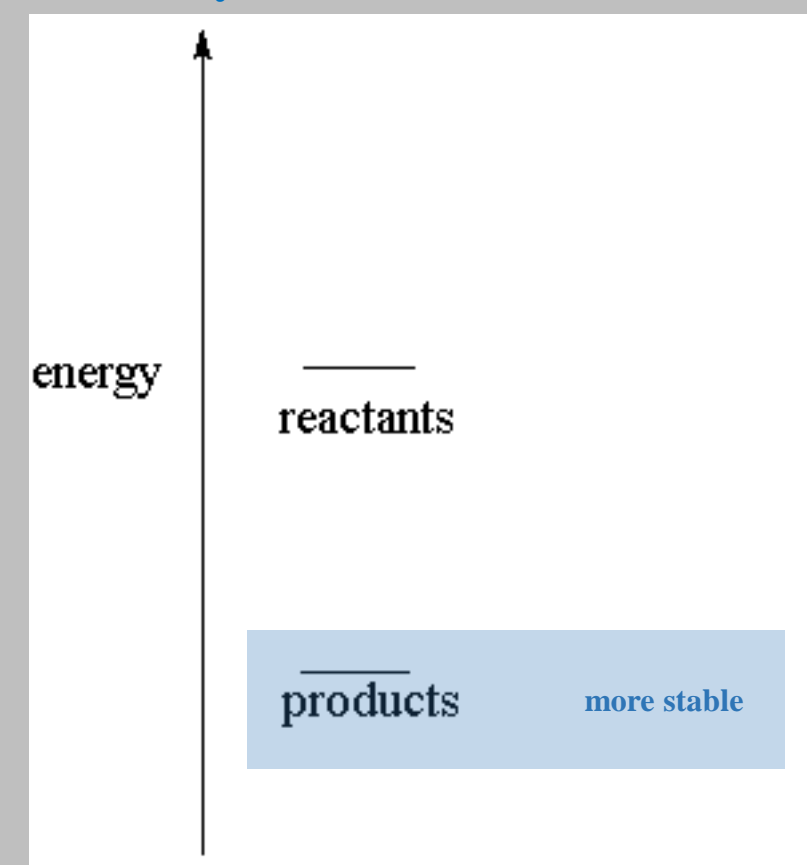
- predicting whether or not a specific reaction takes place spontaneously
- estimating the magnitude of energy exchanges (production/consumption) btw. reactants and their environment
- predicting whether a reaction may be usefully coupled to biological work.

**Kinetics** will tell you how *fast* a reaction will go • **thermodynamics** will tell you if the reaction *should* go.


# Reaction Diagrams



## Thermodynamic Information from (A)



\*thermodynamics isn't dealing w/ time.

- 
- Reaction rates depend on the proportion of reactants that are sufficiently energetic to participate in a given reaction.
  - This proportion is related to temperature and “activation energy” or  $E_a$  ( $\text{kJ mol}^{-1}$ ) – the energy that must be available for the chemical reaction to take place.

**Arrhenius equation (aka: rate constant):** *gives us the relationship between the activation energy and the rate at which the reaction proceeds.*

$$k = Ae^{-E_a/RT}$$

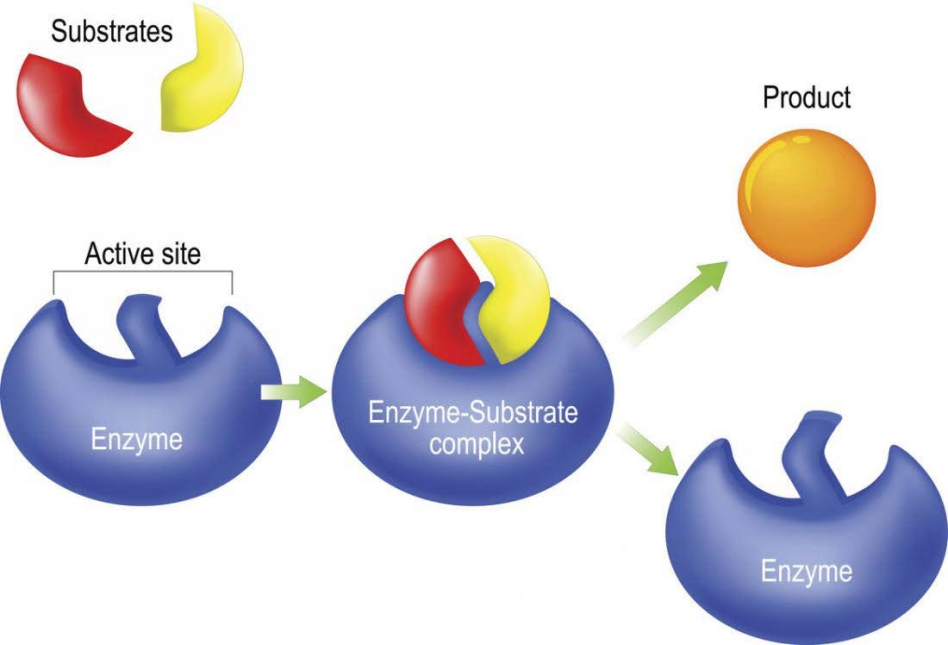
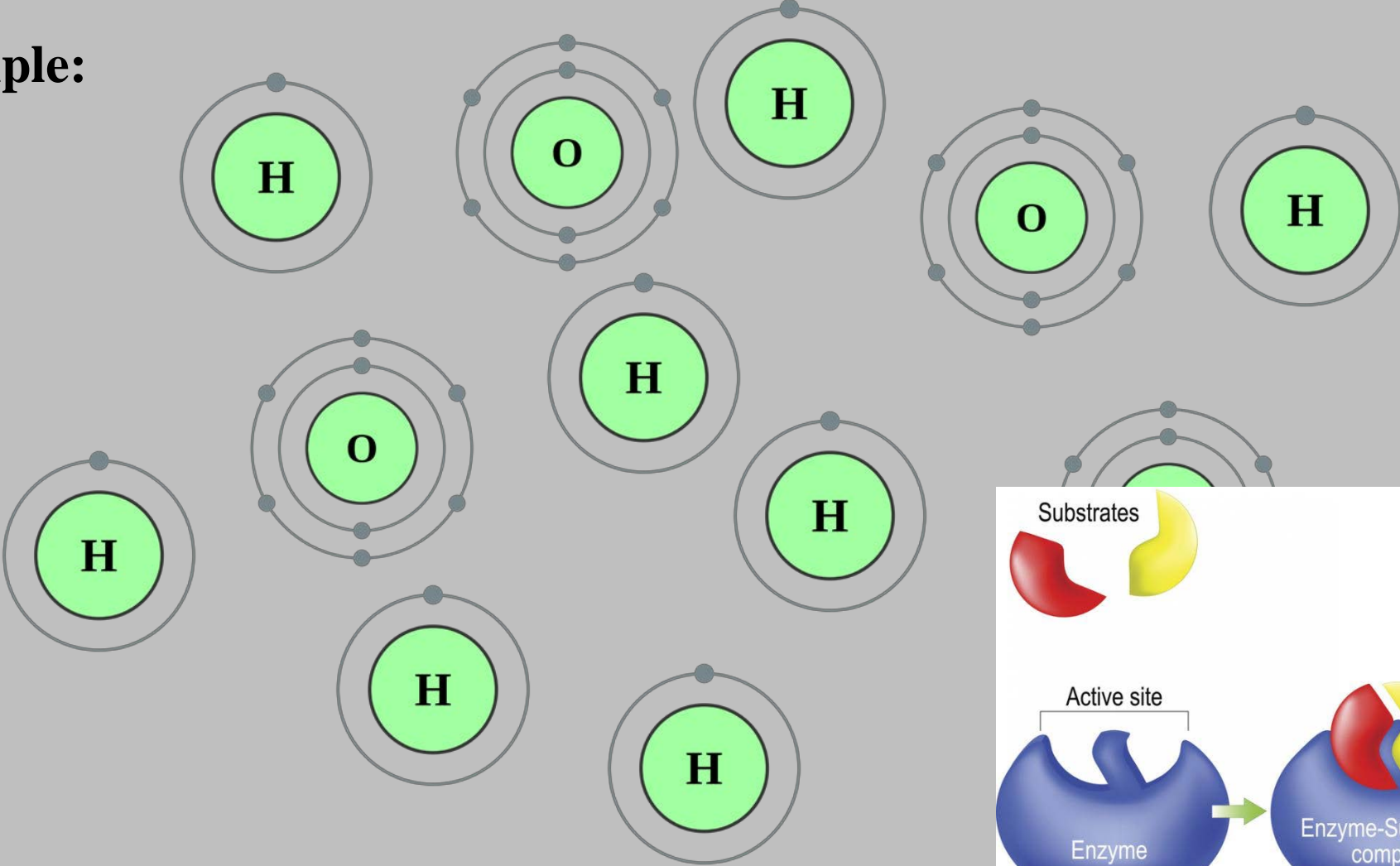
A and  $E_a$  are characteristic reaction constants

R is the gas law constant ( $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$  or  $1.987 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$ )

T is temperature in Kelvin

**\*\*\*In general the higher the activation energy – the slower the reaction.\*\*\***

**Example:**



We use **Gibbs Free Energy** to predict chemical systems and it depends on the state and mass under consideration and.....

- Internal Energy (U sometimes called E)
- Enthalpy (H)
- Entropy (S)
- Temperature (T)



## Internal Energy (U)

Change in internal energy is related to heat exchange between the system and its surroundings and work done by or on the system according to the first **law of thermodynamics**:

$$\Delta U = q + \omega$$

$q$  = heat flow

$\omega$  = work (usually described by pressure-volume changes)

U has the units of Joules

*“energy can be transformed from one form to another, but can be neither created nor destroyed”*



**Enthalpy (H)** – total heat content of a system

$$H = U + PV$$

P= pressure

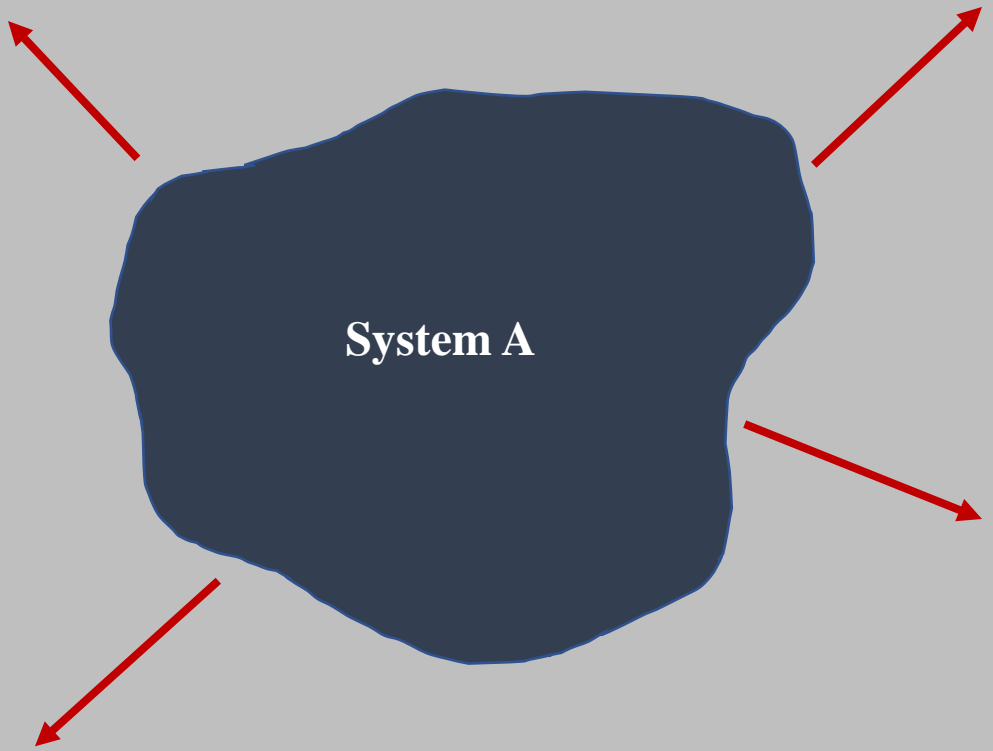
V= volume

Equivalent to the heat added to a substrate from a system as a result of a chemical process at constant pressure. Also known as the heat of reaction.

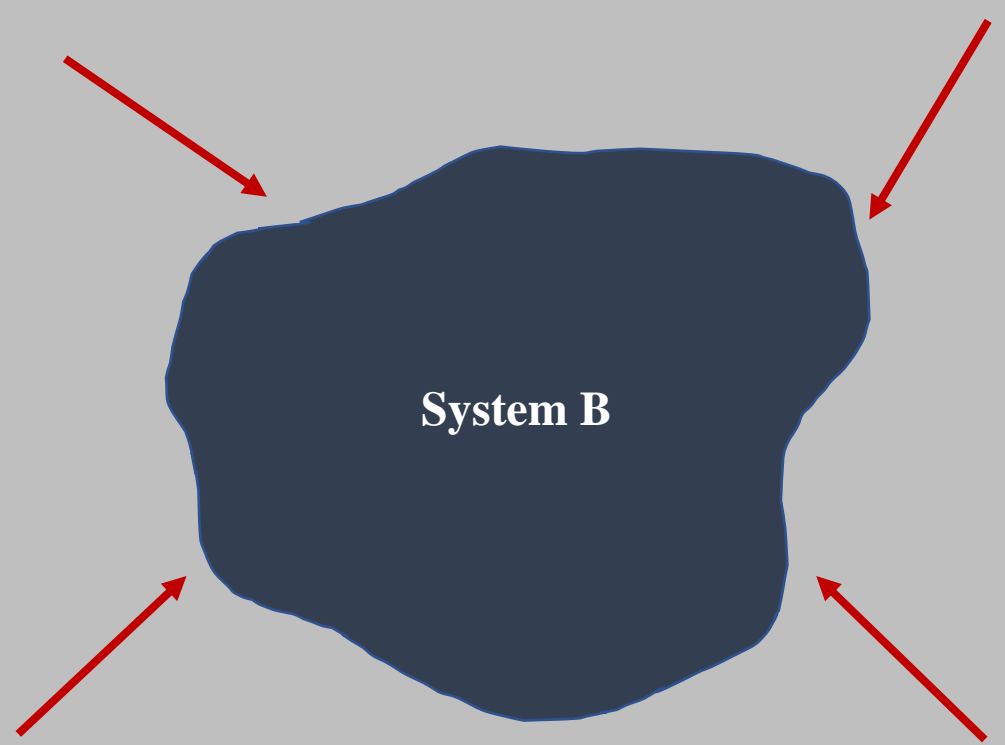
Change in enthalpy:  $\Delta H = U_2 + P_2 V_2 - (U_1 + P_1 V_1)$

$$\Delta H = \Delta U$$





Evolving Heat = Exothermic =  $-\Delta H$

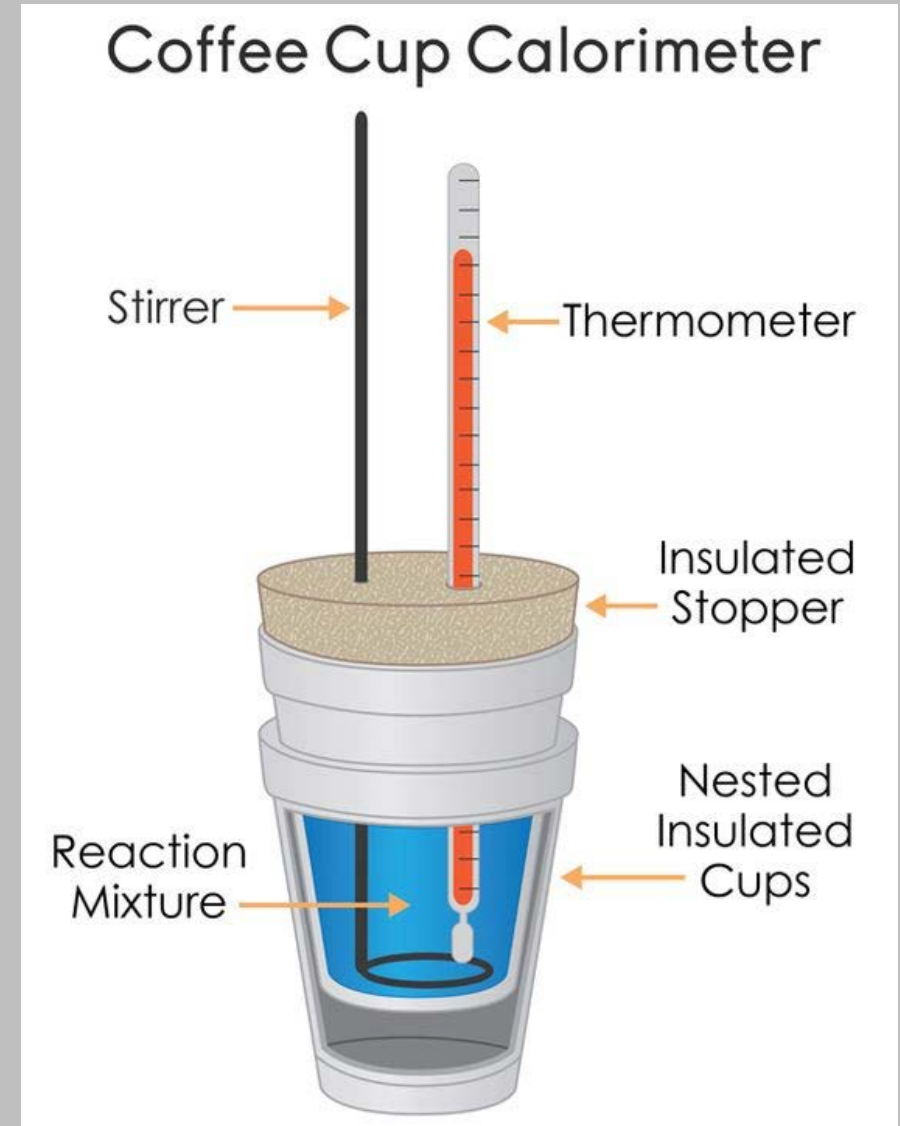


Absorbing Heat = Endothermic =  $\Delta H$

# Heats of Combustion (bomb calorimetry)



# Heats of Formation



Fuel	Heat of Combustion ( $\Delta H_c$ ) - Higher Value Indicated	
	MJ/kg	
<u>Hydrogen</u>	141.9	
<u>Gasoline</u>	47	
<u>Diesel</u>	45	
<u>Ethanol</u>	29.7	
<u>Propane</u>	49.9	
<u>Wood</u>	15	
<u>Coal (lignite)</u>	15	
<u>Coal (anthracite)</u>	36	
<u>Natural gas</u>	54	

## Hess' Law of Constant Heat Summation – allows us to calculate standard enthalpies of reactions:

$$\Delta H^0 = \Delta H_f^0(\text{products}) - \Delta H_f^0(\text{reactants})$$

$\Delta H_f^0$  = standard heat of formation

Standard meaning: 1 atm, pH=7, 25 °C (298.1 K), [1 M]

Use the standard enthalpies of formation in the table below to determine the change in enthalpy for the reactions which follow the table.

Compound	$\Delta H_f^0$ (kJ/mol)	Compound	$\Delta H_f^0$ (kJ/mol)
CH <sub>4</sub> (g)	-74.8	NaHCO <sub>3</sub> (s)	-947.7
CO <sub>2</sub> (g)	-393.5	NaOH(s)	-426.7
CO(g)	-110.5	NH <sub>3</sub> (g)	-46.2
HCl(g)	-92.3	NH <sub>4</sub> Cl(s)	-315.4
H <sub>2</sub> O(g)	-241.8	NO(g)	+90.4
H <sub>2</sub> O(l)	-285.8	NO <sub>2</sub> (g)	+33.9
H <sub>2</sub> S(g)	-20.1	SO <sub>2</sub> (g)	-296.1
H <sub>2</sub> SO <sub>4</sub> (l)	-811.3	SO <sub>3</sub> (g)	-395.2
MgSO <sub>4</sub> (s)	-1278.2	SnCl <sub>4</sub> (l)	-545.2
MnO(s)	-384.9	SnO(s)	-286.2
MnO <sub>2</sub> (s)	-519.7	SnO <sub>2</sub> (s)	-580.7
NaCl(s)	-411.0	ZnO(s)	-348.0
NaF(s)	-569.0	ZnS(s)	-202.9

1. NaOH(s) + HCl(g) → NaCl(s) + H<sub>2</sub>O(g)  $\Delta H^\circ = ???$
2. 2CO(g) + O<sub>2</sub>(g) → 2CO<sub>2</sub>(g)  $\Delta H^\circ = ???$
3. CH<sub>4</sub>(g) + 2O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 2H<sub>2</sub>O(l)  $\Delta H^\circ = ???$
4. 2H<sub>2</sub>S(g) + 3O<sub>2</sub>(g) → 2H<sub>2</sub>O(l) + 2SO<sub>2</sub>(g)  $\Delta H^\circ = ???$
5. 2NO(g) + O<sub>2</sub>(g) → 2NO<sub>2</sub>(g)  $\Delta H^\circ = ???$

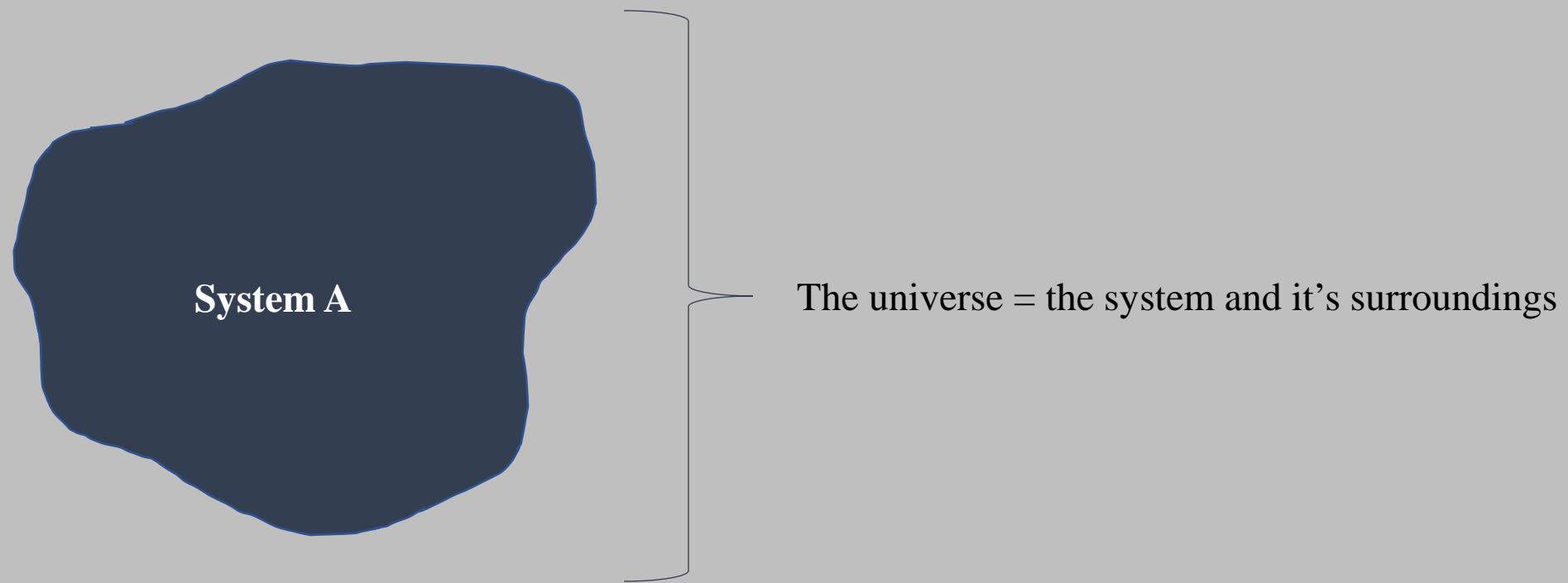
$$\Delta H^0 = (-393.5 + [2 \times -285.8]) - (-74.80 + [2 \times 0.00]) = -890.3 \text{ kJ mol}^{-1}$$

**Exothermic reaction – it's evolving heat.**



# Entropy (S)

**Second law of thermodynamics:** “For any spontaneous process there is an increase in the entropy of the universe.”



Change in entropy of the universe:  $\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$

At constant temperature and pressure, entropy change in the surroundings ( $\Delta S_{surroundings}$ ) is equivalent to the heat added to the surroundings by the system divided by the temperature (K) at which heat is added:

$$\text{Entropy change to surroundings: } \Delta S_{surroundings} = \frac{\Delta H_{system}}{T}$$

$$\text{Change in entropy of the universe: } \Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

$$T\Delta S_{total} = -(\Delta H_{system} - T\Delta S_{system}) \text{ must be negative to be spontaneous}$$

$$\text{Gibbs free energy: } \Delta G = \Delta H - T\Delta S$$

$$\text{Gibbs free energy at standard state } \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

**Gibbs free energy:  $\Delta G = \Delta H - T\Delta S$**

$\Delta G < 0$  (i.e., it's negative) then the reaction is spontaneous – exergonic reaction.

$\Delta G > 0$  (i.e., it's positive) then the reaction not spontaneous and would require energy to proceed in the direction as written – endergonic reaction.

$\Delta G = 0$  the system is at equilibrium

**\*\*  $\Delta G$  is the driving force of the reaction, the more negative  $\Delta G$  the more favorable the reaction.\*\***

## Gibbs free energy for a reaction at standard state:

$$\Delta G^0 = \Sigma(n_i \Delta G_{fi}^0)_{\text{products}} - \Sigma(n_i \Delta G_{fi}^0)_{\text{reactants}}$$

**Table 19.3** • Standard Molar Free Energies of Formation of Some Substances at 298 K

Element/Compound	$\Delta G_f^0$ (kJ · mol <sup>-1</sup> )	Element/Compound	$\Delta G_f^0$ (kJ · mol <sup>-1</sup> )
H <sub>2</sub> (g)	0	CO <sub>2</sub> (g)	-394.4
O <sub>2</sub> (g)	0	CH <sub>4</sub> (g)	-50.87
N <sub>2</sub> (g)	0	H <sub>2</sub> O(g)	-228.6
C(graphite)	0	H <sub>2</sub> O(l)	-237.2
C(diamond)	2.900	NH <sub>3</sub> (g)	-16.4
CO(g)	-137.2	Fe <sub>2</sub> O <sub>3</sub> (s)	-742.2

## Gibbs free energy for a reaction at standard state:



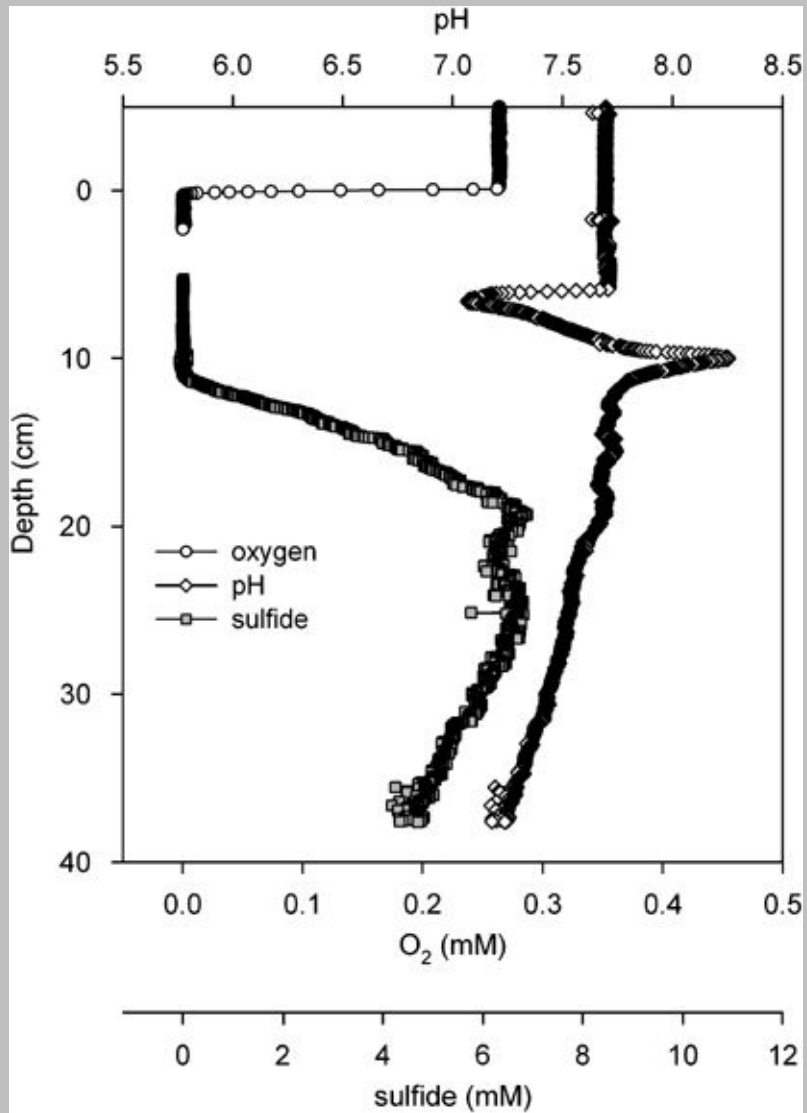
$$\Delta G^0 = \Sigma(n_i \Delta G_{fi}^0)_{products} - \Sigma(n_i \Delta G_{fi}^0)_{reactants}$$

Species	$\Delta G_f^0$ (kJ mol <sup>-1</sup> )
FeO (s)	-251.1
Fe(OH) <sub>2</sub> (precip.)	-486.6
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> (hematite)	-742.7
Fe <sub>3</sub> O <sub>4</sub> (magnetite)	-1012.6
$\alpha$ -FeOOH (goethite)	-488.6
FeOOH (amorph)	-462
Fe(OH) <sub>3</sub> (amorph)	-699(-712)
FeCO <sub>3</sub> (siderite)	-699.7
Fe <sub>2</sub> SiO <sub>4</sub> (fayalite)	-1379.4

Species	$\Delta G_f^0$ (kJ mol <sup>-1</sup> )
N <sub>2</sub> (g)	0
NO (g)	86.57
NO <sub>2</sub> (g)	51.3
N <sub>2</sub> O (g)	104.2

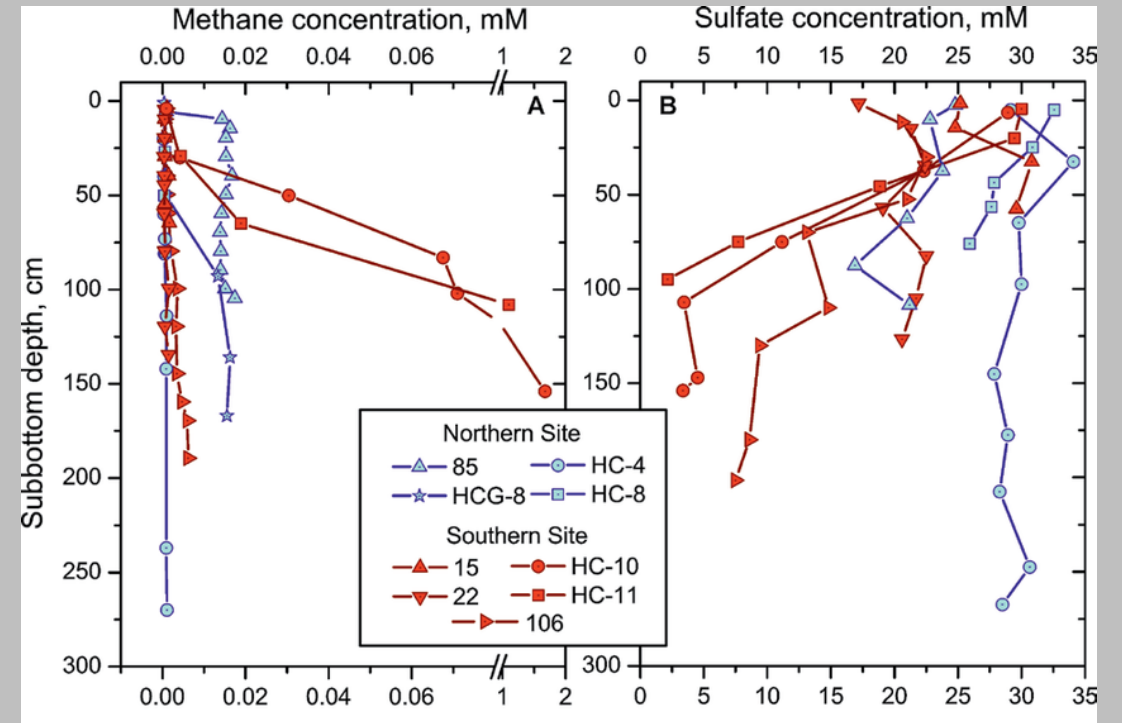


# Beggiatoa inhabited marine sediment



Priesler et al. (2007)

# Methane in Chukchi Sea



Matveeva et al. (2015)

## We can calculate Gibbs under environmental conditions:

General Reaction:  $aA + bB \leftrightarrow cC + dD$

Capital letters are the components reacting

Lower case letters represent the stoichiometric amounts

For any component of the system that deviates from standard conditions:  $\Delta G_i^o = G_i^o + RT \ln a_i$

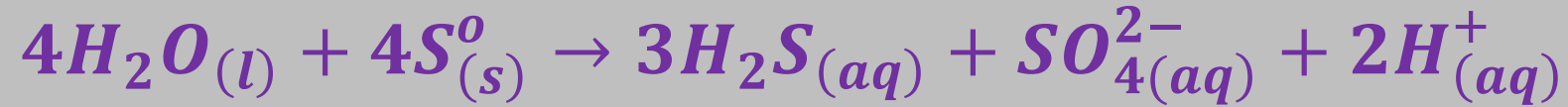
R is the gas constant (= 8.314 kJ mol<sup>-1</sup> K<sup>-1</sup>)

T is temperature in Kelvin (K)

$a_i$  is a quantity known as the activity and it's related to concentration ( $c$ , molar) thru the activity coefficient ( $\gamma_i$ , dimensionless):

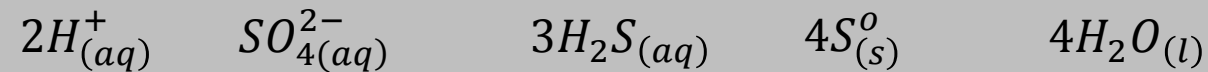
$$a_i = \gamma_i \gamma c_i$$

*\*activity coefficient represents the deviation from ideal behavior .... For ions for example the interactions of ions in a solution cause them to behave differently than what would be predicted from their actual concentrations.*



(1) Gibbs free energy at standard conditions:  $\Delta G^0 = \Sigma(n_i \Delta G_{fi}^0)_{products} - \Sigma(n_i \Delta G_{fi}^0)_{reactants}$

$$\Delta G^0 = 2[0] + [-744.6] + 3[-27.87] - [4(0) + 4(-237.18)] = 120.5 \text{ kJ mol}^{-1}$$



(2) Gibbs free energy at environmental conditions:  $\Delta G = \Delta G^0 + RT \ln(a_C^c a_D^d) / (a_A^a a_B^b)$

*Conditions:*

25 °C,  $H_2S_{(aq)} = 100 \mu\text{M}$ ,  $SO_4^{2-}_{(aq)} = 28 \text{ mM}$ , pH = 7.5, liquid water and solid phase set to 1, assume [] = activity

$$\Delta G = 120.5 + (8.314 \times 10^{-3})(298) \ln(a_{H_2S}^3 a_{SO_4} a_{H^+}^2) = -42.5 \text{ kJ mol}^{-1}$$



## Equilibrium:

Barring kinetic barriers (which can be significant) favorable (i.e.,  $\Delta G^\circ < 0$ ) will continue until the distribution of reacting components reaches equilibrium.

General Reaction:  $aA + bB \rightleftharpoons cC + dD$

We define the distribution of chemical species at equilibrium as:

$$K_{eq} = (a_C^c a_D^d) / (a_A^a a_B^b)$$

Substitute in Gibbs free energy under non-standard conditions:

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

Rearrange to calculate equilibrium constants for  $\Delta G^\circ$ :

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

# Gas Solubility and Henry's Law

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$C_{(aq)i} = P_i K_{Hi}$$

$C_{(aq)i}$  is the concentration of the gas (M)

$P_i$  is the partial pressure of the gas (atm)

$K_{Hi}$  is the Henry's Law constant (M atm<sup>-1</sup>)

Table 3.2 Henry's law constants ( $K_H$ , M atm<sup>-1</sup>), salting out coefficient ( $k_i$ ) and heats of solution ( $\Delta H_{sol}$ ) for some gases of biological interest at 25 °C

Gas	$K_H$	$k_i$	(kJ mol <sup>-1</sup> ) $\Delta H_{sol}$
CO <sub>2</sub> <sup>a</sup>	$3.4 \times 10^{-2}$	0.095	19.6
NH <sub>3</sub>	$5.7 \times 10^1$		
H <sub>2</sub> S	$1.0 \times 10^{-1}$	0.02	
N <sub>2</sub>	$6.5 \times 10^{-4}$	0.131	8.8
O <sub>2</sub>	$1.3 \times 10^{-3}$	0.122	12.5
CO	$9.6 \times 10^{-4}$	0.134	15.9
CH <sub>4</sub>	$1.3 \times 10^{-3}$	0.092	13.4
NO <sub>2</sub>	$1.0 \times 10^{-2}$		
NO	$1.9 \times 10^{-3}$		11.3
N <sub>2</sub> O	$2.5 \times 10^{-2}$		20.1
H <sub>2</sub> O <sub>2</sub>	$1.0 \times 10^5$		
O <sub>3</sub>	$9.4 \times 10^{-3}$		
H <sub>2</sub>	$7.8 \times 10^{-4}$		1.3

<sup>a</sup>CO<sub>2(g)</sub> + H<sub>2</sub>O<sub>(g)</sub> ↔ H<sub>2</sub>CO<sub>3(aq)</sub>.

Data from Stumm and Morgan (1996) and Millero (1996).



## Other things to think about:

Ions interact – that is the electrostatic forces between individual ions can be attractive (different charges) or repulsive (same charges).

The net result is always attractive – ions hold each other!

This restricts their ability to take part in reactions in aqueous systems.

For charged species, concentration (the total amount present in solution, given by  $[x]$  or  $C_i$ ) is almost always an overestimate of reaction potential – that is the amount free and available for a reaction.

At low concentrations we can ignore this, but at higher concentrations these interactions begin to matter.

Activity ( $a_i$ ) = Effective amount (less than total)

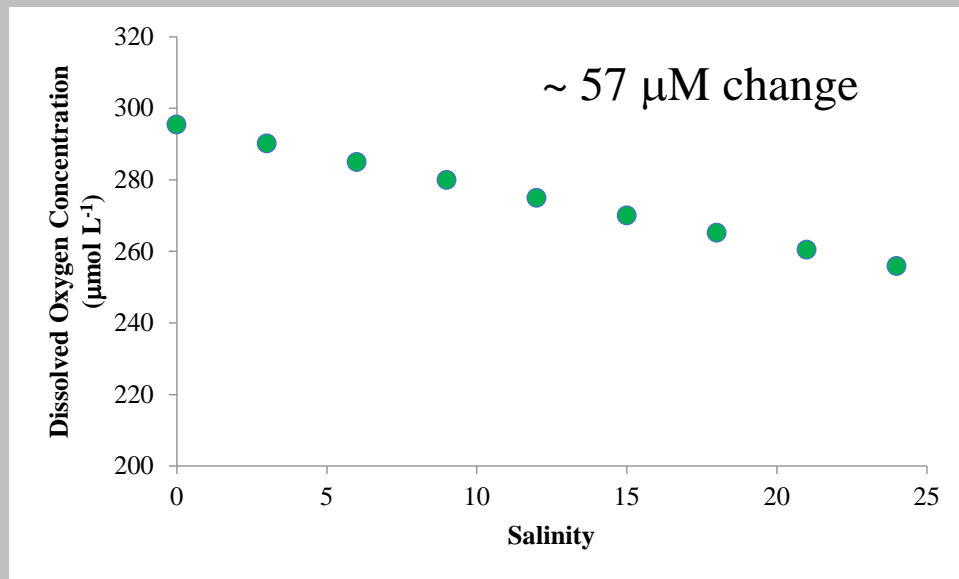
Dilute Solution:  $a_i = C_i$

Concentrated Solution (like seawater):  $a_i < C_i$

So what does this practically mean?

The ionic strength (i.e., the measure of the concentration of ions in that solution) is important to understanding why we observe certain phenomena related to substances dissolving in seawater.

“Salting Out” of Gases as Ionic Strength increases



$$C_{(aq)i} = P_i K_{Hi}$$

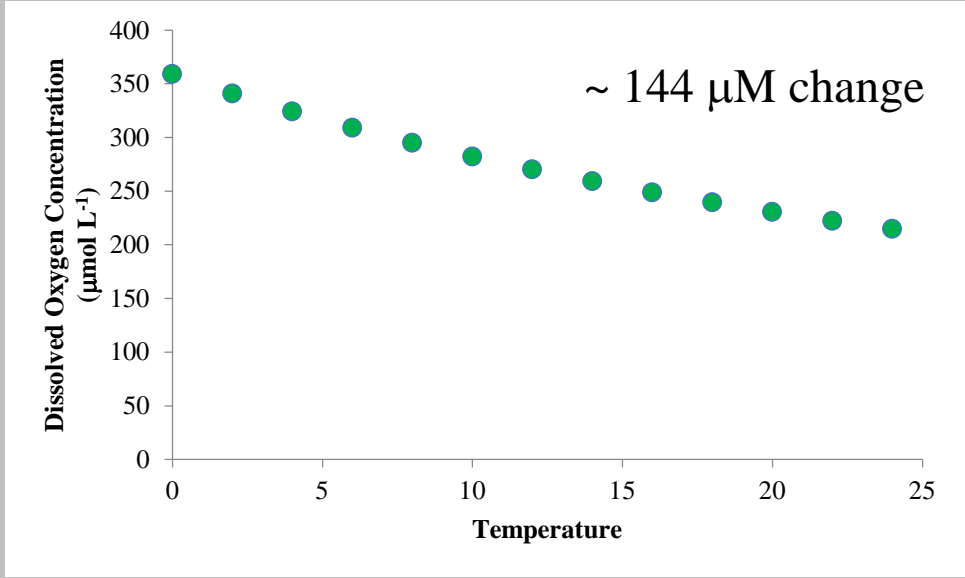
$C_{(aq)i}$  replace with activity coefficient

Temperature held at 18 °C



*What holds more gas? Fresh or salt water?  
How will gas concentration change as temperature increases?*

**Influence of temperature on gas solubility**



Salinity held at 35 ‰

