

Lecture 3: Thermodynamics

Margaret A. Daugherty
Fall 2004

Matter and energy are conserved

Entropy always increases

Absolute zero is unattainable

BIOC 205

BIOC 205

System and Surroundings

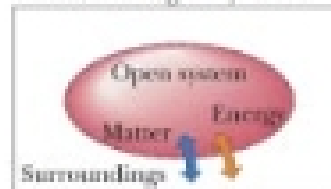
Isolated system:
No exchange of matter or energy



Closed system:
Energy exchange may occur



Open system:
Energy exchange and/or
matter exchange may occur



Harcourt, Inc. Items and derived items copyright © 2002 by Harcourt, Inc.

1st Law of Thermodynamics

Relationship of heat, work, internal energy & Enthalpy

Bookkeeping function to keep track of:
heat transfers
work expenditures

Total E of a system & its surroundings is a constant

$$\Delta E = E_{\text{final}} - E_{\text{start}} = Q + W$$

Q: heat absorbed by system; W: work done on system

Energy cannot be **created** or **destroyed**.

BIOC 205

BIOC 205

Biological Systems and Enthalpy, ΔH :

Definition: $H = E + PV$

For a biological system:

Temperature
Pressure
Volume } **constant!**

Work is a function of V & P

$W = V\Delta P + P\Delta V$; pressure and volume are constant
 $W = 0$

$$\Delta H = \Delta E = Q$$

$\Delta H < 0$ exothermic

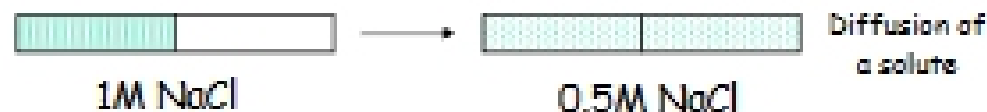
$\Delta H > 0$ endothermic

Enthalpy is equal to the heat absorbed in a biological process

BIOC 205

2nd Law of Thermodynamics

- Systems of molecules have a natural tendency to *randomization or disorder*;
- The degree of randomness or disorder is measured by a function of state called the **entropy** (S);



- The entropy of an isolated system will tend to increase to a maximum value.

For an isolated system, the favored direction:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} > 0$$

BIOC 205

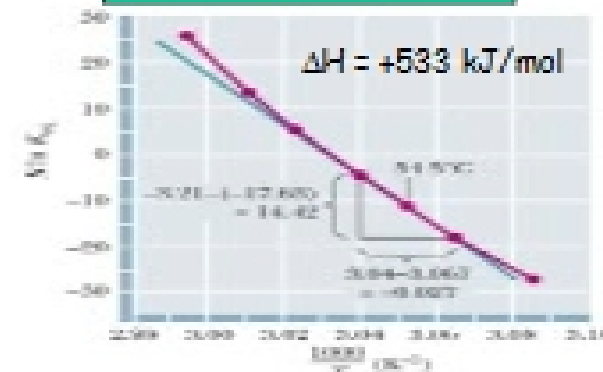
Calorimetry & van't Hoff plots: Determination of enthalpy

$$N \leftrightarrow U$$

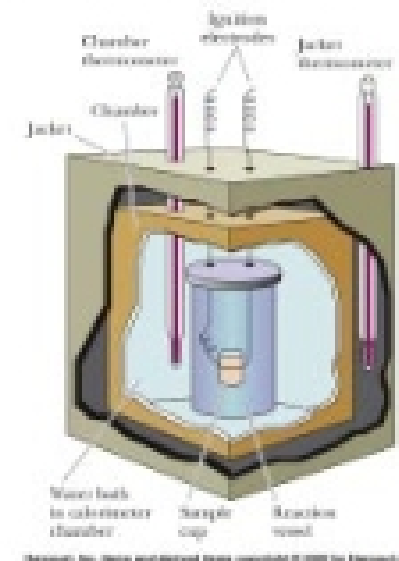
$$K_{eq} = [U]/[N]$$

Measure K as a function of T

$$\Delta H = -R \frac{d \ln K_{eq}}{d(1/T)}$$



Quantification: Biochemistry with a Glass Beaker
Figure 3.2



Reprinted by permission from copyright © 2008 by Pearson, Inc.

BIOC 205

Second Law: Entropy and Disorder

$$\Delta S = \text{entropy}$$

- Systems proceed from an *ordered to a disordered* state
- Reversible processes - entropy of Sys + Sur is unchanged
Irreversible process = entropy of Sys + Sur increases
- All process tend to equilibrium - minimum potential energy

Three cases

$\Delta S = \text{positive}$

Disorder! Reaction will tend to occur

$\Delta S = \text{zero}$

Reaction is reversible; at equilibrium

$\Delta S = \text{negative}$

Order! Reaction is unfavorable

BIOC 205

Entropy: the equations

$$S = k \log W$$

k = Boltzmann's constant
 1.38×10^{-23} J/K

W = # of possible ways to arrange a system at a given temperature

$$dS_{rev} = dq/T$$

Relates entropy to heat absorbed



Third Law:
 Absolute zero is unattainable

What is absolute zero? **A temperature where entropy is zero!**

Absolute zero = 0 K
 Conversion to Celsius = degrees K - 273.15C

The entropy of any perfectly crystalline substance approaches zero as absolute zero is approached

The **heat capacity, C_p** , allows us to have an absolute entropy scale

$$S = \int_0^T C_p d \ln T \quad \text{or} \quad C_p = dH/dT$$

If $\Delta C_p < 0$, molecules become more restricted;
 if $\Delta C_p > 0$, molecules acquire new ways to move

Gibbs Free Energy, ΔG : Is a reaction feasible?

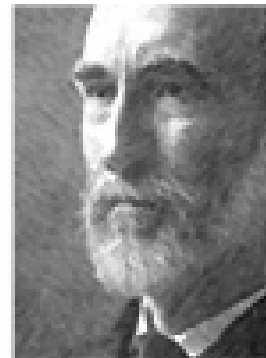
For a reaction $A \leftrightarrow B$

$$K_{eq} = [B]/[A]$$

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

Gibbs Free Energy
 Relates 1st and 2nd Laws of Thermodynamics

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



J. Willard Gibbs
 1839-1903

Three Ways To Have Thermodynamically Favored Reactions
 ($\Delta G = \Delta H - T\Delta S$; $\Delta G < 0$)

