I: Life and Energy

- **Lecture 1**: Life as a thermodynamic system. An attempt at definition.
- Energy, heat, and work: Temperature and thermal equilibrium. The First Law. Thermodynamic states and state functions. Reversible and real processes. The Second Law and free energy. Why do living systems need energy? (B Lentz)

- **Lecture 2**: Solutions and chemical potential; Osmotic pressure (B Lentz).

- **Lecture 3**: Mother Nature plays dice: the Boltzmann distribution, partition functions and entropy. (B Lentz)

- **Lecture 4**: Biology is Binding

Life: An Attempt at Definition

Basic Features

Reproduces itself

Chemical system

Thermodynamic features

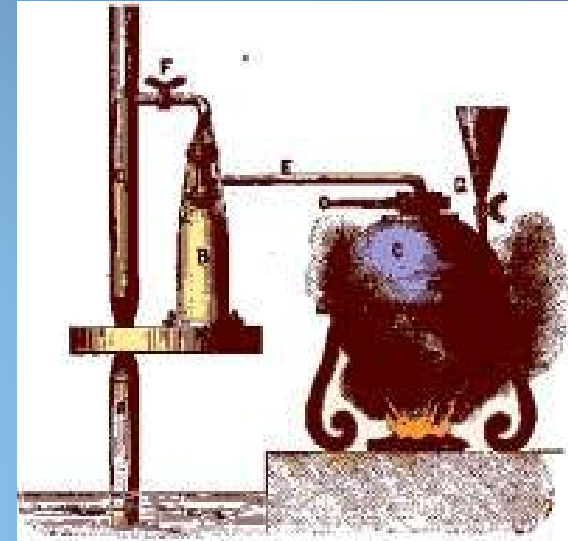capable of doing work

open system
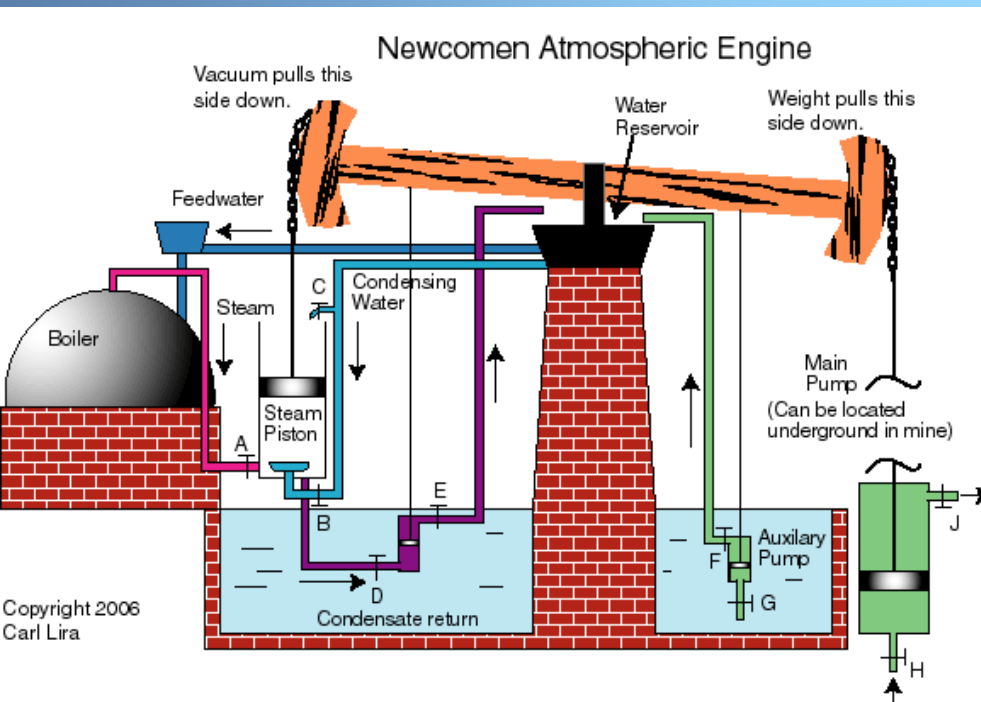
requires energy

organizes itself

Thermodynamics

Thermodynamics got its start in Engineering at the beginning of the 19th Century.

Thomas Savery (1650-1715): Heat machine to raise water from a mine.

Thomas Newcomen (1663-1729): Blacksmith improved Savory pump.
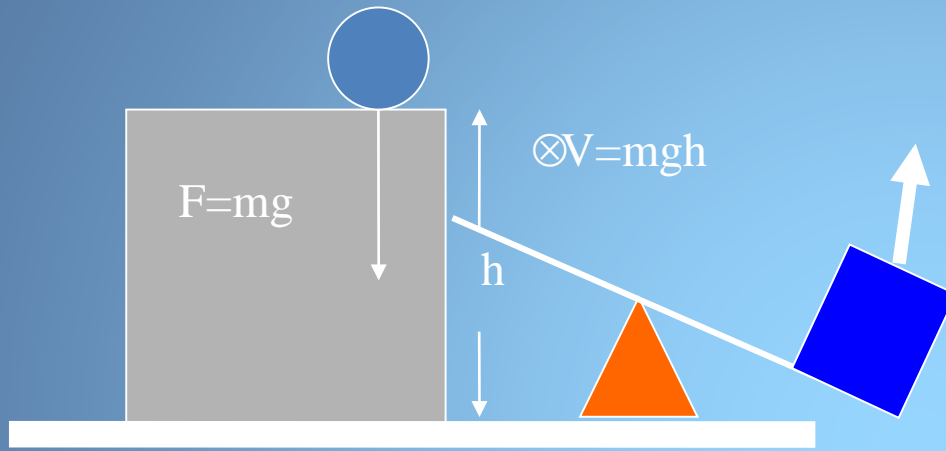

James Watt (1736-1819): Modern steam engine design.

Thermodynamics was developed to improve the efficiency of steam engines.

The Nature of Energy

Potential Energy

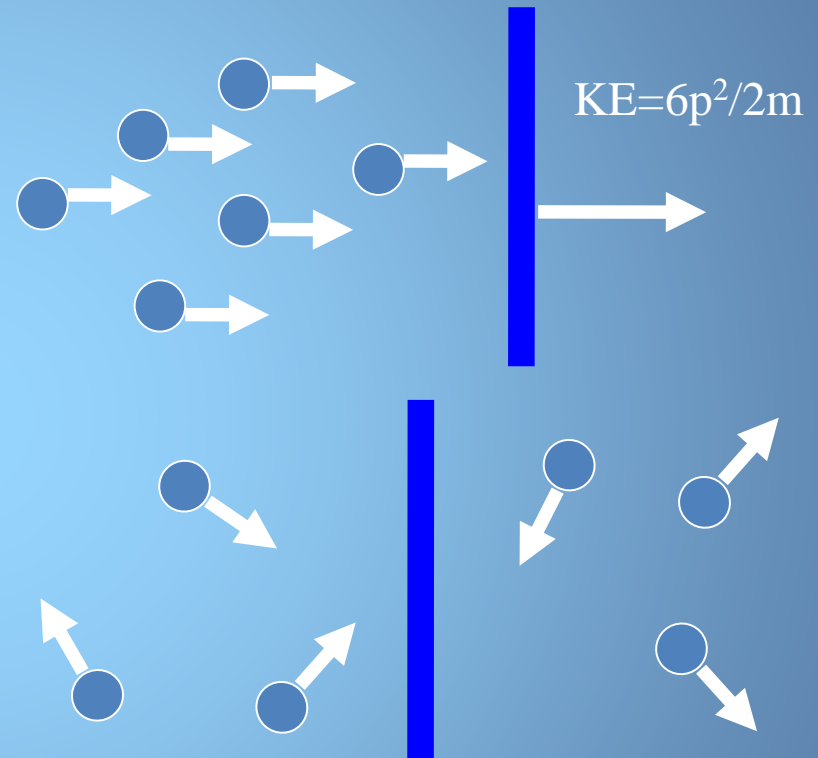$F=mg$

$\otimes V=mgh$

h

Kinetic Energy

$KE=6p^2/2m$

Energy comes in two forms: potential and kinetic.

In either case, it has the property of being directed and organized, or random and non-directed.

Directed energy nearly always has the CAPABILITY to do WORK.

Potential energy is nearly always directed; 8/28/2015 kinetic can be either.

Random energy does sometimes.

1st Law: Energy Is Conserved!

Surroundings

System

w = work done by the system on surroundings

q = heat flow into the system from the surroundings
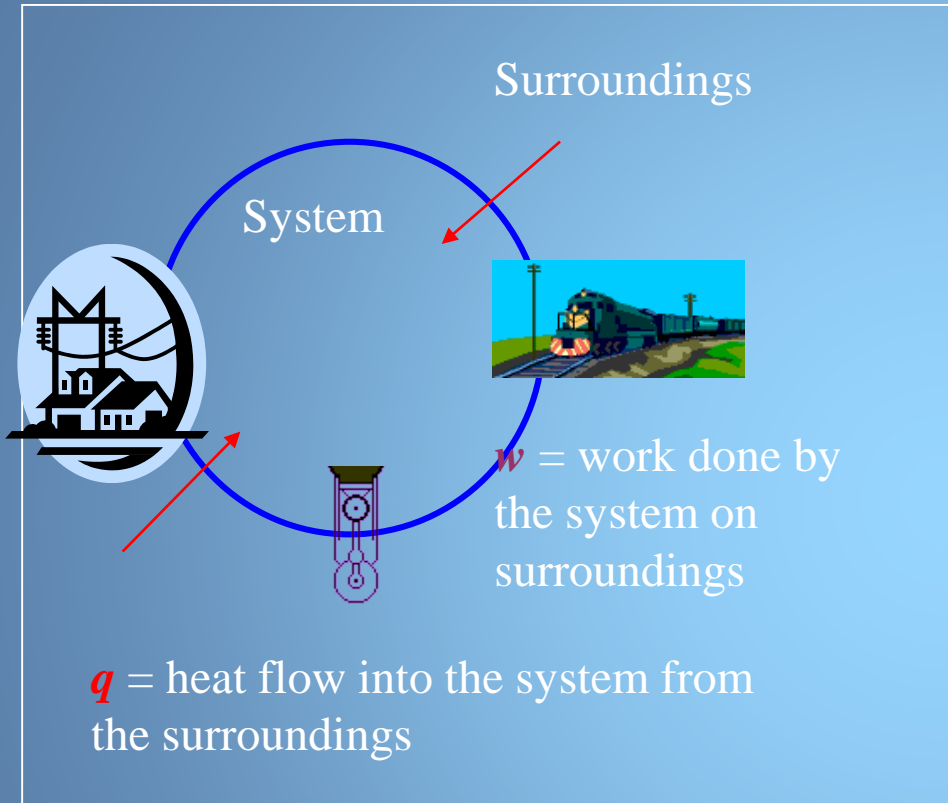
In thermodynamics, the universe is divided into the system of interest and the rest of the universe (the surroundings).

Heat (q) can flow *into* the system.

Work (w) can be done by the system *on* the surroundings.

"Internal Energy" = U

First Law: $\otimes U = q\text{-}w$

Open Systems exchange energy and matter with their surroundings.
Closed Systems exchange energy but not matter with their surroundings.
Isolated Systems exchange neither energy nor matter with surroundings.

This is the convention in physical chemistry; opposite for physics and sometimes for engineering.

State Functions

A State Function depends on the physical state of a system not on the path taken to get to that State.

$$U \text{ is a ``State Function'', i.e., } \Delta U(a \rightarrow b) = -\Delta U(b \rightarrow a)$$

State Functions depend on measurable quantities: Independent Variables.

$$U \text{ is a function of } T, V, \text{ and } N_i$$

The Zeroth Law: Temperature

Two states of material A both in thermal equilibrium with material B are in thermal equilibrium with each other and share a property called *temperature* related to their "hotness".
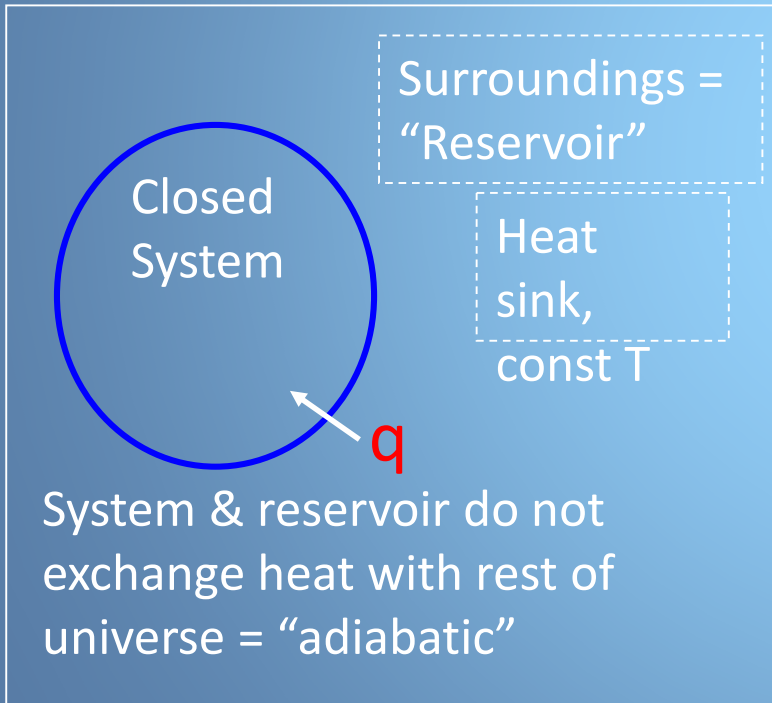

Temperature was first measured using an easily purified material (Hg) having a thermal expansivity $[(\delta V/\delta T)_P]$ that was fairly constant with temperature. Celsius' temperature scale was defined by dividing the change in Hg volume between the melting of ice and the boiling of water (1 atm pressure) by 100. Kelvin's scale was defined by the statistical mechanical properties of an ideal gas, with the units being the same used by Celsius, thus fixing the Boltzmann constant at its current value. Kelvin's scale had the advantage that T=0 when molecular motion stopped.

The Second Law: Get Real! Reversibility is Not!

The "perfect" steam engine is not possible. It is impossible to convert heat completely into work during a real (irreversible) process.

Perpetual Motion Machine!!!!

A system undergoing the process: state A ➔ B ➔ A exchanges no NET work or heat with its environment if it follows a Reversible Path.

Surroundings = "Reservoir"

Closed System

Heat sink, const T

q

System & reservoir do not exchange heat with rest of universe = "adiabatic"

$$dS \equiv \left(\frac{\partial q}{T} \right)_{rev}$$

The entropy is a state function!*

* Follows from thermal equilibrium between System and Reservoir and "Carnot Cycle" (or from Maxwell/Boltzmann).

Heat flow into System is less than or equal to the Entropy Increase of System: Second Law

$$\partial q / T_{R} \leq \partial S_{S}$$

$$dS_{U} = dS_{S} - dq / T_{R} \geq 0$$

The entropy of the universe (the system and its reservoir) increases ($dS_{U} > 0$) for an irreversible (or natural) process.

Equilibrium and the Second Law

Equilibrium: A state from which spontaneous change is not possible.

Since $\Delta S > 0$ for spontaneous processes, if no spontaneous change is possible, the entropy must be maximal.
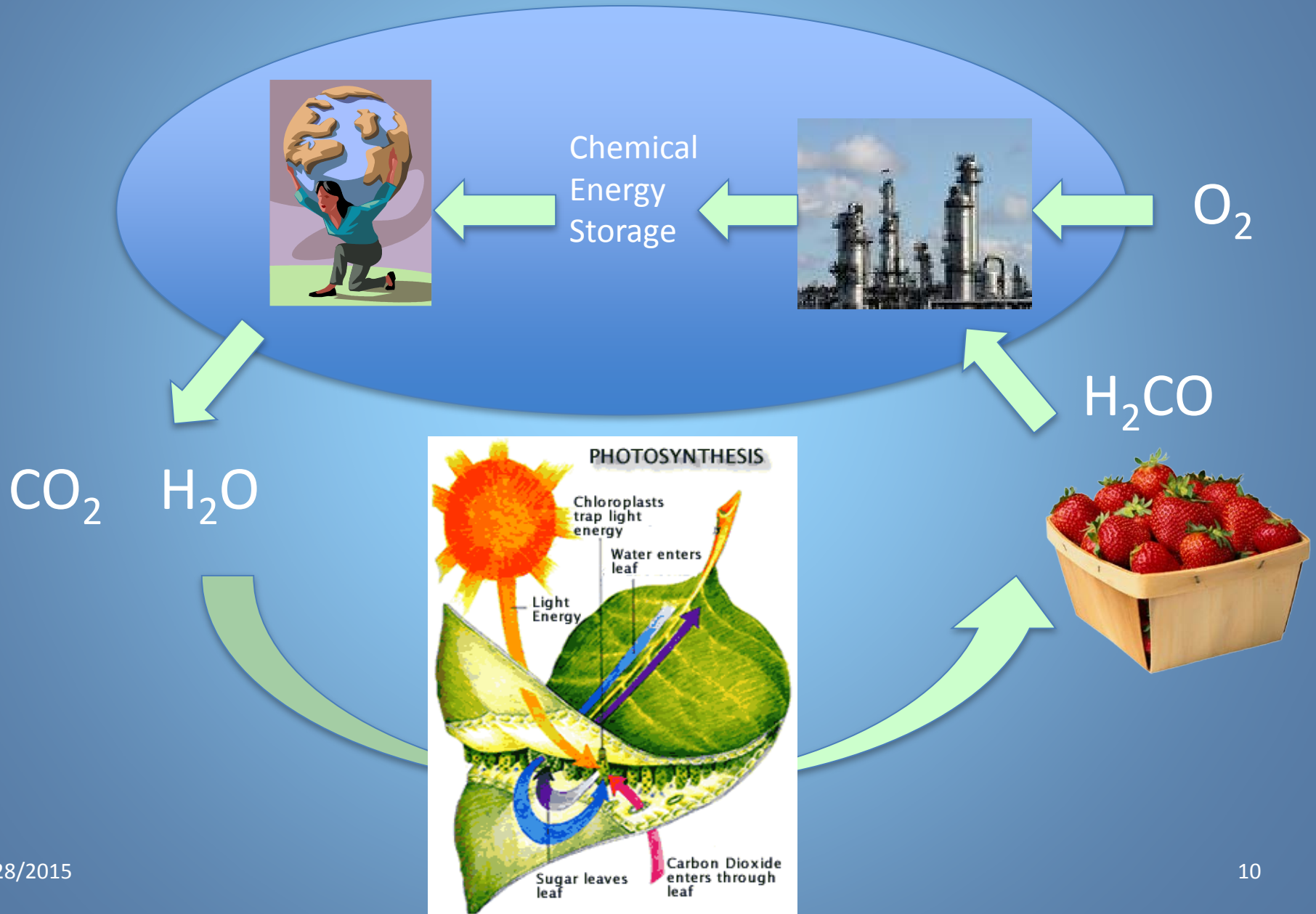
The entropy of a system at equilibrium is maximized.

•• the universe is not at equilibrium (lucky thing for astronomers and cosmologists!)

What the Hell does this mean?

We will see when we consider Boltzmann distribution.

Is a Cell at Equilibrium?

Only if it is dead!

Chemical Energy Storage

O_2

H_2CO

CO_2 H_2O

PHOTOSYNTHESIS

Chloroplasts trap light energy

Water enters leaf

Light Energy

Sugar leaves leaf

Carbon Dioxide enters through leaf

Does Life Follow the Second Law?

No, but it does not violate it!

Biosphere

$\Delta S_{biosphere} < 0$

q

hν

q

q

q

q

q

q

$\Delta S_{surroundings} >> 0$

$\Delta S_{universe} > 0$
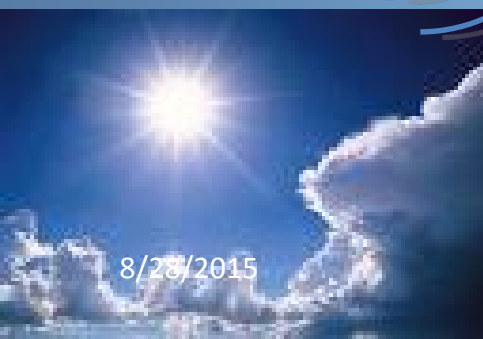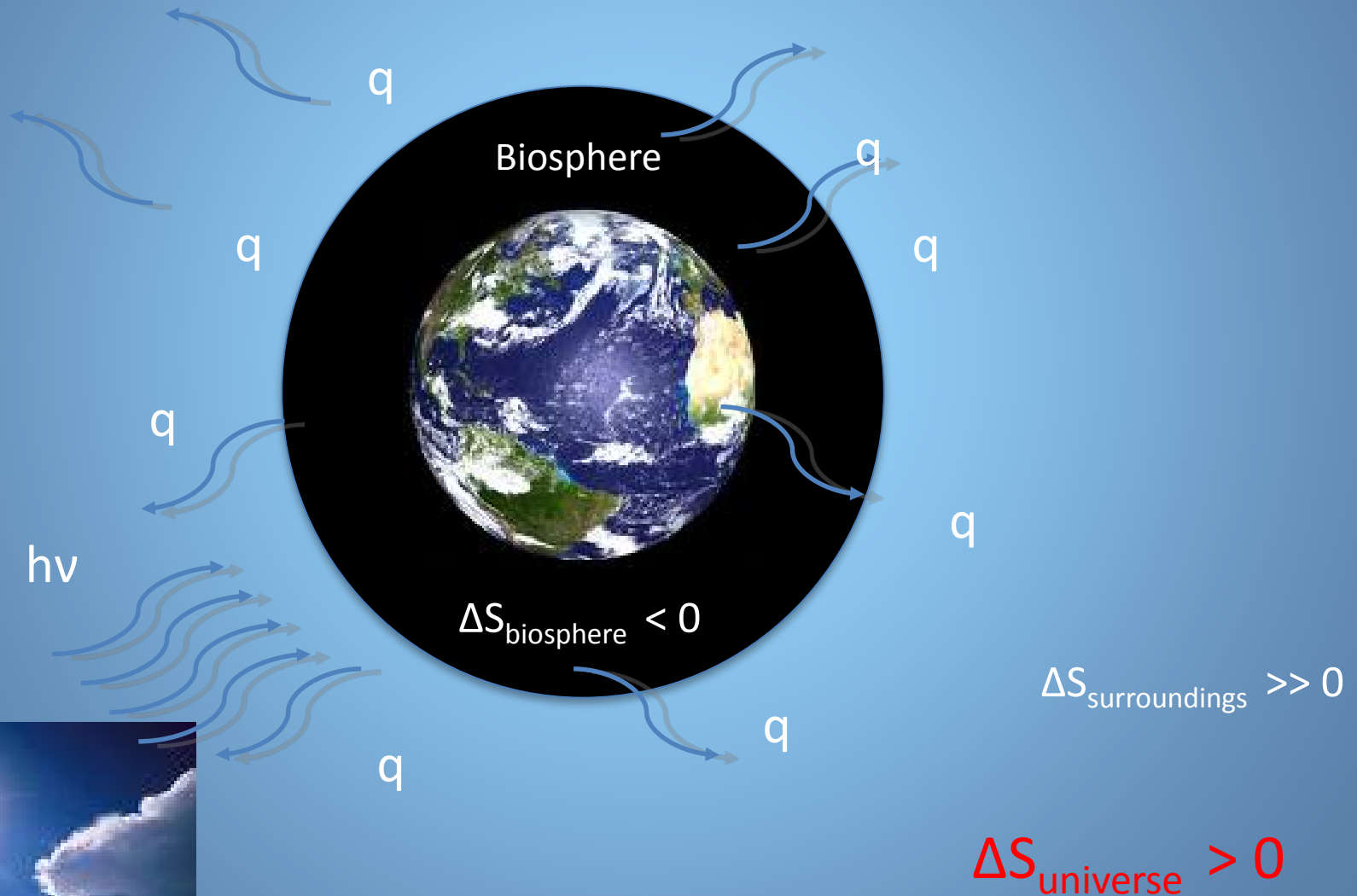
Combined First & Second Laws

Even after correcting for the change in its internal energy, a steam engine can never capture all the heat released by burning coal, unless it is an unreal or virtual "reversible" steam engine.

Recall our basic statement of the Second Law: Real heat flow is less than reversible heat flow

$$\partial q / T_{\mathrm{R}} \leq dS_{\mathrm{S}}$$

Recall also the First Law: $\mathrm{d}U + \delta w = \delta q$. Substituting:

$$\partial w \leq T_R dS_S - dU_S$$

The more common form is one that distinguishes between PV work and other forms of work:

$$dU \leq TdS - PdV - \partial w$$

Arbeit: Useful Work

Recall the Second Law. For work done BY the surroundings, δw is negative.

$$\partial w \leq T_R dS_S - dU_S$$

For a Reversible Process: this "work function" becomes available to do work ON the surroundings.

This "work function" ($-\delta w$) became known as the Helmholtz Energy or "work (Arbeit) available function".

$A(\text{T,V,N}) = U - TS =$
Helmholz Free Energy

The **free energy** is the *Maximum* amount of work you can get out of a system after putting heat in and **is a state function**.

For a reversible process <u>at constant *T*</u>, $dA = -\delta w$
In an irreversible process, $dA < -\delta w$

Free Energy is Minimal at Equilibrium

Based on the definition of free energy, the combined 1st and 2nd Laws, and the 2nd Law requirement that $\Delta S \geq 0$, we conclude that *free energy decreases for spontaneous processes and is stationary at equilibrium*.

$\Delta A \leq 0$; where equality occurs only at equilibrium.

*A is energy **available** for work on the surroundings.*

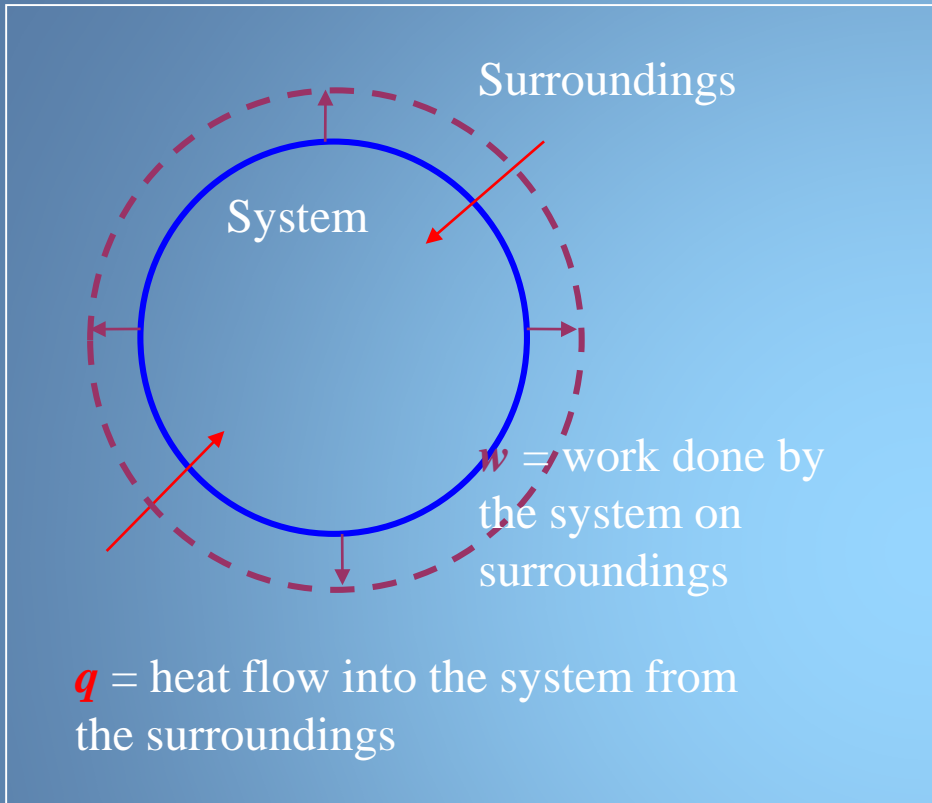Spontaneous change ($\Delta A < 0$) ⇨ available work is lost.

∴ Work can be done on the environment when spontaneous change occurs.

Work in living systems always involves trapping one chemical system in a non-equilibrium state and then **coupling** that system's spontaneous change to non-spontaneous change in another chemical system.

For this, work done in system 2 ≤ - ΔA for system 1.

Why not Equal?

Enthalpy: Changing Variables

Surroundings

System

w = work done by the system on surroundings

q = heat flow into the system from the surroundings

Thus far, V is constant. No PΔV work done on surroundings.

What if V is not constant? Then, P is independent variable.

Heat (q) flow in ⇨ ΔV.

∴ work (w=pΔV) done by the system on the surroundings.

Then U is not a useful state function, and we define a new state function that is determined by T, P, N:
The enthalpy, $H = U + PV$

We then define the corresponding "available work" state function as:

Gibbs Free Energy, $G(T,P,N) = H - TS$

Heat, Heat Capacity, and Entropy

The temperature dependence of the *Heat Capacity* ⇨ All the thermodynamics of a system.

$$C_p = \left(\frac{\partial H}{\partial T} \right)_{P,N_i} ; C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N_i}$$

When no work is done on or by the system, we can write:

$$\Delta S = \int \frac{dq}{T} = \int dT \frac{1}{T} \frac{dq}{dT} = \int dT \frac{C_v}{T}$$

The entropy S of all systems is set equal to zero when the absolute temperature, T is zero (the so-called **Third Law**), ⇒ we can obtain the entropy if we can measure C_V to $T=0°$.

Similarly, we obtain the internal "thermal" energy:

$$\Delta U = \int dq = \int dT \frac{dq}{dT} = \int dT \, C_v$$

Chemical Thermodynamics

Essential for biology!

While Thermodynamics is familiar to engineers and physicists, the thermodynamics most useful in Biophysics is that familiar to chemists: solution, reaction, and phase equilibria.

A new concept: Molar Free Energy = Free Energy per concentration of a molecule.

Need in Lecture 2, but define now.

The Molar Free Energy = Chemical Potential

The **Chemical Potential** is defined as the partial molar free energy for a given component:

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_{j \neq i}} = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,N_{j \neq i}}$$

So far, we have considered only the dependence on *T* and *P* or *V* in defining state functions. We can write the total differential of any state function in terms of these independent variables:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP - dw = -SdT + VdP - dw$$

But now we have a way to express the dependence of *G* on *N_i*:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP - dw + \sum_i N_i \left(\frac{\partial G}{\partial N_i} \right)_{T,P} dN_i = -SdT + VdP - dw + \sum_i \mu_i dN$$

At constant T and P and no work, $dG = \sum_i \mu_i dn_i$

Thermodynamic Formalism Boring but Useful

Differential relationships can be written for all state functions and allow us to use thermodynamics as a mathematical formalism.

State Function Total differentials: Easy to remember & useful:

$$dU \leq TdS - PdV - \partial w + \sum \mu_i dn_i; \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} ; \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} ; \quad \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

Combined 1st & 2nd Laws

$$dG \leq -SdT + VdP - \partial w + \sum \mu_i dn_i; \quad S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i} ; \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i} ; \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

Work Function of Combined Law

$$dH \leq TdS + VdP - \partial w + \sum \mu_i dn_i; \quad T = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} ; \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,n_i} ; \quad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,V,n_j}$$

Combined 1st & 2nd Laws

$$dA \leq -SdT - PdV - \partial w + \sum \mu_i dn_i; \quad S = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i} ; \quad P = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i} ; \quad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$$

Work Function of Combined Law

Maxwell Relationships: http://en.wikipedia.org/wiki/Maxwell_relations

The Gibbs Free Energy is the weighted sum of chemical potentials of each component.

At constant T and P and no work, the total differential of G can be integrated.

Successively add an increment of *each* component in proportion to n_i
Composition and pressure do not change, volume changes proportionally:

$dn_i = n_i \, dx$

$dG = © \big/_i dn_i = \Sigma \big/_i n_i \, dx$

$G(x{=}1) = © \big/_i n_i \, dx = © n_i \big/_i \int dx$

$$G = \sum_i n_i \mu_i$$

Since G must be minimized at equilibrium, mass equilibrium in Open Systems is defined in terms of chemical potential. This is the basis of all forms of chemical and physical mass equilibria.

Study Questions

You should be able to answer easily the following questions. If you can't, please go over these with you Study Group so you are prepared to answer them in recitation.

1. Does the First Law of thermodynamics ring true to your personal experience? Why or why not?

2. What critical observation made the Second Law necessary? Explain.

3. In what sense is the Helmholtz Energy (A) "Free"?

4. How is the Gibbs free energy (G) related to the Helmholtz free energy (in simple words)?

5. From the combined First/Second Law and the definition of A (energy free to perform work), derive the total differential expressions for U and A. The expressions given in lecture have terms in μ_i and n_i. What is the origin and meaning of these?

6. We said that all living systems must be able to do work. Why?

7. If a system can exist in two forms (or states) such that A1 < A2, which form are we more likely to observe?