

Define

Heat (q) - is the energy transferred into or out of a system due solely to differences in temperature.

Heat manifests itself by differences in the velocity of molecules that absorb it.

Temperature

Every molecule has a translational kinetic energy given by $(1/2) mV^2$

Where m is the mass

The average kinetic energy μ

Is given by

$$\langle u \rangle = \left(\frac{1}{2}\right)m\langle v^2 \rangle = \left(\frac{3}{2}\right)k_B T$$

Dividing by 3/2 Boltzmann's constant gives an absolute definition of temperature.

Molecular Energy

There is actually an energy distribution given by

$$d \ln N = \frac{dN}{N} = 2\left(\frac{U'}{\pi}\right)^{0.5} \exp(-U') dU'$$

Where

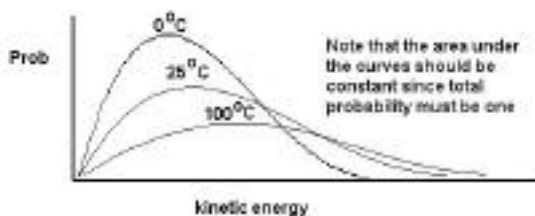
$$U' = \frac{U}{K_B T}$$

Energy

At 300 K

Hydrogen atom	2700 MS ⁻¹
Protein molecule	15
Emulsion droplet	0.001
Billiard Ball	10 ⁻¹⁰

Distribution



Define

Work (W) - is defined as any change (besides thermal) of energy between a system and its surroundings. In most cases the discussions will be concerned with changes in volume and pressure.

Internal Energy (E) - is the total energy within a system

Define

System - A bounded area separated from the rest of the universe which is under study. A system may be open, closed or isolated.

An open system allows for the transfer of both mass and energy between itself and its surroundings. Living organisms are examples of open systems.

Define

A closed system is one that prohibits the transfer of mass with its surroundings, but is open to the exchange of energy. Most of the discussion that follows will concern closed systems.

An isolated system does not permit the transfer of either mass or energy to its environment. A calorimeter is an example of an closed system.

Enthalpy

Enthalpy (H) is defined as the sum of the internal energy of a system plus the mechanical-volume energy associated with the space occupied by the system. The latter is the product of its volume and the external pressure exerted on the system.

$$H = E + PV \quad 1$$

The first law of thermodynamics states that energy is conserved

Enthalpy

For a change of state:

$$\Delta E = \Delta Q - \Delta W \quad 2$$

If the only work done is a change in volume:

$$\Delta E = \Delta Q - P\Delta V \quad 3$$

The enthalpy of the system is:

$$\Delta H = \Delta Q - \Delta W + P\Delta V + V\Delta P \quad 4$$

Enthalpy

If the only work done is PdV, then:

$$\Delta W = P\Delta V \text{ and:}$$

$$\Delta H = \Delta q + P\Delta V \quad 5$$

At a constant volume:

$$\Delta E = \Delta q \quad 6$$

While at constant pressure:

$$\Delta H = \Delta q \quad 7$$

Enthalpy

In living organisms, the changes in pressure are very small so equation 7 nearly applies. Furthermore, in solids and liquids, the volume changes are small so that for biological systems the approximation that the enthalpy change of the system is approximately equal to the internal energy change can be made, i.e.:

$$\Delta H \approx \Delta E \quad 8$$

In practical terms when changes in enthalpy of reactions involving proteins are considered, it can be said that changes in the internal energy of the molecules are approximately equal to their heat content.

Entropy

Define another property of the system
Entropy as:

$$S = k \ln W \quad 9$$

where k is Boltzman's constant
and
 W is equal to the number of ways something
can be arranged.

Entropy

Consider the isothermal expansion of an ideal
gas from volume 1 (V_1) to volume 2 (V_2)

Volume V_1 can be divided into n_1 cells of
volume V so that:

$$V_1 = n_1 V \quad 10$$

The larger volume can be divided into n_2 cells
of volume V so:

$$V_2 = n_2 V \quad 11$$

Entropy

If one molecule is placed in the initial system there
are n_1 ways to do this. For two molecules there are
 n_1^2 arrangements. For a mole of molecules in
volume V_1 , the number of arrangements is:

$$W_1 = n_1^{N_0} \quad 12$$

where N_0 is equal to Avagadro's number. In the
larger volume, V_2 :

$$W_2 = n_2^{N_0} \quad 13$$

Entropy

$$\Delta S = k \ln n_2^{N_0} - k \ln n_1^{N_0} \quad 14$$

or:

$$\Delta S = k \ln(n_2/n_1)^{N_0} \quad 15$$

By definition, R , the gas constant, is equal to k^{N_0}
so:

$$\Delta S = R \ln(n_2/n_1)$$

$$n_1 = \text{and } V_1/V \quad n_2 = V_2/V$$

Entropy

Substitution of these into equation 16 gives:

$$\Delta S = R \ln \left(\frac{V_2/V}{V_1/V} \right) \quad 17$$

Which reduces to:

$$\Delta S = R \ln (V_2/V_1) \quad 18$$

Equation 18 relates the change in entropy directly to
the ratio of the two volumes which is related to the
number of ways of arranging the molecules in these
volumes.

Entropy

Another way to visualize entropy is to consider the
absorption of heat, q , by a system at a constant volume
and pressure.

The absorbed heat must have moved molecules into
higher energy states.

If this process is reversible indicated by q_{rev} , we can
define the change in entropy at a given temperature
as:

$$\Delta S = \Delta q_{\text{rev}}/T \quad 19$$

Entropy

Two observations should be made:

Energy changes in an isolated system are always zero

In all irreversible processes, the entropy of the system plus that of its surrounding increases.

In the "real" world there are no truly reversible processes because there is always some loss of energy to friction and thus to entropy. Thus the entropy of the universe is increasing and will reach its maximum value when no energy differences exist.

Free Energy

Gibb's free energy (G) can now be defined as:

$$G = H - TS \quad 20$$

From the definition of enthalpy equation 1 states that $H = E + PV$, then:

$$G = E + PV - TS \quad 21$$

Thus, the free energy is the total internal energy and mechanical energy of occupying a space in excess of that energy associated with creating the system.

Free Energy

For a differential change in G :

$$dG = dE + PdV + VdP - TdS - SdT \quad 22$$

With proteins work is often done at constant temperature and pressure so that two of the above terms vanish, i.e.:

$$SdT = 0 \text{ and } VdP = 0$$

and from equation 19 :

$$TdS = dq \quad 23$$

Free Energy

Further from the first law (equation 2):

$$dE - dq = -dW$$

consequently, substitution of these four terms into equation 22 yields:

$$dG = -dW + PdV \quad 24$$

which rearranges to:

$$-dG = dW - PdV \quad 25$$

Free Energy

That is, the decrease in free energy is equal to the work done by the system minus the mechanical work done on the system. For any set of conditions, the work done by the system is maximal and can be called q_{\max} , then:

$$-dG = dq_{\max} - PdV \quad 26$$

PdV is work that can not be harnessed in chemical processes as it is used to create the new space required by the system and can be termed as wasted work, or:

$$-dG = dW_{\text{useful}} \quad 27$$

Free Energy

Thus, changes in Gibb's free energy are a measure of the useful work that can be obtained from a system.

A negative value for ΔG suggests that the reaction products have lower energy than do the reactants and that the reaction will proceed.

Free Energy

A positive value suggests that energy must be applied to the system in order for the reaction to proceed.

A useful definition of ΔG for a process in which a system goes from one condition (state) to another is:

$$\Delta G = \Delta H - T\Delta S \quad 28$$

Free Energy

Thus, it has been established that ΔG is useful work.

It is made up of a component related to the change in internal energy of the system (ΔH) and also an entropy term ($T\Delta S$) which measures the change in randomness of the system.

Equilibrium

For a chemical reaction we can define the thermodynamic equilibrium constant K_{eq} as:

$$K_{eq} = \text{Products/Reactants} \quad 29$$

For the reaction $A + B = C + D$ at equilibrium:

$$K_{eq} = (C)(D)/(A)(B)$$

Free Energy

The free energy, ΔG , and the equilibrium constant,

K_{eq} , can be related by the following expression:

$$\ln K_{eq} = \Delta G / RT \quad 30$$

Which rearranges to:

$$\Delta G = -RT \ln K_{eq} \quad 31$$

Free Energy

This is a useful over simplification as it should be obvious from the definition of Gibb's free energy that the value obtained will depend upon the temperature chosen.

Further it has been assumed that K_{eq} is independent of concentration.

This is nearly true for very dilute solutions, but in most cases the use of concentrations in experiments to determine free energy can lead to serious errors.

Partial Molar Quantities

Partial molar volume is equal to the change in a constant number of moles of solvent upon the addition of one mole of solute

$$\bar{V} = dV/dn$$

Free Energy

Can do the same for free energy

$$dG/dn = \bar{G}$$

Define this as chemical potential μ

$$\mu = \bar{G}$$

Activity

Define activity

$$= a/m$$

$$a = m$$

Then

$$\mu_1 = \mu_1^0 + RT \ln a_1$$

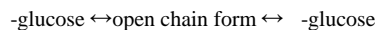
Activity Coefficients

		Concentration	
Ion	0.001	0.01	0.1
H ⁺	0.98	0.93	0.86
OH ⁻	0.98	0.93	0.81
OAc ⁻	0.98	0.93	0.82
H ₂ PO ₄ ⁻	0.98	0.93	0.74
HPO ₄ ⁻²	0.90	0.74	0.45
PO ₄ ⁻³	0.80	0.51	0.16
H ₂ Cit ⁻	0.98	0.93	0.81
H ₂ Cit ⁻²	0.90	0.74	0.45
H ₂ Cit ⁻³	0.80	0.51	0.18

Not all species are reactive

We know that for non enzymatic browning that the form that glucose is in affects its reactivity.

A simple equilibrium can be written as



The activity of the open chain species is what is important

Solvent quality

At high concentrations the activity of a species will depend greatly on the quality of the solvent as well as the presence of other species.

Factors that affect solvent quality will affect activity.

Adsorption

Molecules can adsorb to a number of surfaces or other molecules and lower their activity coefficient.

Interfaces such as air/water and lipid/water as well as the presence of macromolecules can have large effects.

Self association

Amphiphilic molecules can form associations that remove portions of the molecule from the aqueous environment.

Critical micelle concentration is an important consideration.

Other molecules maybe involved in the association

Electric Shielding

Ionizable substance dissociate in water

Osmolarity will be higher than molarity

Presence of other charges can shield charges

Activity will depend on presence of counterions

Ionic strength is important

$$I = \frac{1}{2} \sum m_i Z_i^2$$

Sample Energy

Antibody - Antigen reaction

$$G = H - T S$$

$$G = -7.1 \text{ Kcal/mole}$$

$$H = -9.5 \text{ Kcal/mole}$$

$$S = -8.0 \text{ Eu}$$

What do these values mean?

Calculate

Calculate G at 25 60 and 90C

When

$$H = -3.0 \text{ Kcal}$$

And

$$S = -9 \text{ eu}$$

What is the equilibrium constant at each temperature?