Thermodynamic Potentials

8.1 The Central Equation of Thermodynamics
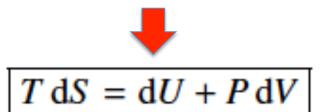
The First Law of Thermodynamics can be written as:

$$đQ = dU - đW,$$

and that for reversible pressure work we can write:

$$đQ_R = dU + P\,dV$$

We have seen that we can write: $đQ_R = T\,dS$

$$\boxed{T\,dS = dU + P\,dV}$$

This is the central equation: although derived for reversible changes only, it applies generally, because all variables are functions of state, so the method of change is not important.

However, it is essential that the system starts and ends in equilibrium so that it is meaningful to talk about pressure, temperature and entropy.

8.2 Entropy of an ideal gas

For a mole of ideal gas we have P = RT/V
and dU = C_V dT (internal energy a function of temperature only).
Therefore we can write:

$$T\, dS = dU + P\, dV \qquad \Rightarrow \qquad dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

integrating

$$S = S_0 + C_V \ln T + R \ln V$$

where S_0 is a constant of integration (note that this constant is not determined in classical thermodynamics but is by statistical thermodynamics).

This relation shows that the

entropy of an ideal gas increases with both T and V

increasing temperature increases the number of available states, since more energy states become available for the atoms.

$$S = S_0 + C_V \ln T + R \ln V$$

For a monatomic gas: $\qquad C_V = \dfrac{3}{2}R = \dfrac{3}{2}N_A k$
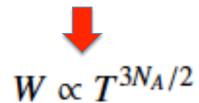
$$S = S_0 + 3/2 \, N_A \, k \, \ln T + R \, \ln V$$

Given Boltzmann's relation $S = k \ln W$:

$$k \ln W = S_0 + 3/2 \, N_A \, k \, \ln T + R \, \ln V$$

$$W \propto T^{3N_A/2}$$

for an Avogadro's number of atoms N_A

8.3 Thermodynamic Potentials

Changes can only occur
if the entropy of the Universe increases

Examples:

-    *we might have two chemicals mixed in a vessel*
whether these react or not depends upon whether the entropy
of the Universe increases as a result of their reaction.

-    *some elements, such as tin, sulphur, carbon*
     can exist in multiple forms or allotropes (like graphite and diamond)
   which is the stable one depends upon whether the entropy
   of the Universe increases as one form converts to another.

This only means that change can occur,
not that it will occur
because potential barriers can make such reactions very slow

Reactions do not usually occur in isolation

we need to consider the surrounding
for instance considering
heat transferred to the environment

In what follows, a subscript 0 on a quantity refers to its value in the surroundings, while plain variables refer to the system of interest.

8.3.1 Enthalpy

If a reaction occurs at constant volume, then the First Law states that:

$$-Q = -\Delta U$$

Let's consider a system in pressure equilibrium with its surroundings (at least at the start and at the end of the change), i.e. $P = P_0$:

$$\Delta U = Q - P_0 \Delta V$$

$$-Q = -(\Delta U + P_0 \Delta V) \qquad \text{the heat given off}$$

Given that $P = P_0$: $$-Q = -(\Delta U + P\Delta V) = -\Delta(U + PV) = -\Delta H$$

$$\boxed{H = U + PV}$$

a function of state called the enthalpy

$$H = U + PV$$

-ΔH is the heat given off in chemical reactions at constant pressure.

The PV term in the enthalpy
corrects for work done during any volume change

In analogy to $\quad C_V = \left(\dfrac{\partial U}{\partial T} \right)_V \quad \Longrightarrow \quad C_P = \left(\dfrac{\partial H}{\partial T} \right)_P$

specific enthalpy capacity

Thermodynamic data books include enthalpies of formation, H_f

The enthalpy of formation of the elements themselves is defined as zero. For instance, both hydrogen in the form of H_2, and oxygen as O_2 have $H_f = 0$.
Water (H_2O) has $H_f = -242$ kJ mole^{-1}

Example:

The enthalpies of formation of carbon monoxide (CO) and carbon dioxide (CO_2) are -110.5 kJ mole^{-1} and -393.5 kJ mole^{-1} respectively.
How much heat is produced per mole of carbon monoxide when it is burnt to produce carbon dioxide?

One mole of CO plus half a mole of O_2 produces one mole of CO_2.
The enthalpy of formation of O_2 is zero by definition,
therefore the heat released is given by:

$$-\Delta H = -(\Delta H_f(CO_2) - \Delta H_f(CO)) = 283 \text{ kJ mole}^{-1}$$

8.3.2 Helmholtz Free Energy

Can a certain reaction take place spontaneously?

including the surrounding

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S \geq 0$$

Consider a reaction taking place at constant volume and
in temperature equilibrium at the start and finish.
The heat given off is given by -Q = -ΔU

The temperature of the surroundings
does not change while heat Q transfers
from it to the system, and so:

$$\Delta S_{\text{surroundings}} = -\frac{Q}{T_0}$$

from the First Law, Q = ΔU
(no work in this case), and so we get:

$$\Delta S - \frac{\Delta U}{T_0} \geq 0$$

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Now since T = T$_0$ at the start and finish (temperature equilibrium), we can write (multiplying by T):

$$T\Delta S - \Delta U \geq 0$$

$$\Delta F \leq 0$$

$$\boxed{F = U - TS}$$

where, the Helmholtz free energy F, is another function of state

chemical reactions at constant volume and temperature only occur spontaneously if ΔF ≤ 0

Helmholtz free energy

$$F = \boxed{U} - \boxed{TS} \qquad \Delta F \leq 0$$

Equilibrium is reached therefore when F is a minimum
at which point dF = 0

The internal energy part enters to account for the heat transferred from the surroundings, in terms of the equivalent entropy change of the surroundings.

The TS part of F is the usual entropy part that gives
$\Delta S \geq 0$ for a thermally isolated system.

it is entropy which determines whether a change is possible or not, and F provides a convenient way of accounting for it.

Changes are favoured either:

- if ΔU < 0 (the reaction gives off heat)
- if ΔS > 0 (there is an increase in entropy).

In some cases both conditions are met,
in others neither condition is met.

In-between case:

- if ΔU > 0 (the reaction absorbs heat) but ΔS > 0.

whether it occurs depends upon the temperature, becoming more favourable as the temperature is increased.

Many such reactions occur: for instance the solution of ammonium nitrate in water is endothermic (it absorbs heat) but it goes ahead anyway because of the large increase in entropy (of the system) that results – needed to offset the decrease in the entropy of the surroundings that has occurred as a result of the absorption of heat.

8.3.3 Gibbs Free Energy

Experimentally it is easier to operate under conditions of
constant pressure rather than constant volume.

We have Q = ΔU, and Q = ΔH
Therefore rather than F = U - TS as the function that determines
whether changes can occur, we get:

$$\Delta G \leq 0$$

where

$$\boxed{G = H - TS = U - TS + PV}$$

Gibbs free energy

G is a minimum in equilibrium,
when dG = 0 for all possible changes

Thermodynamic potentials

- the internal energy U

- the enthalpy H = U + PV

- the Helmholtz free energy F = U - TS

- the Gibbs free energy G = U - TS + PV

like potential energy,
they are minimised in equilibrium.

8.3.4 Why "Free Energy"?

o   the maximum amount of work that can be obtained during a change of a system of constant volume V and temperature T is −ΔF

o   the maximum amount of work that can be obtained during a change of a system of constant pressure P and temperature T is −ΔG

From the first law, the work we can extract from a system, -W is given by:

$$-W = -dU + Q$$

If the volume changes, then we lose some of this in work against the surroundings, P_0V, and so can extract useful work:

$$W_{use} = -W - P_0\,dV = -dU - P_0\,dV + Q$$

$$W_{\text{use}} = -W - P_0\,dV = -dU - P_0\,dV + Q$$

From Clausius' inequality, $Q \leq T_0\,dS$, and therefore:

$$W_{\text{use}} \leq -dU - P_0\,dV + T_0\,dS$$

At constant temperature ($T=T_0$) and pressure ($P=P_0$):

$$W_{\text{use}} \leq -d(U - TS + PV) = -dG$$

$-\Delta G$
is the maximum amount of work
that can be obtained

8.4 Natural variables

The "central equation" T dS = dU + P dV
can be written as

$$dU = T\,dS - P\,dV.$$

and we see that: $$U = U(S, V).$$ U is a function of state

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV.$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Consider subtracting d(TS) to the equation below:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV.$$

Since: $\quad d(TS) = T\,dS + S\,dT.$

$$dU - d(TS) = d(U - TS) = -S\,dT - P\,dV.$$

$$dF = -S\,dT - P\,dV.$$

$$F = F(T, V)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

these equations are useful because F can be calculated in statistical thermodynamics, starting with a microscopic model

In the same way, we can start with:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

and adding d(PV) one obtains: $dH = d(U + PV) = T\,dS + V\,dP$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

If we subtract d(TS) from dH:

$$dH = d(U + PV) = T\,dS + V\,dP$$

$$dG = d(H - TS) = -S\,dT + V\,dP$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

Note that G applies for reactions at constant T and P, and indeed the natural variables for G are T and P

8.5 Example of Use of Gibbs Free Energy

Example 8.2 The density of graphite is $2.25 \times 10^3 \text{ kg m}^{-3}$ while that of diamond is $3.51 \times 10^3 \text{ kg m}^{-3}$. Measured at 298 K, the enthalpy of formation of graphite is 0, while that of diamond is $\Delta H_f = 1.897 \text{ kJ mole}^{-1}$. The difference in entropies of diamond and graphite is

$$S_d - S_g = -3.36 \text{ J K}^{-1} \text{ mole}^{-1}.$$

(a) What is ΔG going from graphite to diamond at 298 K?

(b) Is diamond or graphite the stable form of carbon at 298 K and 1 atm?

(c) Assuming that graphite and diamond are incompressible, at what pressure are they in equilibrium at 298 K?

Answer 8.2   (a) Starting from $G = H - TS$, then

$$\Delta G = G_d - G_g = H_d - H_g - T(S_d - S_g)$$
$$= 1897 \,\mathrm{J\,mole^{-1}} - 298\,\mathrm{K} \times (-3.36\,\mathrm{J\,K^{-1}\,mole^{-1}}) = 2898\,\mathrm{J\,mole^{-1}}.$$

(b) Since $\Delta G > 0$, graphite is the stable form. Diamond can change spontaneously to graphite at 298 K since then $\Delta G < 0$, but we don't see it happen because of a large activation energy.

(c) We use the relation $dG = -S\,dT + V\,dP$ (Eq. 8.36), from which

$$d(G_d - G_g) = (V_d - V_g)\,dP.$$

One mole of carbon has mass 0.012 kg, so the molar specific volumes are $V_g = 0.012\,\mathrm{kg\,mole^{-1}}/2250\,\mathrm{kg\,m^{-3}} = 5.333 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}$ and $V_d = 3.419 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}$. Therefore

$$d(G_d - G_g) = -1.91 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}\,dP.$$

Therefore the difference in G decreases with pressure, and will reach zero when $dP = 2898\,\mathrm{J\,mole^{-1}}/1.91 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}} = 1.5 \times 10^9\,\mathrm{N\,m^{-2}}$, or 15,000 atmospheres. Above this pressure, diamond is the stable form of carbon at 298 K.

8.6 Summary

- Central equation $$T\,dS = dU + P\,dV$$

- Entropy $$S = S_0 + C_V \ln T + R \ln V$$

- Boltzmann relation $$S = k \ln W$$

- Enthalpy $$H = U + PV$$ constant pressure

- Helmoltz Free energy $$F = U - TS$$ constant volume

- Gibbs Free energy $$G = H - TS = U - TS + PV$$

constant pressure