Chemical Thermodynamics

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Introduction

Thermodynamics is a branch of science that originated in the 19th century from experiments on steam engines, but it now spans all the major areas of science from physics to biology as well as engineering. It is a science of the macroscopic world, but it is greatly illuminated by our knowledge of the molecular structure of matter. It is through thermodynamics that we define commonly used terms like heat, work, energy, and temperature. We also define some less commonly used words like entropy, heat capacity, and free energy. In fact, the whole concept of energy, and the relationship between one form of energy and another, was not fully understood before thermodynamics was established.

Thermodynamics leads to relationships between several terms that have the dimension of energy; some are directly related to experimental measurements of heat, some to work, and some are relevant to the concept of equilibrium. We are interested in how these energies change under the externally controlled variables of pressure, volume, and temperature; we therefore start with a definition of these variables.

The external variables

Volume is straightforward; it is a measure of three-dimensional space (SI unit m$^3$). Pressure is the force per unit area (SI unit of force is the Newton (N), and of pressure is the Pascal, Pa = N/m$^2$). Pressure is more commonly expressed in the unit atmospheres (1atm = 101325Pa).

Temperature is the tricky variable. We know that heat flows from a hotter to a colder body. We also know that the atoms and molecules in a hot body are moving more rapidly than in a cold body (the atoms in a gas at room temperature are typically moving at supersonic speeds). As solids, liquids, and gases, expand roughly linearly with temperature, we can construct the commonly used thermometers for measuring temperature. Fahrenheit, and Celsius, defined scales of temperature from the expansion of liquids with certain fixed points on their scales. Other properties of matter such, as its electrical resistance, or the potential that exists at the junction of two metals, also vary linearly with temperature over a limited range of temperature, hence $T$ can be measured by a platinum resistance thermometer, or by a thermocouple.

The well-known gas law for perfect or ideal gases, which is called an equation of state, is
This equation was known long before the laws of thermodynamics were established. \( R \) is called the gas constant, and \( n \) is the number of moles of gas. But for this equation to be true it was found that \( T \) had to be measured in a temperature scale that had a zero at approximately \(-273^\circ C\). \( RT \) has the dimensions energy/mole, and \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \), or \( 0.0825 \text{ L atm K}^{-1} \text{ mol}^{-1} \).

A precise definition of temperature, and its measure by the kelvin scale, \( 0K = -273.15^\circ C \) (one cannot have a temperature below 0K), arises from the second law of thermodynamics, which we examine later. The kelvin scale also comes from the statistical theory developed by Boltzmann in which thermodynamics is given an interpretation through the energy levels available to individual atoms and molecules. *If temperature appears in any thermodynamic equation it must be taken in the kelvin scale.*

**The laws**

Thermodynamics is based on three laws. The first law is the Conservation of Energy. We can convert energy from one form to another but it cannot change in a closed system (this ignores mass to energy conversion which occurs in nuclear reactions).

The second law is concerned with spontaneous change and results from the important observation that heat always flows from hotter to colder bodies. The second law also holds the key to whether changes occur reversibly or irreversibly; reversibility in thermodynamics is associated with an idealized experiment in which we have a system in equilibrium, and any external influences move the position of the equilibrium very slowly. Chemical reactions can be carried out reversibly or irreversibly, and the heat or work that can be extracted from the reaction are different in the two cases.

The third law is a conclusion drawn from the statistical behavior of matter that only one state is possible for a perfect crystalline lattice at absolute zero. From this law it can be deduced that one can approach absolute zero to any prescribed temperature, but one can never reach absolute zero.

**The system**

A concept central to thermodynamics is that of the ‘system’. The system is something we focus attention on; outside it we have the ‘surroundings’, to which the system is connected. For example, a water ice mixture in a vessel might be the system and the refrigerator in which it is kept could be the surroundings. A system is ‘open’ if it can exchange matter and energy with its surroundings. It is closed if it can exchange energy but not matter, and it is isolated if neither matter nor energy can
be exchanged. Changes to the system are called isothermal if the temperature is kept constant, isobaric if the pressure is kept constant, and an adiabatic system is one that is in thermal isolation.

The state of a system is defined by its composition and any two of the three variables (P,V,T), the third variable being determined by the other two according to an appropriate equation of state. The various thermodynamic energy terms are called functions of state, and for a system in equilibrium (one not changing with time), the functions of state have values which are independent of the history of the system (how it got to be in the condition it is in). The consequence of this is that changes in a function of state do not depend on the route by which one goes from one state to another. Thus changing from state \( a \) to state \( b \) changes a general state function (\( F \)) according to the rule

\[
\Delta F = F_b - F_a
\]

The use of the symbol \( \Delta \) is important in thermodynamics; it emphasizes that we are mainly interested in changes of state function rather than in their absolute values; indeed in most cases the absolute value cannot be defined and in consequence we define sensible arbitrary zeros.

**The first Law**

Heat and work are both consequences of the energy change in a system. The energy contained in a system is called internal energy and is given the symbol \( U \). If we change a system from state \( a \) to state \( b \) then the change in internal energy is equal to the heat added to plus the work done on the system, according to the equation

\[
\Delta U = U_b - U_a = q_{\text{in}} + w_{\text{on}}
\]

Going from \( a \) to \( b \) always gives the same change in \( U \) but the values of \( q \) and \( w \) depend on the route taken; **heat and work are not state functions**.

The most common type of work that we encounter in chemical reactions comes from the change in volume against an external pressure, and this is the only one we deal with here; it is usually only a large quantity for gases whose volumes vary appreciably with pressure. If we keep the pressure constant then \( w_{\text{on}} = -P \Delta V \). Note the negative sign, because only if \( \Delta V \) is negative (a compression), have we done positive work on the system. For a constant pressure system

\[
\Delta U = q_{\text{in}} - P \Delta V
\]
a) If there is no change in volume then \( w_{on} \) is zero, so \( \Delta U \) is equal to the heat added to the system. Suppose, for example, we carry out a chemical reaction in a thermally sealed container (an adiabatic system) and keep the volume constant. If the reaction is exothermic (gives out heat), the temperature will rise but \( \Delta U \) will be zero because no heat is transferred to the surroundings. If now we place the system in a thermostat bath (an isothermal system), the heat generated by the reaction will be transferred to the bath, hence \( q_{to} \) will be negative and \( \Delta U \) will be negative for the system. For an endothermic reaction (one in which the system gets colder), \( \Delta U \) will be zero for an adiabatic system and positive for an isothermal system. To summarize: \( \Delta U \) is the heat given to the system in a reaction at constant volume.

b) For a system at constant pressure any change in volume will also contribute to \( \Delta U \). However, as we have not specified whether the system is adiabatic or isothermal we are not yet in a position to say what this change will be.

The position is clarified by introducing a new state function \( H \) called the enthalpy.

\[
H = U + PV
\]

For a constant pressure change (going from state a to state b)

\[
\Delta H = H_b - H_a = U_b - U_a + P(V_b - V_a)
\]

or,

\[
\Delta H = \Delta U + P \Delta V
\]

Combining (4) and (6), we see that the change in \( H \) for an isothermal system is equal to the heat given to the system at constant pressure.

\[
\Delta H = q_{to}
\]

Most chemical reactions are indeed carried out under constant pressure, therefore \( H \) is a more important quantity in chemistry than is \( U \). In a thermally sealed (adiabatic) reaction no heat is given to or taken from the system, hence \( \Delta H \) is zero. In an isothermal system at constant pressure \( \Delta H \) is the heat transferred to the system from the surroundings. If the reaction is exothermic \( \Delta H \) is negative, and if the reaction is endothermic \( \Delta H \) is positive.

**Applications**

\( U \) and \( H \) will change if we change the phase of the system. For example, if we condense steam at 100°C to water at 100°C heat is evolved; the process is exothermic
and both $\Delta U$ and $\Delta H$ will be negative. If we boil water at 100°C to give steam at 100°C we have to add heat to the system (both $\Delta U$ and $\Delta H$ are positive). We conclude that both U and H increase on passing from water to steam at 100°C. There are likewise increases on going from ice to water at 0°C, and in both cases we can attribute these facts to the loss of binding energy (a negative quantity) as the molecules get further apart on going from solid to liquid to gas.

In the combustion of fuels, as described by an equation such as

$$C_3H_8 (g) + 5O_2 (g) = 3CO_2(g) + 4H_2O(g) \quad (8)$$

heat is evolved, hence $\Delta H$ for the reaction is negative. $\Delta H$ is the difference between the total enthalpies of the products and the total enthalpies of the reactants, –2046kJ/mol for a system kept at 298K. An important method for determining the enthalpy change in a reaction is to use Hess’s law, that the heat change at constant pressure or constant volume in a chemical reaction is the same whether it takes place in one stage or several stages; this follows from the definition of a state function.

By convention the enthalpies of neutral molecules are referred to arbitrary standards (called standard states) in which the elements have zero enthalpies. Enthalpies on this scale are called enthalpies of formation, and are given the symbols $\Delta H_f^\circ$. Note that although $\Delta$ is used in this symbol it is better to consider enthalpies of formation as absolute quantities because $\Delta H$ for a reaction such as (8) is equal to the difference between the enthalpies of formation of the products and the enthalpies of formation of the reactants. Standard states refer to the phases of the elements at the temperature and pressure specified (tables usually give values at 298K); they may be gases, liquids, or solids, and if solids then the most stable phase at that temperature is the standard. For example, the standard state of O$_2$ is a gas at 1atm, of Hg is a liquid, and of C is solid graphite.

Example: we can determine the enthalpy of formation of C$_3$H$_8$(g) by measuring the heat of the following reaction at constant pressure

$$3C(s) + 4H_2(g) = C_3H_8(g) \quad (9)$$

As the enthalpies of formation of the reactants are, by definition, zero, $\Delta H_f^\circ$ for the product is equal to $\Delta H$ for the reaction.

Values for the enthalpies of formation at 298K have been tabulated for most common molecules. For C$_3$H$_8$(g), CO$_2$(g) and H$_2$O(g) the values are -104, -394, and -242kJ/mol, respectively. Thus the enthalpy change for the reaction (8) at 298K is given by
\[ \Delta H = 3(-394) + 4(-242) - (-104) - 5(0) = -2046 \text{kJ/mol} \]

At other temperatures the value would be a little different but we usually ignore the difference unless we are working at very high temperatures or need a very accurate value. Although enthalpies vary with temperature, enthalpy differences usually vary rather little. The main changes are when there is a change in phase of one or more component, for example, having water as a product in a reaction produced as liquid rather than gas.

**Heat Capacity**

The quantity that measures the change of the enthalpy with temperature is called the heat capacity (in early work called the specific heat), or more exactly the heat capacity at constant pressure; its symbol is \( C_p \) and it is defined by

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (10) \]

As \( H \) is a function of \( P \) and \( T \), this is the slope of \( H(P,T) \) along the line of constant \( P \). The change of \( H \) for a small change of \( T \), \( \delta T \), would then be \( C_p \delta T \). An old unit, the calorie, which is still widely used, is defined as the amount of heat required to raise the temperature of 1g of liquid water by 1°C, and this is roughly constant between 0 and 100°C. Thus \( C_p \) for water is roughly 1cal/g deg, or 18cal/mol deg; in SI units it is roughly 75J/mol deg. Raising the temperature of water from 0 to 100°C changes \( H \) by roughly 7.5kJ/mol.

For more precise work \( C_p \) is can be expressed as a power series in \( T \) (it is usually sufficient to go up to quadratic terms), and then changes in \( H \) from one temperature to another can be obtained from the integral

\[ H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p \, dT \quad (11) \]

Quite clearly we can get the changes in the enthalpy of a reaction such as (8) from the appropriate differences between the heat capacities according to the formula

\[ ( \frac{\partial \Delta H}{\partial T} )_p = \Delta C_p \quad (12) \]

where \( \Delta C_p \) is the sum of the product heat capacities minus the sum of the reactant heat capacities.
Just to complete the story, as $U$ is related to heat at constant volume, the heat capacity at constant volume is defined by

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v$$  \hspace{1cm} (13)

but only for gases is the difference between $C_p$ and $C_v$ significant. Indeed, for a reaction we can usually ignore the difference between $U$ and $H$ unless gases are involved and there is a change in the number of moles of gas between reactants and products.

**Pressure changes**

The work done on a system if it expands against a constant external pressure, such as atmospheric pressure, is $-P_{\text{ext}} \Delta V$ (expanding into a vacuum produces zero work as the external pressure is zero). If the volume change is infinitesimal ($dV$) the work done will be $-P_{\text{ext}} dV$, and for a larger change from $V_1$ to $V_2$, we must evaluate the integral

$$W_{\text{on}} = - \int_{V_1}^{V_2} P_{\text{ext}} \, dV \hspace{1cm} (14)$$

We can also use this formula to calculate the work done on the system if the external pressure is not constant. The only case of general interest is if the change in volume is made in what is called a reversible process; this means having the external pressure in almost complete balance with the internal pressure at all times. For example, by taking a gas in a cylinder with a piston and slowly applying an increasing pressure on the piston to compress the gas. This would be reversible because if we slowly relaxed the external pressure the gas would expand back to its original volume. To calculate the work done for a reversible change on a gas, we replace the external pressure by the internal pressure, and use the ideal gas law to replace the pressure in (14) by $RT/V$ (for one mole), and then evaluate the standard integral to give the following constant temperature result:

$$W_{\text{on}} = - RT \int_{V_1}^{V_2} \frac{1}{V} \, dV = -RT \ln(V_2/V_1) \hspace{1cm} (15)$$

The ideal gas law can again be used to produce a similar formula with $V_2/V_1$ being replaced by $P_1/P_2$. If, for example, we double the volume then the work done on one mole of a gas (the work produced), is from (15),

$$w_{\text{on}} = -RT \ln 2 = -1.7\text{kJ/mol} \hspace{1cm} (16)$$

**The First Law and Microscopic Energies**
Atoms and molecules have energies and we can relate these to the macroscopic energies that arise in thermodynamics; for this discussion we will ignore the difference between \( U \) and \( H \), which we have seen is generally small. For a low pressure gas we can multiply the molecular energy by Avogadro’s constant, \( 6.022 \times 10^{23} \text{ mol}^{-1} \), to get energy per mole, and this will be good enough for gases at any pressure unless we are doing very accurate work. However, remember that enthalpies of formation are relative to the enthalpies of the elements in their standard states, and so we must measure individual atomic or molecular energies with the same reference state; the simplest approach is to use bond dissociation energies.

Although molecular energies can be expressed in joules, a more common unit for dissociation energies and ionization potentials is the electron volt (eV). Also, spectroscopic energies are often expressed in wave numbers (cm\(^{-1}\)). The conversion factors to molar energies are as follows:

\[
1 \text{eV is equivalent to } 96.49 \text{kJ/mol} \\
1 \text{cm}^{-1} \text{ is equivalent to } 0.01196 \text{kJ/mol}
\]

We start with a simple example of a diatomic molecule.

\[
\text{H}_2(\text{gas}) \Rightarrow 2\text{H(g)}
\]

The dissociation energy of \( \text{H}_2 \) is 4.476eV or 432kJ/mol, thus as the enthalpy of formation of \( \text{H}_2 \) is zero, the enthalpy of formation of \( \text{H(g)} \) is 216kJ/mol. Going further, we can use the dissociation energy of \( \text{H}_2\text{O} \) for the process

\[
\text{H}_2\text{O(}g) \Rightarrow \text{OH}(g) + \text{H(g)}
\]

which is 5.12eV, or 494kJ/mol, together with the enthalpy of formation of \( \text{H}_2\text{O(g)} \) which is -242kJ/mol, to give the enthalpy of formation of \( \text{OH(g)} \) as 36kJ/mol.

We can also use ionization potentials to calculate the enthalpies of formation of gaseous ions. For example,

\[
\text{H}_2\text{O(g)} \Rightarrow \text{H}_2\text{O}^+(g) + e
\]

The ionization potential of \( \text{H}_2\text{O} \) is 12.6eV, or 1218kJ/mol, hence the enthalpy of formation of \( \text{H}_2\text{O}^+ \) is \( 1218 - 242 = 976 \)kJ/mol. However, this approach does not give the enthalpies of formation of ions in solution, because the stabilization energy of ions by solvation is usually very large, particularly when they are in polar solvents.
like water (if this were not so then molecules such as NaCl would not dissociate to ions in water). For solvated ions one uses a completely different standard from that used for neutral molecules, and this is that the enthalpy of formation of $\text{H}^+(\text{aq})$ is zero.

Liquids and solids have lower energies than gases because there are attractive forces between the molecules called van der Waals’ forces. These produce stabilization energies of about 0.1 eV (10 kJ/mol), or more for polar molecules due to electrostatic energies. These intermolecular forces therefore lower the enthalpies of liquids and solids relative to gasses. As there is not a great deal of difference between the binding energies in liquids and solids, the enthalpy changes on melting (heats of fusion) are rather small (water is 6 kJ/mol, benzene is 10 kJ/mol), and they are noticeably less than the enthalpy changes on vaporization (water is 44 kJ/mol, benzene is 43 kJ/mol). An important point to note is that from (10) we see that a non-zero enthalpy changes at a phase change leads to infinite values for the heat capacities at the temperature of a phase change.

The Second Law

The first law is a law of conservation, the second law is a law of dissipation. In historical times it was much more difficult to get it accepted by all scientists, but it is now recognized as one of the pillars of science. Note that it is not a law that can be proved from the laws of classical mechanics because from Newton’s laws it follows that all classical motion is precisely reversed if we go from +time to -time.

The main thrust of the second law is to enable us to understand the processes of spontaneous change; gases expand into a vacuum, they do not create a vacuum; if we use the brake to stop a car the brake gets hot, but if we heat the brake we do not move the car; put ice in hot water and it melts, hot water does not spontaneously produce ice.

It was first thought that spontaneous change went in the direction of lower energy, but this was seen to be false when it was noted that chemical reactions can be either exothermic or endothermic. Energy is important but another factor called entropy is involved. In fact for an isolated system entropy is the only factor that matters because the energy of an isolated system is conserved. Entropy is a word coined by Clausius in 1854 meaning literally ‘to give a direction’. From the microscopic picture of matter (the work of Boltzmann) we can associate entropy with randomness, and the law of dissipation is a law of increasing randomness.

Classical thermodynamics emerged from the study of steam engines, machines that convert heat to work. The earliest steam engines had a single cylinder with a
piston. Steam was introduced causing the piston to move out, and the cylinder was then cooled to make the piston move back again; in both movements work could be extracted. If steam is condensed and cooled to 0°C the energy released is about 52kJ/mol, and the question is how much work can be extracted. Clearly not all, because some energy will be transferred as heat to the cylinder. The efficiency is defined by the ratio of the work extracted to the heat provided. The first engines only had efficiencies of about 1% and it required great inventiveness to bring this figure up to that of modern engines with efficiencies of about 20%.

A major discovery concerning the efficiencies of steam engines was made by Carnot (1824). His analysis was based on an idealized engine in which the expansion and contraction of an ideal gas is used to produce work by transferring heat from a hot to a cold reservoir. The analysis of what is called the Carnot cycle (details in standard texts) assumes that the work is produced by a reversible process in which the expansions and contraction of the gas is infinitely slow.

Let us think of two reservoirs at temperatures $T_1$ (the source), and $T_2$ (the sink). Let the heat given to these two reservoirs be $q_1$ and $q_2$, respectively; $q_1$ will be negative if we extract heat from the source. When $T_1 > T_2$ we can extract work from the heat engine. However, if $T_1 < T_2$ we can use an engine (pump) to do work and transfer heat from the colder to the hotter reservoir; this is the principle behind the refrigerator.

It is obvious that we have zero work (out or in) if $T_1 = T_2$. Carnot’s discovery was that the maximum efficiency for the machine for fixed reservoir temperatures is given by the formula

$$-(w/q_1) = (T_1 - T_2)/T_1$$

We only have an efficiency of 1 (100%) if $T_2$ is absolute zero.

By the conservation of energy

$$w + q_1 + q_2 = 0$$

and using this to replace $w$ in (17) we have an equation which can be rearranged to give

$$q_2/q_1 = -(T_2/T_1)$$

which can be rewritten

$$(q_1/T_1) + (q_2/T_2) = 0$$
This equation is the basis of a conservation law (like (18)), and it implies that there is a state function, equal to \( q/T \), whose change is zero if we go around a Carnot cycle. It was this function that Clausius called the entropy, and it is given the symbol \( S \). In a reversible process we write

\[
S = q_{\text{rev}}/T \tag{21}
\]

where \( q_{\text{rev}} \) is the heat given to the system. Expression (21) is general for all reversible processes, not just those defined by the Carnot cycle. The entropy change in a reversible cycle is zero. The important extension of this idea made by Clausius is that for an \textit{irreversible} change of an isolated system the entropy always increases, and this is the principle behind our understanding of the direction of spontaneous change. Note that entropy has the dimensions of energy/deg.

To gain further insight into the concept of entropy we pass to the ideas of statistical mechanics developed by Boltzmann. His name is associated with the famous equation

\[
S = k \ln(W) \tag{22}
\]

In this equation \( k \) is known as Boltzmann’s constant, and \( W \) is the number of microstates of the system that are consistent with its macroscopic state. A microstate is a particular way in which the total energy is distributed amongst the energy states of the individual molecules. \( W \) is clearly related to a probability, the more microstates there are, the greater the probability for that macroscopic state. Because we multiply probabilities of individual events to arrive at a total probability, so through the use of the logarithmic function in (22), we add individual entropy contributions to get a total entropy \((\ln(P_1P_2) = \ln P_1 + \ln P_2)\).

So, spontaneous change is in the direction of increasing randomness for a closed system. To paraphrase the famous statement of the second law by Clausius, 'The entropy of the universe is increasing'. However, we are usually not interested in what is happening to the universe, rather, what is happening in, say, a reaction vessel that is in thermal contact with its surrounds. In our vessel we may boil a liquid (increasing its entropy), or freeze a liquid (decreasing its entropy). We are not really concerned with what is happening to the heater in the first case or the freezer in the second. In order to understand spontaneous change in a system that is in contact with its surrounds we have to introduce another type of thermodynamic state function, which is called the free energy.

There are two free energy functions, one useful for changes at constant volume, and one for changes at constant pressure. The latter is much the more important in
chemistry and is the only one we consider in detail; it is called the Gibb’s energy. It is given the symbol $G$ and is defined by

$$G = H - TS$$

(23)

If we make a change in the system keeping the temperature constant, then the change in $G$ is given by

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

(24)

For a change at constant pressure we have (from (7)), $\Delta H = q$, so that (24) becomes

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

(25)

We now see from (21), that in a reversible process at constant $T$ and $P$, $\Delta G = 0$, and in an irreversible process ($dS > q_{irrev}/T$), $\Delta G$ is negative. Thus, an irreversible or spontaneous process (again at constant $T$ and $P$) is one that leads to a decrease in $G$. Spontaneous processes for an adiabatic system at constant pressure are those that lead to a decrease in an energy term, but it is $G$, not $U$ or $H$ that must decrease.

From (24), we see that spontaneous change can be due to a decrease in $H$ or an increase in $S$. Below $0^\circ C$ liquid water freezes, both $H$ and $S$ decrease but $H$ wins. Above $0^\circ C$ ice melts, both $H$ and $S$ increase but $S$ wins.

For a chemical reaction we can take the $\Delta$ in (24) to be the difference between the thermodynamic quantities of products and reactants. We have seen that $\Delta H$ is the heat we can extract from a spontaneous chemical reaction at constant pressure (eg on combustion of a fuel). We will now show that $\Delta G$ is the maximum work that can be extracted from a reaction, this maximum being obtained if we carry out the reaction in a reversible mode. The simplest practical method of establishing reversibility is to carry out the reaction in an electrochemical cell where by applying an external emf we can move the reaction in either direction. We contrast the non reversible combustion of a fuel with the potentially reversible oxidation of a fuel in a fuel cell.

We start again with the definition of $G$

$$G = H - TS = U + PV - TS$$

(26)

and for a small change at constant $T$ and $P$
\[
dG = dU + PdV - TdS
\]  \hspace{1cm} \text{(27)}

From the first law (4)
\[
dU = dq_{\text{to}} + dw_{\text{on}}
\]  \hspace{1cm} \text{(28)}

and we can take \(w_{\text{on}}\) in two parts, that due to the volume change \((-PdV)\) and the rest \(w'\), thus
\[
dG = dq_{\text{to}} + w' - TdS
\]  \hspace{1cm} \text{(29)}

If the process is reversible, \(dq_{\text{to}}\) equals \(TdS\), so that
\[
dG = w'
\]  \hspace{1cm} \text{(30)}

Just as there are two state functions which relate to heat change, \(H\) for constant pressure and \(U\) for constant volume, so there are two state functions for maximum work, \(G\) for constant pressure and \(A\), the Helmholtz energy, for constant volume.
\[
A = U - TS
\]  \hspace{1cm} \text{(31)}

\(A\) is also equal to the total work in a reversible process at constant temperature both that due to volume change and the remainder.

\textbf{Changes in free energy with pressure and temperature}

For an infinitesimal reversible change involving only PV work we can combine the first and second laws ((4) and (21)) to give
\[
dU = -PdV + TdS
\]  \hspace{1cm} \text{(32)}

Then from (5) and (23)
\[
dG = d(U + PV - TS) = VdP - SdT
\]  \hspace{1cm} \text{(33)}

This gives rise to the important equations
\[
(\frac{\partial G}{\partial P})_T = V, \quad \text{and} \quad (\frac{\partial G}{\partial T})_P = -S
\]  \hspace{1cm} \text{(34)}

for the change in \(G\) with temperature or pressure. These are particularly important for our understanding of how phases change on changing \(P\) or \(T\) (the most stable phase at a particular \((T, P)\) is the one having the lowest value of \(G\)).
For a perfect gas we can integrate (34) at constant temperature (dT=0) between two pressure limits $P_1$ and $P_2$, to give

$$G(P_1) - G(P_2) = \int_{P_1}^{P_2} V dP = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \left( \frac{P_1}{P_2} \right)$$

(35)

If we take $P_2$ to be 1atm, and $P_1$ to be any other pressure $P$, and write $G(1\text{atm}) = G^\circ$, then this becomes

$$G(P) = G^\circ + RT \ln P$$

(36)

Where $P$ is measured in atmospheres. This is an important equation not only because it gives the free energy of a gas at any pressure $P$ with respect to the free energy at 1atm (the standard state of the gas), but also because it is the archetype of a class of expressions relating the free energies at one condition to the free energies in some chosen standard state; this is widely used for the thermodynamics of solutions.

**Standard States**

We have already mentioned standard states for enthalpies, and those for free energies are defined along the same lines with zeros for the elements in their normal phases; the symbol for the free energies of formation is $\Delta G_f^\circ$. However, entropies do not have an arbitrary zero because the third law of thermodynamics (based on the statistical interpretation of entropy) makes the entropies of all perfect crystals at absolute zero equal to zero. Entropies at other temperatures can be calculated by various means (usually from heat capacities). Thus entropies can be found in tables as $S^0_{298}$, but the symbol $\Delta S$ will still mean the difference between the entropies of the final and the initial state (eg reactants and products), and the fact that entropy is treated differently from enthalpy and free energy does not cause any problems because differences are our main concern.

**Free Energy and Equilibrium constants**

The simplest assumption we can make about the total free energy of a mixture of chemical species is to take the free energy per mole of each species, multiply by the number of moles, and add these together for all components. This works very well for mixtures of gases, but is generally rather inaccurate for solutions because molecules in a liquid can interact with one another quite strongly. To get around this problem a new state function is introduced for mixtures called the chemical potential, which is given the symbol $\mu_i$, and which is the effective free energy per mole of species $i$ in the mixture. The total free energy is then

$$G = \sum n_i \mu_i$$

(37)
We do not give a formal definition of $\mu_i$ at this point but note that it can be referred to the chemical potential of a standard state $\mu_i^o$ in an expression similar to (36)

$$\mu_i = \mu_i^o + RT \ln a_i$$

(38)

where $a_i$ is called the activity; for a perfect gas $a_i$ is the pressure in atmospheres and for solutions it can be related to concentrations. In a sense $a_i$ is introduced here to clean up the mathematics but it is related to observable quantities in certain ideal situations.

We can now apply (37) to give the change in free energy in a chemical reaction. We write

$$\Delta G = \Sigma n_p \mu_p - \Sigma n_r \mu_r$$

(39)

where the first sum is over products and the second is over reactants. Using (38) we can write

$$\Delta G = \Delta G^o + RT(\Sigma n_p \ln a_p - \Sigma n_r \ln a_r) = \Delta G^o + RT \ln K_a$$

(40)

where

$$K_a = (\Sigma n_p \ln a_p - \Sigma n_r \ln a_r) = \Pi(a_p)^{np} / \Pi(a_r)^{nr}$$

(41)

and

$$\Delta G^o = \Sigma n_p \mu_p^o - \Sigma n_r \mu_r^o$$

(42)

$K_a$ is the product of the activities of the products each raised to the appropriate power $n_p$, divided by the product of the activities of the reactants, each raised to the appropriate power $n_r$. $\Delta G^o$ is the appropriate difference between the chemical potentials of the standard states.

At a position of equilibrium $\Delta G$ is zero (no work can be obtained by moving reactants to products or vice versa), hence at equilibrium we have

$$\Delta G^o = -RT \ln K_a$$

(43)

or equivalently

$$K_a = \exp(-\Delta G^o/RT)$$

(44)

$K_a$ is called the thermodynamic equilibrium constant. The position of equilibrium in a reaction is an extremely important topic in chemistry as it tells us whether a reaction will go to completion or not.
Consider a chemical reaction in which reactants and products can be taken as perfect gases.

\[ H_2 + Cl_2 = 2HCl \]  \( (45) \)

(This potentially explosive reaction is just to illustrate the method of analysis). The activities of the components are just the pressures of the gases at 1 atm, so we have from (41)

\[ K_a = \frac{(P(HCl))^2}{(P(H_2).P(Cl_2))} \]  \( (46) \)

The free energies of formation of \( H_2 \) and \( Cl_2 \) are zero by definition, as they are the standard states of the elements, and the free energy of formation of \( HCl \) is \(-95\) kJ/mol. Therefore \( \Delta G^0 \) for the reaction is \(-95\) kJ/mol. We therefore have from (44), at 298K,

\[ K_a = \exp \left(\frac{95000}{8.314 \times 298}\right) = \exp(38.3) = 4.5 \times 10^{16} \]  \( (47) \)

We see from (45) that if the reaction (44) went to equilibrium then

\[ P(HCl) = 2.1 \times 10^8 \ \{ P(H_2). P(Cl_2) \}^{1/2} \]  \( (48) \)

all pressures being in atmospheres.

Now we take an example of a reaction in solution. In this case we can approximate the activities by the concentrations in moles per liter (this is very approximate as it does not take solvent effects into account).

\[ CO_3^{2-} + H^+ = HCO_3^- \]  \( (49) \)

\[ K_a = [HCO_3^-]/[CO_3^{2-}][H^+] \]  \( (50) \)

From standard tables we find

\[ \Delta G^0 = -587 + 528 + 0 = 59 \text{ kJ/mol} \]  \( (51) \)

so from (44), at 298K,

\[ K = \exp(59000/8.314 \times 298) = 2.2 \times 10^{10} \]  \( (52) \)

This means (from (49))

\[ [HCO_3^-]/[CO_3^{2-}] = 2.2 \times 10^{10} [H^+] \]  \( (53) \)
At a pH of 7, say, the concentration of $\text{H}^+$ is $10^{-7}$ moles/liter so at this pH there is 2200 times more $\text{HCO}_3^-$ than $\text{CO}_3^{2-}$.

Note that equilibrium constants are always dimensionless (as they must be from the definition (44)). Expressions such as (46) and (50) may appear to have dimensions but they do not as the units in which the quantities appear are always specified; atmospheres for the pressure of gases, or moles per liter for solutions, for example.

The End