

Notes on Basic Thermodynamics

The First Law

The First Law of Thermodynamics: *Energy cannot be created or lost, it can only be changed in form.*

Energy can take the form of heat (thermal energy), kinetic energy, potential energy, electrical energy, magnetic energy and electromagnetic energy (radiation).

Heat and the Thermodynamic System

In thermodynamics we are normally concerned with the energy balance of a system of some kind. The basic model system (Figure 1) is a container which has some matter (gas, liquid or solid) inside and have an internal energy U . It also has a specified volume V , temperature T and pressure P . The walls of the system may or may not (according to design) permit the transfer of heat energy q into or out of the system. As a result, the system internal energy may change by an amount ΔU , and its volume, temperature and pressure may also change as a result. The system may also do some work w on the external environment or have work done on it.

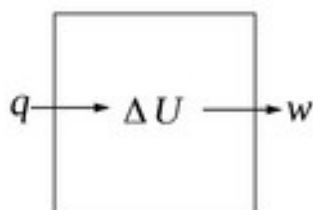


Figure 1. The basic system

The quantities may have positive or negative values according to the following conventions.

Heat:

$$\begin{aligned} q \text{ is } +ve \text{ if endothermic system (heat in)} \\ q \text{ is } -ve \text{ if exothermic system (heat out)} \end{aligned} \quad (1)$$

Internal energy:

$$\begin{aligned} \Delta U = \text{change in internal energy:} \\ +ve \text{ if energy increases} \\ -ve \text{ if energy decreases} \end{aligned} \quad (2)$$

Work:

$$\begin{aligned} w = \text{work done by the system:} \\ +ve \text{ if work done by the system} \\ -ve \text{ if work done on the system} \end{aligned} \quad (3)$$

The First Law applied to the basic system establishes the relation:

$$q = \Delta U + w \quad (4)$$

from which many thermodynamic relations are derived.

The Ideal Gas

An ideal gas is one which obeys the following equation of state.

$$PV = nRT, \quad (5)$$

where P is the gas pressure (Pa), V is the system volume (m^3), T is the system temperature (K), n is the number of moles of gas (mol) and R is the universal gas constant ($8.1446 \text{ J mol}^{-1} \text{ K}^{-1}$). The internal energy U of an ideal gas is

$$U = \frac{3}{2} nRT. \quad (6)$$

Most gases are good approximations to an ideal gas, so it is a good model system to study.

Gas Expansion and Work

In many circumstances a system does work when gas expansion takes place. It is useful to know how much work can be done when this occurs. For this purpose the system is viewed as a piston (Figure 2) that moves in response to the internal pressure P or external pressure P_{ext} .

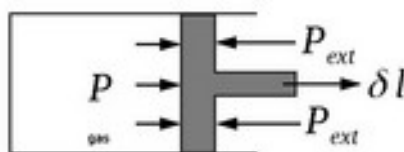


Figure 2. Work done by a volume of gas

The work δw done by the enclosed volume of gas is

$$\delta w = f \delta l = P_{ext} A \delta l = P_{ext} \delta V, \quad (7)$$

where δl is the piston displacement, δV is the change in volume, A is the area of the piston cross section, f is the force exerted on the piston and P_{ext} is the pressure external to the piston. The amount of work done depends on how the expansion is carried out. Two important examples are: an *irreversible* expansion against a constant external pressure (Case 1) and internal and external pressures are out of balance; and a *reversible expansion* (Case 2), where internal and external pressures are always in balance.

Case 1. *Constant external pressure.*

$$\delta w = P_{ext} \delta V. \quad (8)$$

So

$$\begin{aligned} w &= \int_{V_1}^{V_2} P_{ext} dV \\ &= P_{ext} (V_2 - V_1) \\ &= P_{ext} \Delta V. \end{aligned} \quad (9)$$

From (9) w is +ve if $V_2 > V_1$ i.e. ΔV +ve, and w is -ve if $V_2 < V_1$ i.e. ΔV -ve.

Case 2. Reversible expansion.

A *reversible* change is one accomplished by infinitesimal changes, such that throughout all forces are in balance and the system remains in equilibrium with its surroundings. In this case

$$P_{ext} = P. \quad (10)$$

Where P is the pressure of the gas inside the piston. So

$$\begin{aligned} w &= \int_{V_1}^{V_2} P dV \\ &= \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ w &= nRT \log \frac{V_2}{V_1}. \end{aligned} \quad (11)$$

Heat Capacity

Two definitions of heat capacity arise in thermodynamics: one where heat is added to a system that retains the same volume; and one where heat is added to a system that retains the same pressure. These are defined as:

C_v is the heat required to raise the temperature of one mole of a substance by 1 K, under *constant volume* conditions.

C_p is the heat required to raise the temperature of one mole of a substance by 1 K, under *constant pressure* conditions.

Constant Volume:

At constant volume, no work is done by the system i.e. $w=0$, so for an ideal gas equation (4) becomes

$$q = \Delta U + w = \Delta U = \frac{3}{2}R(T_2 - T_1) = \frac{3}{2}R\Delta T. \quad (12)$$

Since

$$C_v = q / \Delta T \quad (13)$$

then

$$C_v = \frac{3}{2}R. \quad (14)$$

Constant Pressure:

Under a *reversible* constant external pressure equation (4) becomes

$$q = \Delta U + P_{ext} \int_{V_1}^{V_2} dv. \quad (15)$$

So

$$q = \Delta U + P_{ext} \Delta V. \quad (16)$$

Since $\Delta V = V_2 - V_1$, then by the ideal gas law (5) for one mole of gas

$$\Delta V = \frac{RT_2}{P_{ext}} - \frac{RT_1}{P_{ext}} = \frac{R\Delta T}{P_{ext}}. \quad (17)$$

Then

$$C_p = \frac{q}{\Delta T} = \frac{\Delta U}{\Delta T} + R, \quad (18)$$

and so

$$C_p = C_v + R. \quad (19)$$

Other Properties of Gas Expansions

Isothermal Expansion.

In an isothermal expansion $\Delta T = 0$ and therefore $\Delta U = 0$. So

$$q = w = nRT \log \frac{V_2}{V_1} \quad (20)$$

for a reversible expansion.

Irreversible Adiabatic Expansion

In an adiabatic expansion $q = 0$ and therefore $\Delta U = -w$. So for an irreversible expansion

$$\Delta U = -P_{ext} \Delta V. \quad (21)$$

For an ideal gas

$$\Delta U = \frac{3}{2} nR \Delta T, \quad (22)$$

so

$$\frac{3}{2} nR \Delta T = -P_{ext} \Delta V \quad (23)$$

and

$$\Delta T = -\frac{2}{3} \frac{P_{ext}}{nR} \Delta V. \quad (24)$$

If $\Delta V > 0$ i.e. $V_2 > V_1$, ΔT is $-ve$ and $T_1 > T_2$. The temperature falls in adiabatic expansions.

Reversible Adiabatic Expansion

For a reversible expansion the internal pressure P and external pressure P_{ext} are equal:

$$P = P_{ext} = \frac{nRT}{V} \quad (25)$$

also

$$\delta U = nC_v \delta T \quad (26)$$

and

$$\delta U = -P_{ext} \delta V. \quad (27)$$

So

$$nC_v \delta T = -\frac{nRT}{V} \delta V, \quad (28)$$

which leads to

$$C_v \int_{T_1}^{T_2} \frac{\delta T}{T} = - \int_{V_1}^{V_2} \frac{R}{V} \delta V. \quad (29)$$

Integration gives

$$C_v \log \frac{T_2}{T_1} = -R \log \frac{V_2}{V_1}. \quad (30)$$

So

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{-R/C_v} \quad (31)$$

and then

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_2}{V_1} \right)^{-R/C_v} \quad (32)$$

or

$$P_2 V_2^{(1+R/C_v)} = P_1 V_1^{(1+R/C_v)}. \quad (33)$$

Let

$$\gamma = 1 + R/C_v = (C_v + R)/C_v = C_p/C_v \quad (34)$$

so

$$P_1 V_1^\gamma = P_2 V_2^\gamma, \quad (35)$$

i.e.

$$P_1 V_1^\gamma = \text{Const}. \quad (36)$$

Equation (36) applies to an adiabatic expansions.

The Virial Theorem

The Virial Theorem provides a means to calculate the pressure in a non-ideal gas. For a gas consisting of n atoms, in a cubic vessel of dimension $l \times l \times l$, the virial Φ is defined as

$$\Phi = \left\langle - \sum_{i=1}^n \sum_{\alpha=1}^3 x_i^\alpha f_i^\alpha \right\rangle, \quad (37)$$

where

$$f_i^\alpha = f_i^{\alpha'} + f_i^{\alpha''} \quad (38)$$

is the α component of the force on atom i and

$$f_i^{\alpha'} = w_i^\alpha \delta(x_i^\alpha - l) \quad (39)$$

is the (instantaneous) wall force (with magnitude w_i^α and cell width l) and

$$f_i^{\alpha''} = \sum_{j \neq i}^n f_{ij}^\alpha \quad (40)$$

is the force arising from atomic interactions (assumed to be pair interactions).

Consider the term $x_i^\alpha \dot{x}_i^\alpha$ then

$$\frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) = \dot{x}_i^\alpha \dot{x}_i^\alpha + x_i^\alpha \ddot{x}_i^\alpha. \quad (41)$$

Then

$$\ddot{x}_i^\alpha = \frac{1}{x_i^\alpha} \left(\frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) - \dot{x}_i^\alpha \dot{x}_i^\alpha \right), \quad (42)$$

so from Newton's law

$$f_i^{\alpha''} = \frac{m_i}{x_i^\alpha} \frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) - \frac{m_i}{x_i^\alpha} \dot{x}_i^\alpha \dot{x}_i^\alpha. \quad (43)$$

From equations (38),(39) and (43) equation (37) becomes

$$\Phi = \left\langle - \sum_{i=1}^n \sum_{\alpha=1}^3 w_i^\alpha \delta(x_i^\alpha - l) x_i^\alpha \right\rangle + \left\langle - \sum_{i=1}^n \sum_{\alpha=1}^3 m_i \frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) \right\rangle + \left\langle \sum_{i=1}^n \sum_{\alpha=1}^3 m_i \dot{x}_i^\alpha \dot{x}_i^\alpha \right\rangle. \quad (44)$$

which becomes

$$\Phi = -3PA - \sum_{i=1}^n \sum_{\alpha=1}^3 \frac{m_i}{\tau} \int_0^{\tau \rightarrow \infty} \frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) dt + 2K, \quad (45)$$

where PA is the area force of the confining vessel ($A=l \times l$) and K is the system kinetic energy. The middle term right can be integrated to give

$$- \sum_{i=1}^n \sum_{\alpha=1}^3 \frac{m_i}{\tau} \int_0^{\tau \rightarrow \infty} \frac{d}{dt}(x_i^\alpha \dot{x}_i^\alpha) dt = - \sum_{i=1}^n \sum_{\alpha=1}^3 \frac{m_i}{\tau} [x_i^\alpha \dot{x}_i^\alpha]_0^\tau = 0. \quad (46)$$

This follows because x_i^α and \dot{x}_i^α are not correlated¹ and have zero average values.

Finally

$$\Phi = -3PV + 2K, \quad (47)$$

or on rearrangement

$$P = (2K - \Phi) / 3V. \quad (48)$$

Note that if the virial is zero then

$$PV = \frac{2}{3}K. \quad (49)$$

This result applies to an ideal gas.

Enthalpy

Enthalpy is a key variable in thermodynamics, taking into account the internal energy of a system and the system pressure. It is a *state function* of the system - under the same conditions of temperature and pressure a given quantity of matter will always have the same enthalpy.

The enthalpy H of a system is defined by the equation

$$H = U + PV \quad (50)$$

where U is the system internal energy, P is the pressure and V is the system volume. The differential form is

¹ This is not strictly true. At the walls the velocity is momentarily zero, but being zero contributes nothing to the average.

$$dH = dU + PdV + VdP. \quad (51)$$

Under constant pressure conditions $dP=0$, so

$$dH = dU + PdV, \quad (52)$$

which means that

$$\int_a^b dH = \int_a^b dU + P \int_a^b dV, \quad (53)$$

and therefore

$$\Delta H = \Delta U + P \Delta V. \quad (54)$$

Gas Reactions

Consider the reaction



Then

$$\begin{aligned} PV(\text{products}) &= (c+d)RT \\ PV(\text{reactants}) &= (a+b)RT \end{aligned} \quad (56)$$

and so

$$\Delta(PV) = (c+d-a-b)RT, \quad \text{or} \quad \Delta(PV) = \Delta nRT, \quad (57)$$

where

$$\Delta n = c+d-a-b, \quad (58)$$

is the change in molarity of the species present.

The change in enthalpy due to a chemical reaction is

$$\Delta H = \Delta U + \Delta(PV) \quad \text{or} \quad \Delta H = \Delta U + \Delta nRT. \quad (59)$$

Standard enthalpies for the elements are defined as zero at standard temperature and pressure (STP)².

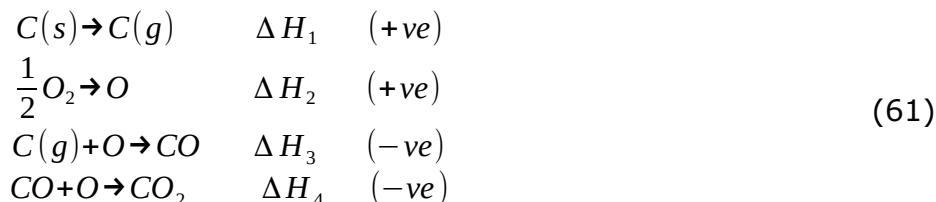
Enthalpy of Formation and Hess's Law

The *Enthalpy of Formation* of a compound is the change in enthalpy when one mole of a compound is formed from reactants.

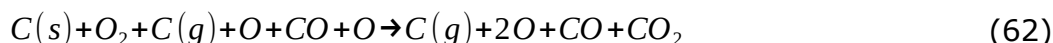
Hess' Law states that the enthalpy of formation is independent of the reaction pathway and is the sum of enthalpy changes of all intermediate steps. For example the reaction



can be represented by a series of intermediate reactions:



The reaction can therefore be written as the sum of all the reactions



2 Standard temperature and pressure (STP) is 25 Celsius and 1 atmosphere.

Cancelling the components that appear on both sides of (62) gives equation (60) as expected. The enthalpy change for the reaction (61) is

$$\Delta H = \Delta H_1 + 2\Delta H_2 + \Delta H_3 + \Delta H_4 = \Delta H_f(\text{CO}_2), \quad (63)$$

Which is the enthalpy of formation of CO_2 . These results may be represented by the following figure (Figure 3).

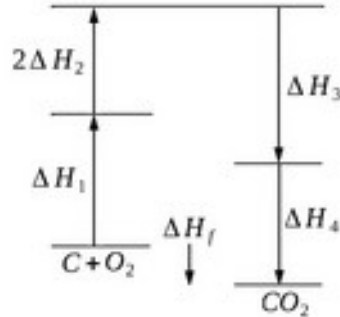


Figure 3. Hess's law and the Formation of CO_2

Entropy and the Second Law

Entropy is defined by the integral

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T}. \quad (64)$$

Which gives the change in entropy on changing from state 1 to state 2 by a *reversible* process. In molecular terms (i.e. in the language of statistical thermodynamics) entropy is a measure of the degree of disorder in system. However, classical thermodynamics pays no heed to this. Like enthalpy, entropy is a *state function* of the system.

The Second Law of Thermodynamics states: *In a spontaneous process, the entropy of a system plus its surroundings always increases.*

Entropy and Reversible Isothermal Expansion

Since $\Delta U = 0$ at fixed T

$$q_{rev} = w = RT \log \frac{V_2}{V_1}, \quad (\text{at fixed } T). \quad (65)$$

For a reversible expansion from V_1 to V_2 . From (64) it follows that

$$\Delta S_g = R \log \frac{V_2}{V_1}, \quad (\text{at fixed } T). \quad (66)$$

where ΔS_g is the change in entropy of the gas. The corresponding change in entropy for the surroundings

$$\Delta S_s = -R \log \frac{V_2}{V_1} \quad (67)$$

since the surroundings lost the energy $-q_{rev}$ to the gas under isothermal conditions. It follows that

$$\Delta S_g + \Delta S_s = 0, \quad (68)$$

meaning the overall change in entropy is zero in this case. So in a reversible process, the entropy remains constant.

Entropy and Irreversible Isothermal Expansion

The change in entropy for an *irreversible* expansion is the same as (67), since entropy is a state function i.e. it is a property of the system under the prescribed thermodynamic conditions, not of the process by which that state is achieved. If the gas expands from V_1 to V_2 without doing work (e.g. into an evacuated vessel) then

$$q_{rev}=0 \text{ and } \Delta S_s=0. \quad (69)$$

In this case

$$\Delta S_g + \Delta S_s = R \log \frac{V_2}{V_1} \quad (70)$$

and the total entropy increases.

The Temperature Dependence of Entropy

A reversible temperature change is one in which the temperature of the system differs only infinitesimally from the temperature of the surrounding heat bath. Thus equilibration is maintained throughout.

So we have

$$\Delta S = \int \frac{dq_{rev}}{T}, \quad (71)$$

where, under constant pressure conditions for n moles of a substance

$$dq_{rev} = n C_p dT. \quad (72)$$

so

$$\Delta S = n \int_{T_1}^{T_2} \frac{C_p}{T} dT = n C_p \log \frac{T_2}{T_1}, \quad (73)$$

which is the system entropy change going from temperature T_1 to T_2 . So we have

$$\begin{aligned} \Delta S &= n C_p \log \frac{T_2}{T_1} \text{ for constant pressure} \\ &\text{and} \\ \Delta S &= n C_v \log \frac{T_2}{T_1} \text{ for constant volume.} \end{aligned} \quad (74)$$

Thermal Equilibrium

Suppose we have a system 1 at a temperature T_1 and a system 2 at a temperature T_2 where $T_2 > T_1$. If the two systems are brought into thermal contact, experience shows that they will equilibrate to the same temperature T , where $T_2 > T > T_1$. For systems 1 and 2 the entropy changes at constant pressure are

$$\begin{aligned} \Delta S_1 &= n C_p \log \frac{T}{T_1} \\ &\text{and} \\ \Delta S_2 &= n C_p \log \frac{T}{T_2} \end{aligned} \quad (75)$$

The total change in entropy of both systems combined is

$$\Delta S = \Delta S_1 + \Delta S_2 = nC_p \log \frac{T^2}{T_1 T_2} \quad (76)$$

Let

$$T_1 = T - \Delta T \quad \text{and} \quad T_2 = T + \Delta T \quad (77)$$

Then equation (76) becomes

$$\Delta S = nC_p \log \frac{T^2}{(T^2 - \Delta T^2)} \quad (78)$$

From which it is apparent that $\Delta S > 0$ i.e. the entropy increases.

Entropy and Changes of State

Take for example melting under constant temperature conditions. The melting temperature is T_m and the change in entropy is

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T_m} = \frac{1}{T_m} \int_1^2 dq_{rev} \quad (79)$$

At constant pressure

$$dq_{rev} = dH, \quad (80)$$

so

$$\Delta S = \frac{\Delta H}{T_m} = \frac{\text{Enthalpy of melting}}{\text{Temperature of melting}} \quad (81)$$

The entropy for a change of state can often be estimated using *Trouton's rule* which states that the entropy of vaporization (or boiling) ΔS_{vap} , is approximately the same for a wide range of liquids and is given approximately by

$$\Delta S_{vap} = 10.5R, \quad (82)$$

where R is the universal gas constant. From equation (81) this means that

$$T_b = \frac{\Delta H_b}{10.5R}, \quad (83)$$

is the approximate boiling temperature.

Entropy and the Third Law

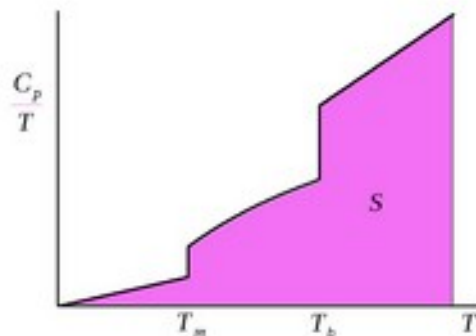


Figure 4. Calculating Entropy using the Third Law

The Third Law of Thermodynamics states: *The entropy of a perfect crystal at 0 K is zero.*

This means that entropy at a given temperature T can be calculated from the dependence of C_p or C_v on temperature. For example Figure 4 shows how the entropy may be calculated from zero Kelvin, the heating of the solid to the melting point T_m , the latent heat of melting ΔH_m , through heating of the liquid to the boiling point T_b and the latent heat of boiling ΔH_b , and on through the heating of the gas to the required temperature at T , as encapsulated by the equation:

$$S = \int_0^{T_m} \frac{C_p^s}{T} dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} \frac{C_p^l}{T} dT + \frac{\Delta H_b}{T_b} + \int_{T_b}^T \frac{C_p^g}{T} dT. \quad (84)$$

For equation (84) to be practical, the specific heats of the solid, liquid and gas at constant pressure (C_p^s , C_p^l and C_p^g respectively) must be a known function of temperature over the whole temperature range $0 \rightarrow T$. Entropies determined this way are known as *third law entropies*.

Free Energy

The free energy of a system is the energy that is available to do work. The common forms of free energy are Helmholtz free energy which applies in constant volume conditions and the Gibbs free energy which applies in constant pressure conditions.

The Helmholtz free energy A is defined as

$$A = U - TS \quad (85)$$

where U is the system internal energy, T is the absolute temperature and S is the entropy. The differential form is

$$dA = dU - TdS - SdT. \quad (86)$$

The Gibbs free energy G is defined as

$$G = H - TS \quad (87)$$

where H is the system enthalpy, T is the absolute temperature and S is the entropy. Since it is a function of both enthalpy and entropy, the free energy (both Gibbs and Helmholtz) is a *state function* of the system. In what follows we focus mostly on the Gibbs free energy.

At constant temperature, the relation (87) is often expressed as

$$\Delta G = \Delta H - T \Delta S, \quad (\text{at fixed } T). \quad (88)$$

From the definition of the enthalpy (50) we can write the Gibbs free energy as

$$G = U + PV - TS \quad (89)$$

where P is the system pressure and V the volume. The differential form of the Gibbs free energy is

$$dG = dU + PdV + VdP - TdS - SdT. \quad (90)$$

Under constant pressure $dP = 0$ so (90) becomes

$$dG = dU + PdV - TdS - SdT, \quad (\text{at fixed } P). \quad (91)$$

At both constant pressure and temperature $dP = 0$ and $dT = 0$, so (90) then becomes

$$dG = dU + PdV - TdS, \quad (\text{at fixed } P \text{ and } T). \quad (92)$$

We also recognise from equation³ (16) that $dU + PdV$ equals the heat dq input to the system, so (92) becomes

$$dG = dq - Tds, \quad (\text{at fixed } P \text{ and } T). \quad (93)$$

We also note that, for a *reversible* process

$$dq_{\text{rev}} = TdS, \quad (94)$$

and so (93) can be written as

$$dG = dq - dq_{\text{rev}}. \quad (95)$$

It follows that

$$dG = 0 \quad (\text{fixed } P \text{ and } T). \quad (96)$$

for a reversible process and

$$dG < 0 \quad (\text{fixed } P \text{ and } T). \quad (97)$$

So dG is *-ve* for a spontaneous process. Equation (97) follows because $q_{\text{rev}} > q$ for a non reversible process.

Like the enthalpy, the free energy G° of the chemical elements at STP is defined to be zero.

Free Energy of Formation

The standard free energy of formation ΔG_f° of a given chemical compound is the free energy change when one mole of the compound is formed from its constituent elements at STP. ΔG_f° is formally given by the equation

$$\Delta G_f^\circ = \Delta H_f^\circ - T \Delta S_f^\circ, \quad (98)$$

where ΔH_f° is the change in enthalpy for the chemical reaction between the elements resulting in one mole of the compound and ΔS_f° is the corresponding change in entropy for the same reaction, both standardised for STP. These are obtained experimentally. For example, with the enthalpy change obtained using Hess's law (see equation (63) and preceding discussion) and the entropy change obtained as a difference in third law entropies of the elements and products (see discussion leading to equation (84)).

Free Energy and Chemical Equilibrium

Equation (90) may be written as

$$dG = dq + VdP - TdS - SdT \quad (99)$$

and we also note that for a *reversible* process

$$dq = dq_{\text{rev}} = TdS. \quad (100)$$

So (99) becomes

$$dG = VdP - SdT, \quad (101)$$

and so at *constant temperature*

$$dG = VdP, \quad \text{at fixed } T. \quad (102)$$

For an ideal gas we have

$$dG = \frac{nRT}{P} dP, \quad (103)$$

and so

³ In differential form.

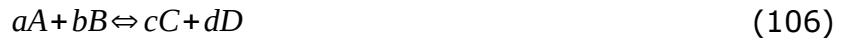
$$\Delta G = nRT \log \frac{P_2}{P_1}. \quad (104)$$

Since G is a state function, equation (104) holds for irreversible processes as well as reversible ones. Given the free energy G^o of a gas at standard temperature and pressure, equation (104) allows us to write

$$G = G^o + nRT \log P, \quad (105)$$

in which P_1, P_2 are expressed in atmospheres so that $P_1=1$ and $P_2=P$.

For the chemical reaction



we have

$$\Delta G = cG_C + dG_D - aG_A - bG_B. \quad (107)$$

On inserting equation (105) this becomes

$$\Delta G = \Delta G^o + RT \log \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}. \quad (108)$$

At equilibrium the reaction can proceed no further, which means the free energy driving the reaction must be at minimum, so $\Delta G=0$ and (108) becomes

$$\Delta G^o = -RT \log K, \quad (109)$$

where K is the equilibrium constant

$$K = \left[\frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \right]_{eq} \quad \text{at equilibrium.} \quad (110)$$

It is apparent that a knowledge of the standard free energies of formation of the reactants and products permits a determination of the equilibrium constant for any postulated reaction.

Electrical Cells

In an electrical cell we need to allow for the fact that work may be done electrically as well as by system expansion. From equation (4) we obtain

$$dU = dq + dw, \quad (111)$$

where dw is the infinitesimal work. We can now write equation (90) as

$$dG = dq - dw + PdV + VdP - TdS - SdT, \quad (112)$$

which for processes at fixed T and P becomes

$$dG = dq - dw + PdV - TdS \quad (\text{fixed } T \text{ and } P). \quad (113)$$

For a reversible process, this further reduces to

$$dG = -dw + PdV. \quad (114)$$

As noted above the work done is electrical as well as from expansion so

$$dw = dw_e + dw_{pV}, \quad (115)$$

where w_e is electrical work and w_{pV} is work done by expansion. We may note that

$$PdV - dw_{pV} = 0 \quad (116)$$

since these quantities are the same. Therefore (114) becomes

$$dG = -dw_e, \quad (117)$$

and so

$$\Delta G = -nF \Delta E, \quad (118)$$

where F is Faraday's unit of charge (96,486 coulombs), n is the number of moles of charge moved and ΔE is the difference in electrical potential between the electrodes of the system (i.e. the *voltage*). Equation (118) allows us to write

$$\Delta G^{\circ} = -nF \Delta E^{\circ}, \quad (119)$$

where ΔG° is the free energy under STP conditions and ΔE° is the associated voltage.

The free energy is defined by the chemical state of the system. For a reaction of the form given in (106) (in solution) the free energy difference is given by

$$\Delta G = \Delta G^{\circ} + RT \log \frac{(C)^c (D)^d}{(A)^a (B)^b}. \quad (120)$$

Combining this with equations (118) and (119) gives

$$\Delta E = \Delta E^{\circ} + \frac{RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}, \quad (121)$$

where $[A]$ is the concentration of a species A . Equation (121) is known as the Nernst Equation and describes how the voltage of an electrical cell varies with the concentrations of the electrolytes.

The Temperature Dependence of Equilibrium

At constant temperature we have

$$\Delta G = \Delta H - T \Delta S, \quad (122)$$

and

$$\Delta G = -RT \log K. \quad (123)$$

So

$$\log K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}. \quad (124)$$

If the thermal capacity C_p is constant at all temperatures then both ΔH and ΔS are constants. In which case, at temperatures T_1 and T_2

$$\log K_2 - \log K_1 = -\frac{\Delta H}{RT_2} + \frac{\Delta H}{RT_1}, \quad (125)$$

or equivalently

$$\log \frac{K_2}{K_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (126)$$

which describes how the equilibrium constant changes with temperature.

Phase Equilibria

Let G_1 be the free energy of a phase 1 and G_2 be the free energy of a phase 2. Then at equilibrium

$$G_1 = G_2 \text{ or } dG_1 = dG_2. \quad (127)$$

Now for a reversible process (see equation (101))

$$dG = VdP - SdT. \quad (\text{reversible process}) \quad (128)$$

At equilibrium

$$dG_1 = V_1 dP - S_1 dT = V_2 dP - S_2 dT = dG_2. \quad (129)$$

So

$$(V_1 - V_2) dP = (S_1 - S_2) dT \quad (130)$$

and

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{\text{vap}}}{T \Delta V}. \quad (131)$$

This leads to the Clausius-Clapeyron Equation:

$$\frac{dP}{dT} = \frac{1}{T} \frac{(H_g - H_l)}{(V_g - V_l)}. \quad (132)$$

Since

$$V_g - V_l \approx V_g = \frac{nRT}{P} \quad (133)$$

then

$$\frac{1}{P} \frac{dP}{dT} = - \frac{\Delta H_{\text{vap}}^{\circ}}{nRT^2} \quad (134)$$

or

$$\frac{d \log P}{d(1/T)} = - \frac{\Delta H_{\text{vap}}^{\circ}}{R}. \quad (135)$$

Integrating (135) gives

$$\log \frac{P_2}{P_1} = - \frac{\Delta H_{\text{vap}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (136)$$

which describes how vapour pressure varies with temperature.

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