

Mass action

This material involves more extensive use of thermodynamics than is usually covered in first year physics, but the material is not intrinsically more difficult than other 3rd year electrical engineering topics. It is somewhat lengthy but it should be understood in order to follow the arguments about recombination in this chapter.

The Law of Mass Action governs chemical reactions of the form $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ or [electron-hole pair] \rightarrow [Si bond]. The notation used is as follows: when ν_i molecules of initial reactant N_i produces ν_j molecules of product N_j , we write $\sum_i \nu_i N_i = 0$. This means that the ν_i

are negative numbers since they represent reactants used up in the reaction. For example, in the production of water where $2\text{H}_2\text{O} \leftrightarrow 2\text{H}_2 + \text{O}_2$ we write $-2 \text{H}_2 - 1 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ or

$-2 \times 2\text{H} - 1 \times 2\text{O} + 2 \times (2\text{H} + \text{O}) = 0$ or, without the symbols,

$-2 \times 2 - 1 \times 2 + 2 \times 3 = 0$. For a reaction described this way, if the number of moles of the i^{th} constituent (reactant or product) is n_i and if $\sum n_i = n$ where n is the total number of moles of material, then the concentration of the i^{th} constituent is n_i/n . The Law of Mass Action is then

$$\left(\frac{n_1}{n}\right)^{\nu_1} \left(\frac{n_2}{n}\right)^{\nu_2} \dots \left(\frac{n_i}{n}\right)^{\nu_i} \dots = \prod_i \left(\frac{n_i}{n}\right)^{\nu_i} = f(T) \quad (1)$$

where $f(T)$ is a function of the temperature if the pressure of the system is constant.

In order to see how the Law of Mass Action comes about we confine ourselves to a system of ideal gases for which the Ideal Gas Law $PV = nRT$ holds. For such a system the partial pressure of each gas is given by $P_i = \frac{n_i}{n} P$ where P is the total pressure. The pressure can be

kept constant by allowing the reaction to take place in a vessel with one end a piston that exerts a constant force on the gas mixture. To proceed we need to review the First law of thermodynamics and the concept of entropy. We then define some new thermodynamic quantities designed for the specific problem at hand, called the Enthalpy and the Gibbs Function.

The First Law says that the change in energy U of a gas is equal to the heat added to the

gas less the work done by the expansion (change in volume) of the gas:

$$dU = dQ - dW \quad (2)$$

The heat $dQ = TdS$, where T is the temperature and S is the entropy. The work done by the gas is

$dW = PdV$. Work done on the gas is $dW = -PdV$. Thus, if the volume decreases as work is done on the gas, $dW < 0$. The entropy dS is given by

$$dS \geq dQ/T \quad (3)$$

where the equality holds only for reversible processes. An example of a reversible process is one in which the volume of gas increases infinitesimally slowly as the gas does work on a piston. An irreversible process would be the rapid expansion of the gas volume with resulting turbulence set up in the gas. For a reversible process dU can be integrated exactly: dU is a perfect differential in the mathematical sense.

If we allow the possibility of a mixture of gases which can react chemically, to dU we must add a term $\sum_i \mu_i dn_i$ which represents the energy extracted from or added to the system

when dn_i moles react, depending on whether the reaction is exothermic or endothermic, respectively. μ is called the chemical potential: it represents the amount of energy absorbed or released per mole in a chemical reaction. Then

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (4)$$

(for a reversible process). Since dU is a perfect differential for a reversible process we may write it in the form

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V} dn_i \quad (5)$$

where $T = \left(\frac{\partial U}{\partial S} \right)_{V, n_i}$, $P = - \left(\frac{\partial U}{\partial V} \right)_{S, n_i}$ and $\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V}$. The subscripts on the

partials explicitly indicate the variables that are kept constant. The energy depends explicitly on S , V and n (or several n_i) - these are the natural variables for U and they are called extensive

variables; they depend on the amount of material in the system. If we write dU generally as $dU \leq TdS - PdV + \sum_i \mu_i dn_i$ then we see that when a small change in S , V or n doesn't

change U , that U must be a minimum. This is the equilibrium state of the system. For a system where the volume is allowed to change but the pressure is kept constant, the energy will no longer be a minimum in equilibrium and we must look for another function or potential to describe the system. The quantities P , T and μ are called intensive variables: they do not depend on the amount of material in the system (T doesn't double if the amount of material is doubled).

To find the new potentials we use a method developed by Euler. Suppose the extensive variables S , V and n are increased by an amount θ and the intensive variables are kept unchanged. Then U would change by the same factor θ :

$$\theta dU = T\theta dS - P\theta dV + \mu\theta dn \quad (6)$$

(we consider just one species of gas in this example to simplify the notation). Put another way,

$$U(\theta S, \theta V, \theta n) = \theta U(S, V, n) \quad (6')$$

If this expression is differentiated with respect to θ we find

$$\frac{d}{d\theta}(\theta U(S, V, n)) = U(S, V, n) = \frac{d}{d\theta} U(\theta S, \theta V, \theta n) = \frac{d}{d\theta} U(\theta X_j) \quad (7)$$

where $X_1 = S$, $X_2 = V$, $X_3 = n$ etc. Then we have

$$U = \sum_j \frac{\partial U(\theta X_j)}{\partial(\theta X_j)} \frac{\partial(\theta X_j)}{\partial\theta} = \sum_j \frac{\partial U(\theta X_j)}{\partial(\theta X_j)} X_j = TS - PV + \mu n \quad (8)$$

When there is more than one species of gas the term μn is replaced by $\sum_i \mu_i n_i$. Before

proceeding we calculate the entropy and chemical potential of an ideal gas where $dn = 0$: the results will be needed shortly.

For an ideal mono-atomic gas at constant temperature

$$U = \frac{3}{2} nRT \quad (9)$$

From the first law we then have

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{\frac{3}{2} nRdT}{T} + \frac{nR}{V}dV \quad (10)$$

When this is integrated we get

$$S = nR \ln\left(\frac{T}{T_0}\right)^{\frac{3}{2}} + nR \ln\left(\frac{V}{V_0}\right) + S_0 \quad (11)$$

where $S = S_0$ when $T = T_0$ and $V = V_0$. If we now take into consideration the chemical potential of the gas and write the energy again as $U = TS - PV + \mu n = 3/2 nRT$, we can express the chemical potential as

$$\mu = -\frac{TS}{n} + \frac{PV}{n} + \frac{3}{2} RT = -T\frac{S}{n} + \frac{5}{2} RT \quad (12)$$

In terms of the entropy calculated above we obtain

$$\mu = -RT \ln\left(\frac{T}{T_0}\right)^{\frac{3}{2}} - RT \ln\left(\frac{V}{V_0}\right) - T\frac{S_0}{n} + RT \ln\left(e^{\frac{5}{2}}\right) \quad (13)$$

which can be simplified to

$$\mu = RT \ln\left\{\left(\frac{T_0}{T}\right)^{\frac{3}{2}} \left(\frac{V_0}{V}\right) e^{\frac{5}{2}}\right\} - T\frac{S_0}{n} \quad (14)$$

The quantity $\frac{S_0}{n}$ is the entropy of 1 mole of gas at temperature T_0 and volume V_0 .

Note that if the volume of the gas is constant so no work is done by or on the gas,

$dU = dQ = 3/2 nRT$. Then $\frac{dQ}{dT} = \frac{3}{2}nR = C_v$, which is the heat capacity of the gas at constant

volume.

Suppose now that instead of holding the volume of the gas constant we hold the pressure constant. We define a new potential H called the *enthalpy* as

$$H = U + PV \quad (15)$$

If we take the differential of H we get

$$dH = dU + PdV + VdP = TdS + VdP + \mu dn \quad (16)$$

The natural variables of H are those that appear as differentials: S, P and n. $V = \left(\frac{\partial H}{\partial P} \right)_{S,n}$.

If the pressure and number of moles of gas are constant so

$dP = dn = 0$, $dH = TdS = dQ$ and $\frac{dQ}{dT} = \frac{dH}{dT} = C_p$, the heat capacity at constant pressure¹.

Finally, we define the quantity

$$G = H - TS \quad (17)$$

called the Gibbs Function. G is very handy for calculations involving chemical reactions taking place at constant temperature and pressure. This is the case for reactions in a vessel in contact with a heat reservoir and sealed by a movable piston that applies a constant force. From

$$G = H - TS = U + PV - TS \quad (18)$$

we get

$$dG \leq TdS - PdV + \mu dn + PdV - VdP - TdS - SdT = \mu dn - VdP - SdT \quad (19)$$

If the temperature, pressure and number of moles of gas are constant, dG is negative or zero for an irreversible or reversible process, respectively, which implies G is a minimum.

We are now ready to see what happens when a chemical reaction defined by $\sum_i \nu_i N_i = 0$ takes place. Recall that ν_i is the number of *molecules* of substance N_i while n_i is the number of

¹ If P is constant, from $dU = \frac{3}{2} nRdT = dQ - PdV$ we get, with

$$P = \text{constant} = \frac{nRT}{V}, \quad dQ = \frac{5}{2} nRdT. \quad \text{Thus } C_p = \frac{dQ}{dT} = \frac{5}{2} nR.$$

moles. From $G = U + PV - TS$ and $U = TS - PV + \sum \mu_i n_i$ we see

$$G = \sum \mu_i n_i \quad (20)$$

and

$$dG = \sum \mu_i dn_i \quad (21)$$

if T and P are constant.

We can now derive the Law of Mass Action for a mixture of ideal mono-atomic gases that undergo a chemical reaction. First we note that since ideal gases do not interact except to undergo a chemical reaction, their energies and entropies add. Suppose there are n_i moles of gas of type i (species N_i) and that the total number of moles of gas is $\sum_i n_i = n$. The energy of

species i is

$$U_i = \frac{n_i}{n_o} U_{oi} + \frac{3}{2} n_i R(T - T_o) \quad (22)$$

where U_{oi} is the energy of n_o moles of the gas that occupy a volume V_o when $T = T_o$. Similarly, the entropy of gas of species i is

$$S_i = \frac{n_i}{n_o} S_{oi} + \frac{3}{2} n_i R \ln \left(\frac{T}{T_o} \right) + n_i R \ln \left(\frac{V}{V_o} \times \frac{n_o}{n_i} \right) \quad (23)$$

S_{oi} is the entropy of n_o moles of gas when $T = T_o$ and $V = V_o$; the factor $\frac{n_o}{n_i}$ is due to the entropy

of mixing (it is, obviously, present only when more than one species of gas is present). The total energy and entropy are

$$U = \sum_i U_i = \sum_i n_i \left(\frac{U_{oi}}{n_o} \right) + \frac{3}{2} R(T - T_o) \sum_i n_i \quad (22')$$

and

$$S = \sum_i S_i = \sum_i n_i \left(\frac{S_{oi}}{n_o} \right) + \frac{3}{2} R \ln \left(\frac{T}{T_o} \right) \sum_i n_i + R \sum_i n_i \ln \left(\frac{V}{V_o} \times \frac{n_o}{n_i} \right) \quad (23')$$

The independent variables in the expressions are n_i , T and V .

As a check on the validity of these expressions we can use them to derive the ideal gas law

$PV = nRT$: from $dU = TdS - PdV + \sum \mu_i dn_i$ we have $\mathbf{P} = -\left(\frac{\partial U}{\partial V}\right)_{S, n_i}$. By manipulating the

partial derivatives the pressure can be expressed as

$$\mathbf{P} = + \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial U)_{V, n_i}} \quad (24)$$

This is done as follows: if U and the n_i are held constant, $dU = 0$ and $dn_i = 0$ for all i . Then

$dU = TdS - PdV + \sum \mu_i dn_i$ becomes $0 = TdS - PdV$ or $\mathbf{P} = T \left(\frac{\partial S}{\partial V}\right)_{U, n_i}$. The temperature T is

given by $T = \left(\frac{\partial U}{\partial S}\right)_{V, n_i}$ or $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, n_i}$, and Equation 24 follows directly.

Similarly

$$\frac{1}{(\partial S / \partial U)_{V, n_i}} = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} = \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \left(\frac{\partial T}{\partial S}\right)_{V, n_i} \quad (25)$$

so we can write the pressure as

$$\mathbf{P} = \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial U)_{V, n_i}} = \left(\frac{\partial S}{\partial V}\right)_{U, n_i} \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \left(\frac{\partial T}{\partial S}\right)_{V, n_i} = \left(\frac{\partial U}{\partial T}\right)_{V, n_i} \frac{(\partial S / \partial V)_{U, n_i}}{(\partial S / \partial T)_{V, n_i}} \quad (26)$$

From the expressions for the energy and the entropy we can calculate:

$$\left(\frac{\partial U}{\partial T}\right)_{V, n_i} = \frac{3}{2} R \sum_i n_i \quad (27)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U, n_i} = \left(\frac{\partial S}{\partial V}\right)_{T, n_i} = \frac{R}{V} \sum_i n_i \quad (28)$$

(using the fact that for the perfect gas if U is constant, T is constant) and

$$\left(\frac{\partial S}{\partial T}\right)_{V, n_i} = \frac{3}{2} \frac{R}{T} \sum_i n_i \quad (29)$$

From these partials we then get

$$P = \frac{3}{2} R \sum_i n_i \times \frac{\frac{R}{V} \sum_i n_i}{\frac{3}{2} \frac{R}{T} \sum_i n_i} = \frac{RT}{V} \sum_i n_i = \frac{nRT}{V} \quad (30)$$

so the ideal gas law has indeed been recovered. If P is multiplied by the concentration n_i/n of species i we find the partial pressure $P_i = n_i \frac{RT}{V}$ of the i^{th} species.

Now assume that the mixture of gases undergoes a chemical reaction that produces new gas molecules, and that the temperature and pressure are maintained at constant values by using a heat reservoir and a constant pressure piston. Then with

$$G = \sum_i \mu_i n_i \quad (31)$$

we have

$$dG = \sum_i \mu_i dn_i \quad (32)$$

Let the number of moles be expressed in terms of the number of molecules by $dn_i = \nu_i dx$ (this means dn is $\frac{1}{\text{Avogadro's Number}}$ times a dimensionless differential dx). If in the chemical

reaction ν_i is a negative number this implies that n_i moles of gas i will be used up; if ν_i is positive n_i moles will be created. $dG = \left(\sum_i \mu_i \nu_i\right) dx$ and at equilibrium, when the reaction is over, G is a

minimum so $dG = 0$. This implies that

$$\sum_i \mu_i \nu_i = 0 \quad (33)$$

since a small change in dx must leave G unchanged (the meaning of a minimum). Now at constant volume the differential change in the energy U is

$$dU = TdS + \sum_i \mu_i dn_i \quad (34)$$

If we differentiate this expression with respect to n_k we get

$$\frac{\partial}{\partial n_k} \left(\sum_i \mu_i dn_i \right) = \frac{\partial}{\partial n_k} (dU - TdS) \quad (35)$$

Since $\frac{dn_i}{dn_k} = \delta_{ik}$ where δ_{ik} is the Kronecker delta (defined as $\delta_{ik} = 0, i \neq k, \delta_{ik} = 1, i = k$), we

find the chemical potential

$$\mu_k = \left(\frac{\partial U}{\partial n_k} \right)_{V, T, n_i} - T \left(\frac{\partial S}{\partial n_k} \right)_{V, T, n_i}, \quad i \neq k \quad (36)$$

With

$$U = \sum_k n_k \left(\frac{U_{ok}}{n_o} \right) + \frac{3}{2} R(T - T_o) \sum_k n_k \quad (37)$$

the differentiation yields

$$\frac{\partial U}{\partial n_k} = \frac{U_{ok}}{n_o} + \frac{3}{2} R(T - T_o) \quad (38)$$

Now if we use Equation 23 for the entropy,

$$S = \sum_k n_k \left(\frac{S_{ok}}{n_o} \right) + \frac{3}{2} R \ln \left(\frac{T}{T_o} \right) \sum_k n_k + R \sum_k n_k \ln \left(\frac{V n_o}{V_o n_k} \right), \text{ differentiation gives us}$$

$$\frac{\partial S}{\partial n_k} = \frac{S_{ok}}{n_o} + \frac{3}{2} R \ln \left(\frac{T}{T_o} \right) + R \ln \left(\frac{V n_o}{V_o n_k} \right) - R \quad (39)$$

Putting all the terms together we get the chemical potential in terms of the initial energy and entropy, the temperature, the volume and the number of moles of the gases:

$$\mu_k = \frac{U_{ok}}{n_o} + \frac{5}{2} RT - \frac{3}{2} RT_o - \frac{TS_{ok}}{n_o} - \frac{3}{2} RT \ln \left(\frac{T}{T_o} \right) - RT \ln \left(\frac{V n_o}{V_o n_k} \right) \quad (40)$$

We can now manipulate this expression into a more useful form by using the Ideal Gas Law

$PV = nRT$ to write $\frac{V_o}{n_o} = \frac{RT_o}{P_o}$ and $\frac{V}{n_k} = \frac{RT}{P_k}$. Then the product $\frac{V n_o}{V_o n_k}$ becomes

$$\frac{V n_o}{V_o n_k} = \frac{RT}{P_k} \frac{P_o}{RT_o} = \frac{T P_o}{T_o P_k}. \quad \text{Finally, with a little algebraic manipulation the chemical}$$

potential of the k^{th} species is found to be

$$\mu_k = \frac{U_{ok} - \frac{3}{2} n_o RT}{n_o} + RT \left(\frac{5}{2} - \frac{S_{ok}}{R n_o} - \frac{5}{2} \ln \left(\frac{T}{T_o} \right) + \ln \left(\frac{P_k}{P_o} \right) \right) \quad (41)$$

or

$$\mu_k = F_k(T) + RT \ln \left(\frac{P_k}{P_o} \right) \quad (42)$$

where $F_k(T)$ is a function only of the temperature. This is the key result, for if we now re-write the equation describing the chemical reaction

$$\sum_k \mu_k \nu_k = 0 \quad (33)$$

in terms of Equation 42 for μ_k we obtain

$$\sum_{\mathbf{k}} v_{\mathbf{k}} \left(F_{\mathbf{k}} (T) + RT \ln \left(\frac{P_{\mathbf{k}}}{P_{\mathbf{o}}} \right) \right) = 0 \quad (43)$$

or,

$$RT \sum_{\mathbf{k}} v_{\mathbf{k}} \ln \left(\frac{P_{\mathbf{k}}}{P_{\mathbf{o}}} \right) = - \sum_{\mathbf{k}} v_{\mathbf{k}} F_{\mathbf{k}} (T) = A (T) \quad (44)$$

where A(T) is a function only of T. If we divide both sides of this expression by RT we have

$$\sum_{\mathbf{k}} \ln \left(\frac{P_{\mathbf{k}}}{P_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = \ln \prod_{\mathbf{k}} \left(\frac{P_{\mathbf{k}}}{P_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45)$$

or, using the relation between the partial pressures of the gases, $\frac{P_{\mathbf{k}}}{P} = \frac{n_{\mathbf{k}}}{n_{\mathbf{o}}}$

$$\sum_{\mathbf{k}} \ln \left(\frac{n_{\mathbf{k}} P}{n_{\mathbf{o}} P_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = \ln \prod_{\mathbf{k}} \left(\frac{n_{\mathbf{k}} P}{n_{\mathbf{o}} P_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45')$$

or

$$\ln \prod_{\mathbf{k}} \left(\frac{n_{\mathbf{k}} P}{n_{\mathbf{o}} P_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = - \frac{A (T)}{RT} \quad (45'')$$

By taking the anti-logarithm of both sides of this last equation we get the Law of Mass Action:

$$\prod_{\mathbf{k}} \left(\frac{n_{\mathbf{k}}}{n_{\mathbf{o}}} \right)^{v_{\mathbf{k}}} = \left(\frac{P}{P_{\mathbf{k}}} \right)^{\sum_{\mathbf{k}} v_{\mathbf{k}}} e^{-\frac{A(T)}{RT}} = \left(\frac{P}{P_{\mathbf{k}}} \right)^{\sum_{\mathbf{k}} v_{\mathbf{k}}} K(T) = f (T) \quad (46)$$

where f(T) is a function only of the temperature if P is constant. That is, the product of the concentrations $n_{\mathbf{k}}/n_{\mathbf{o}}$ raised to the power $v_{\mathbf{k}}$ is a function only of the temperature if the pressure P is constant.