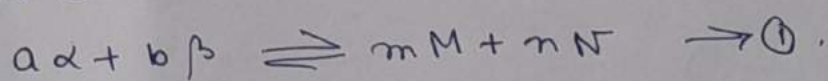


①

Degree of advancement of reaction (De Donder's treatment of chemical equilibrium)

For a closed system, if in a chemical reaction, when all the reactants are converted to the product, the progress of the reaction is said to be 100%. This is also expressed by saying that one unit of the reaction has occurred. At this stage, the equilibrium is reached at ~~50%~~ when progress of the reaction is 50%, the concentration of the reactants becomes equal to the concentrations of the products and the equilibrium constant $K=1$ (Perfect equilibrium). But for a reversible reaction, the progress of the reaction is never 100%. i.e. all the reactants do not get converted into the products. In that case, a variable " ξ " is introduced, by De Donder to express the progress of the reaction or advancement of the reaction and is called the degree of advancement of a chemical reaction.

Let us consider a reaction.



The Gibbs's free energy, $G = f(T, P, n)$,

Hence, it can be given by.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n} dP + \left(\frac{\partial G}{\partial n_i}\right)_{P, T} dn_i$$

$$\text{or } dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N \rightarrow \textcircled{2}$$

At constant temp^r and pressure.

$$(dG)_{T, P} = \mu_A dn_A + \mu_B dn_B + \mu_M dn_M + \mu_N dn_N \rightarrow \textcircled{3}$$

where dn_A , dn_B , dn_M and dn_N are the small change in the no of moles of A, B, M and N respectively.

(2)

and μ_A, μ_B, μ_M & μ_N are their chemical potentials.
If the reaction advances by ξ unit, then the n_i 's
can be written as.

$$\left. \begin{aligned} n_A &= n_A^0 - a \xi \\ n_B &= n_B^0 - b \xi \end{aligned} \right\} \text{Indicate consumption,} \\ \left. \begin{aligned} n_M &= n_M^0 + m \xi \\ n_N &= n_N^0 + n \xi \end{aligned} \right\} \text{Indicate formation,} \quad \rightarrow (4)$$

where n_i^0 's are the number of moles of the chemical species at the initial state, i.e. before the reaction is advanced by ξ unit.

Differentiating eqn (4)

$$\begin{aligned} dn_A &= -a d\xi, & dn_B &= -b d\xi \\ dn_M &= +m d\xi, & dn_N &= +n d\xi \end{aligned} \quad \rightarrow (5)$$

[n_i^0 's are constant for a closed system].

Substituting these values in equation no (2)

$$(dG)_{T,P} = -a \mu_A d\xi - b \mu_B d\xi + m \mu_M d\xi + n \mu_N d\xi.$$

$$(dG)_{T,P} = [(m \mu_M + n \mu_N) - (a \mu_A + b \mu_B)] d\xi \rightarrow (6)$$

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = [(m \mu_M + n \mu_N) - (a \mu_A + b \mu_B)] \rightarrow (7)$$

The partial derivative $\left(\frac{\partial G}{\partial \xi} \right)_{T,P}$ gives the rate of change of the Gibbs free energy with the advancement of the reaction.

The term $\left(\frac{\partial G}{\partial \xi} \right)_{T,P}$ is called the reaction potential, and is given by ΔG

$$\text{Reaction potential} = \Delta G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} \rightarrow (8)$$

(3)

Thus, the reaction potential is the rate of change of total free energy per unit advancement of the reaction at constant T and P . It is similar to the free energy change (ΔG) of a reaction.

The negative of reaction potential i.e. the decrease of reaction potential is called chemical affinity and denoted by A_f , i.e.

$$A_f = -\left(\frac{\partial G}{\partial \xi_r}\right)_{T,P} \rightarrow (9)$$

For a system to be present in equilibrium the value of $\left(\frac{\partial G}{\partial \xi_r}\right)_{T,P}$ must be zero.

When $\left(\frac{\partial G}{\partial \xi_r}\right)_{T,P}$ is negative, i.e. free energy of the reaction mixture ^{decreases} as the reaction advances. Then A_f is positive, means that the ^{forward} reaction is spontaneous.

If the derivative is positive, the affinity is negative, i.e. the ~~reaction~~ forward reaction is non-spontaneous and the backward reaction is spontaneous.

From eqnⁿ (5), we have.

$$d\xi_r = -dn_A/a = -dn_B/b = dn_M/m = dn_N/n$$

This quantity $d\xi_r$ is called the differential advancement or the increment of the degree of advancement of the reaction.

(A)

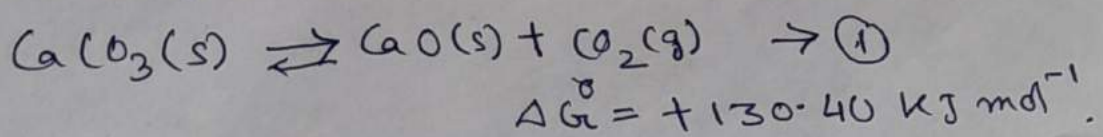
Coupling of Exoergic and Endoergic reactions.

An exoergic (exothermic) reaction is a reaction that releases energy while an endoergic (endothermic) reaction is one that requires an input of energy to take place.

For an exoergic reaction the free energy change during the reaction ΔG is less than zero ($\Delta G < 0$), and the reaction is spontaneous. ~~The~~ But the reactions which are endoergic ($\Delta G > 0$) are not spontaneous i.e. they are thermodynamically forbidden reactions. ~~These~~ This type of reactions require energy to be externally applied to occur. However, such reactions can be made to proceed in the desired direction by coupling with a separate exothermic (thermodynamically favourable) reaction, often via a shared intermediate. The two reactions are allowed to take place simultaneously.

Since Gibbs free energy is a state function the ΔG value of each half reaction may be summed to yield the combined ΔG of the coupled reaction.

One example of the coupling of reactions is the decomposition of CaCO_3 .

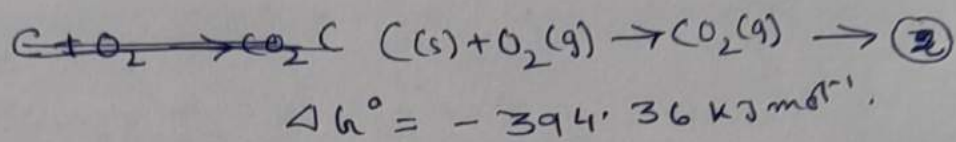


The strongly (+)ve ΔG for this reaction indicates that the reaction is reactant favoured, (not spontaneous)

(5)

If the reaction temperature is raised above 837°C , this reaction becomes spontaneous and favours the product.

Now, let us consider a second and completely different reaction that can be coupled to this reaction. The ~~constant~~ For the reaction, combustion of coal (burning of coal), the ΔG value is $\Delta G^{\circ} = -394.36 \text{ kJ mol}^{-1}$, which is greater than the energy required to decompose CaCO_3 ($130.40 \text{ kJ mol}^{-1}$).



If the reactions ① & ② are coupled,



$$\Delta G^{\circ} = 130.40 \text{ kJ mol}^{-1} + (-394.36 \text{ kJ mol}^{-1})$$
$$= -263.96 \text{ kJ mol}^{-1}$$

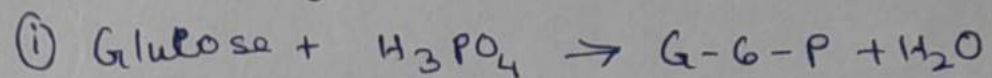
Here Hen' law ~~was~~ applied and the combined reaction is product favoured (spontaneous). ~~and~~

Let us consider another biological example. P

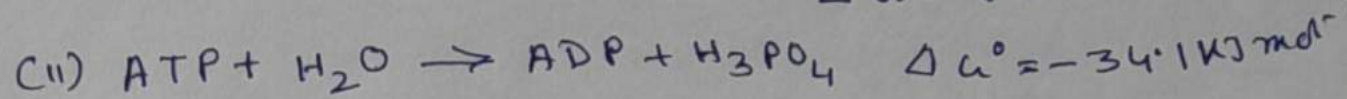
To take part in our metabolic system glucose must be first converted into activated complex glucose-6-phosphate (G-6-P). This conversion is endoergic ($\Delta G^{\circ} = +12.5 \text{ kJ mol}^{-1}$). Thus it is non spontaneous. But it can be ~~drive in~~ pushed to occur by coupling it with another reaction i.e. the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) which is highly exoergic ($\Delta G^{\circ} = -34.1 \text{ kJ mol}^{-1}$).

(6)

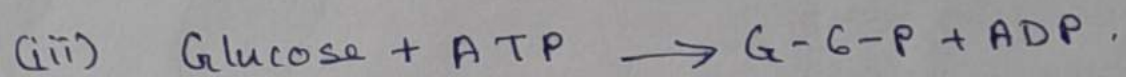
The coupling of the two reactions may be represented by the following steps.



$$\Delta G^\circ = +12.5 \text{ kJ mol}^{-1}$$



and the coupled reaction is



$$\Delta G^\circ_{(iii)} = \Delta G^\circ_{(i)} + \Delta G^\circ_{(ii)} = \Delta G = -21.7 \text{ kJ mol}^{-1}$$

The negative value of free energy change indicates that the reaction proceeds spontaneously.

Thus, the concept of coupled reaction is very useful in carrying out many non-spontaneous reactions on a large industrial scale as well as in a number of biological reactions.