

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 12.1

Free Energies of Reaction

CHEMICAL EQUILIBRIUM AND DYNAMICS



Jacobus Henricus van't Hoff

Using the ideas of reaction rates van't Hoff described the dynamics of chemical equilibrium. This is one of the most important topics in chemistry.

van't Hoff *also* published a paper early in his career that described a tetrahedral model for the carbon atom. This was not included in his thesis because it was *too controversial to be accepted*.

van't Hoff was awarded the first Nobel Prize in Chemistry

THERMODYNAMICS AND EQUILIBRIUM

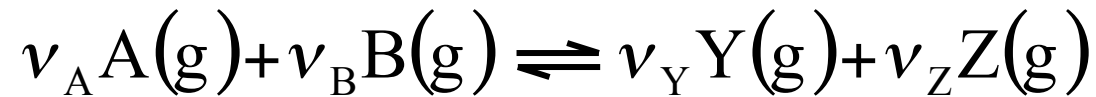
Many of the most important applications of thermodynamics are to systems at chemical equilibrium.

At constant T and P (where most benchtop chemistry takes place) we know that the condition for equilibrium is $\Delta G = 0$. If we are *not* at equilibrium, we can predict whether a reaction will proceed towards equilibrium by the sign of ΔG , which dictates whether a process will proceed spontaneously.

With the knowledge of thermodynamics that we have developed, we can calculate and make predictions about G , for example the temperature dependence. What we need in order to apply this to chemical equilibrium is to derive the relationship between G and the equilibrium constant for a chemical reaction.

EXTENT OF REACTION

Start with a gas phase reaction described by a balanced chemical equation,

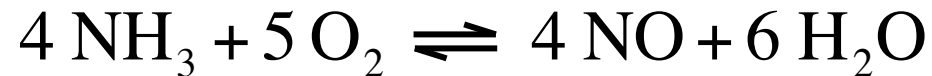


Define the *extent of reaction*, ξ ,

| | <u>reactants</u> | <u>products</u> |
|------------------------------|----------------------------|----------------------------|
| | $n_A = n_{A0} - \nu_A \xi$ | $n_Y = n_{Y0} + \nu_Y \xi$ |
| number of moles of B | $n_B = n_{B0} - \nu_B \xi$ | $n_Z = n_{Z0} + \nu_Z \xi$ |
| Initial number of moles of B | | |
| unitless | | |
| must have units of moles | | |

Self-assessment

For the reaction:



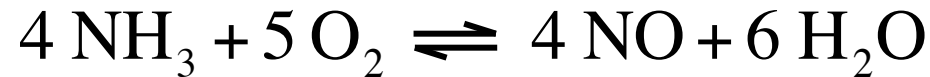
with initial amounts of NH_3 , O_2 , NO , and H_2O of 2, 2, 1, and 0 moles, respectively:

what are the amounts of NH_3 , O_2 , NO , and H_2O at reaction extent $\xi = 0.25$ moles?

what is the maximum possible reaction extent?

Self-assessment Explained

For the reaction:



with initial amounts of NH_3 , O_2 , NO , and H_2O of 2, 2, 1, and 0 moles, respectively:

what are the amounts of NH_3 , O_2 , NO , and H_2O at reaction extent $\xi = 0.25$ moles?

1, 0.75, 2, and 1.5 moles, respectively

what is the maximum possible reaction extent?

0.4 moles (at which point no O_2 remains to react)

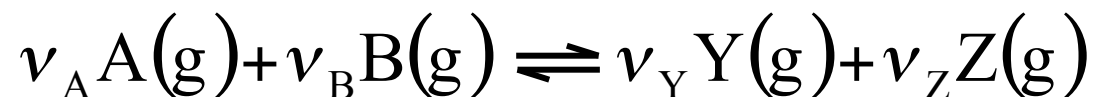
reactants

$$n_{\text{A}} = n_{\text{A}0} - \nu_{\text{A}} \xi$$

products

$$n_{\text{Y}} = n_{\text{Y}0} + \nu_{\text{Y}} \xi$$

EXTENT OF REACTION (CONT.)



ξ varies from 0 to a maximum value dictated by the stoichiometry.

For example, if $\begin{cases} n_{A0} = \nu_A \text{ moles} \\ n_{B0} = \nu_B \text{ moles} \end{cases}$ then ξ can vary from 0 to 1 mol

(Note that in this case ξ cannot exceed 1 since n_A and n_B would become negative)

reactants

$$n_A = n_{A0} - \nu_A \xi$$

$$n_B = n_{B0} - \nu_B \xi$$

products

$$n_Y = n_{Y0} + \nu_Y \xi$$

$$n_Z = n_{Z0} + \nu_Z \xi$$

Differentiate

change in the number of moles for each reactant and product

Note the sign

Proportionality constant

change in the extent of reaction

$$dn_A = -\nu_A d\xi$$

$$dn_B = -\nu_B d\xi$$

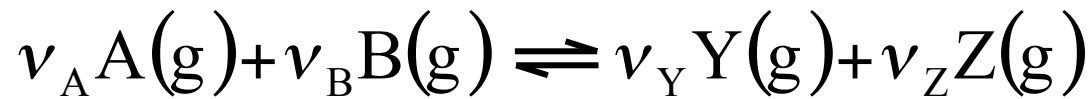
reactants

$$dn_Y = \nu_Y d\xi$$

$$dn_Z = \nu_Z d\xi$$

products

CONNECTING TO GIBBS FREE ENERGY



Consider G , which is a function of T, P, n_A, n_B, n_Y, n_Z :

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_j} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_j} dP + \left(\frac{\partial G}{\partial n_A} \right)_{T, P, n_{j \neq A}} dn_A \\ + \left(\frac{\partial G}{\partial n_B} \right)_{T, P, n_{j \neq B}} dn_B + \left(\frac{\partial G}{\partial n_Y} \right)_{T, P, n_{j \neq Y}} dn_Y + \left(\frac{\partial G}{\partial n_Z} \right)_{T, P, n_{j \neq Z}} dn_Z$$

Using: $\left(\frac{\partial G}{\partial T} \right)_P = -S$ $\left(\frac{\partial G}{\partial P} \right)_T = V$ $\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{P, T, n_{j \neq A}}$

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

At constant T and P , (i.e., G only depends on change in n):

$$dG = \sum_j \mu_j dn_j = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

GIBBS FREE ENERGY OF REACTION

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \quad (\text{constant } T \text{ and } P)$$

Rather than having dG in terms of differentials for every component we can use stoichiometry to rewrite it in terms of the change in a single variable, $d\xi$:

$$dn_A = -\nu_A d\xi \quad dn_B = -\nu_B d\xi \quad dn_Y = \nu_Y d\xi \quad dn_Z = \nu_Z d\xi$$

$$dG = (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \quad (\text{constant } T \text{ and } P)$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

$\Delta_r G$ is the change in the Gibbs energy when the extent of reaction changes by one mole. Units are energy/mol. Note that $\Delta_r G$ only has meaning if a balanced chemical equation has been specified.

$$dU = \delta q + \delta w$$



Next: Equilibrium Constants K_p , K_c , and K_a