Chemical Equilibrium

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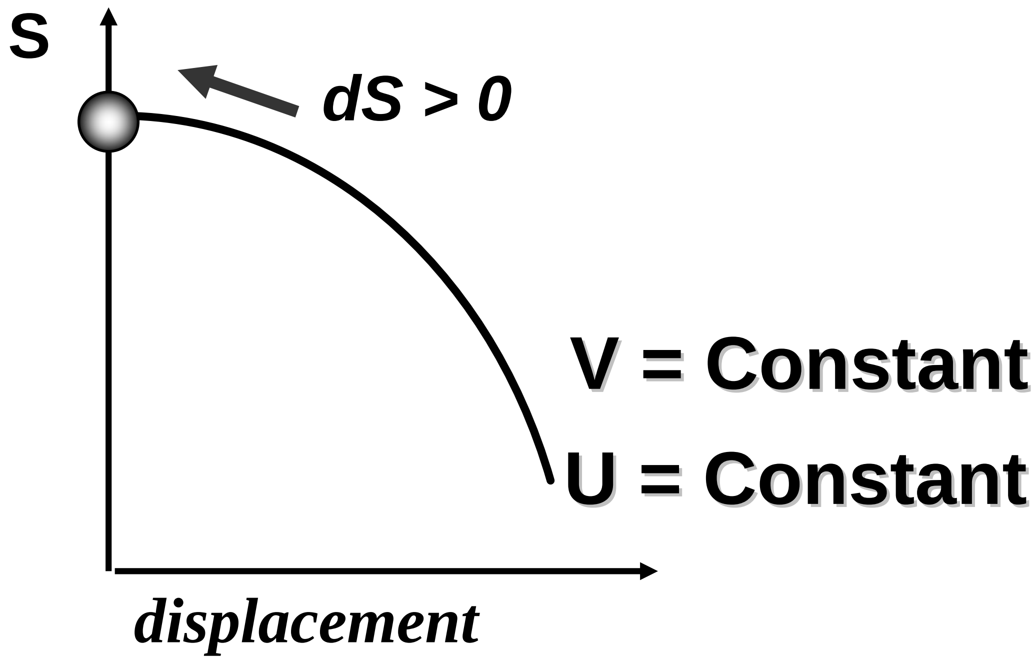
The maximum entropy principle



$$dS\,|_{U,V} \geq 0$$

For any spontaneous process

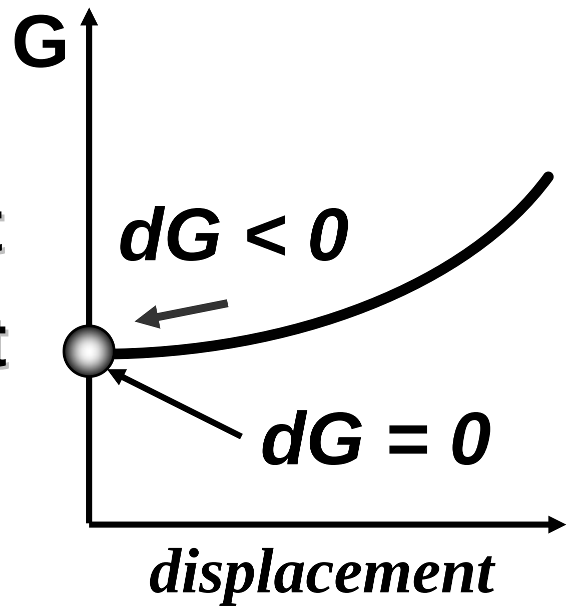
Gibbs function – Criterion for equilibrium

- Recall the Gibbs function

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

T = Constant

P = Constant



$$dG|_{T,P} \leq 0$$

Chemical potential

- For a multicomponent system, define the chemical potential of component i, symbolized by μ_i, as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j,j\neq i}}$$

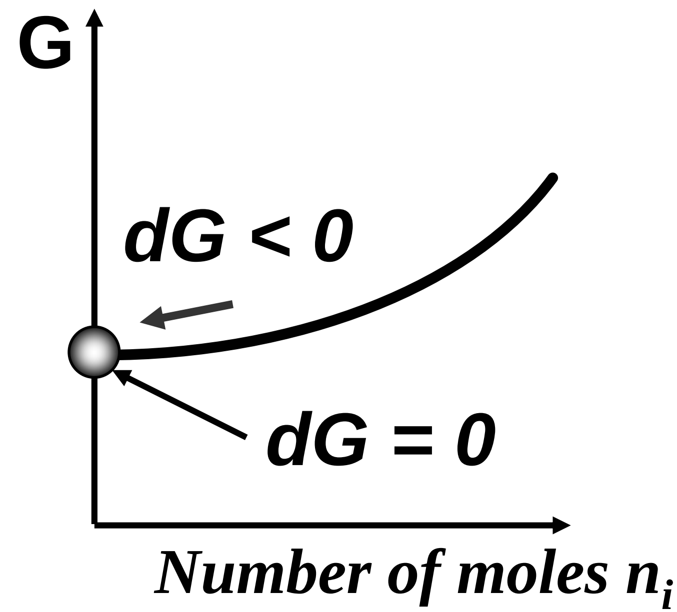
Chemical potential

- The Gibbs function has been shown to be:

$$G = \sum_{i=1}^{C} n_i \mu_i$$

- And the condition for equilibrium takes the form:

$$dG\,|_{T,P} = \sum_{i=1}^{C} \mu_i dn_i = 0$$



Single phase of a pure substance

- Let n be the number of moles
- Then G=n μ
- The chemical potential is then:

$$\mu = \frac{G}{n} = \bar{g}$$

Ideal gas mixture

- The enthalpy and entropy of an ideal gas mixture are:

$$H = \sum_{i=1}^{C} n_i \bar{h}_i(T) \qquad S = \sum_{i=1}^{C} n_i \bar{s}_i(T, p_i)$$

- $p_i = y_i p$ is the partial pressure of component i (the pressure that component i will have if it occupies the same volume as the mixture at the same temperature)

The Gibbs function for a mixture of ideal gases

- For each gaseous species i that comprises an ideal gas mixture at constant T and constant P, we have:

$$\bar{g}_i = \bar{h}_i - T\bar{s}_i$$

- Associate a sub-volume v_i with each of the C-components:

$$Td\bar{s}_i = d\bar{u}_i + pd\bar{v}_i \quad \Rightarrow \quad d\bar{s}_i = \bar{c}_{v_i}\frac{dT}{T} + \bar{R}\frac{d\bar{v}_i}{\bar{v}_i}$$

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The Gibbs function for a mixture of ideal gases

$$d\bar{s}_i = \bar{c}_{v_i} \frac{dT}{T} + \bar{R} \frac{d\bar{v}_i}{\bar{v}_i}$$

- The individual volumes $\bar{v}_i$ are the `internal degrees of freedom' which may adjust themselves so that the system attains equilibrium.
- An expression for the molar entropy can be calculated for any ideal gas species occupying volume $\bar{v}_i$ at some temperature T by integrating that volume from some reference state.

The Gibbs function for a mixture of ideal gases

$$d\bar{s}_i = \bar{c}_{v_i} \frac{dT}{T} + \bar{R} \frac{d\bar{v}_i}{\bar{v}_i}$$

- Introduce $\bar{v}_i^{ref}$: the volume that a mole of isolated gas would occupy at some temperature T and some reference pressure P^{ref}.
- Integrate from $\bar{v}_i^{ref}$ to $\bar{v}_i$ with constant T:

$$\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R} \ln \frac{\bar{v}_i}{\bar{v}_i^{ref}}$$

The Gibbs function for a mixture of ideal gases

$$\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R}\ln\frac{\bar{v}_i}{\bar{v}_i^{ref}}$$

- Since for an ideal gas:

$$\frac{\bar{v}_i}{\bar{v}_i^{ref}} = \frac{p^{ref}}{p_i}$$

- We conclude: $\bar{s}_i(\bar{v}_i) - \bar{s}_i(\bar{v}_i^{ref}) = \bar{R}\ln\frac{p^{ref}}{p_i} = \bar{R}\ln\frac{p^{ref}}{y_i p} =$

$$= -\bar{R}\ln\frac{y_i p}{p^{ref}}$$

where, the partial pressure of component i is:

$p_i = y_i p$

The Gibbs function for a mixture of ideal gases

$$\bar{s}_i(T,P) = \bar{s}_i^0(T) - \bar{R}\ln\frac{y_i\,p}{p_{ref}}$$

- Here $p_i = y_i p$ is the partial pressure of component i – the pressure that the component i will have at temperature T occupying the mixture volume.

$$pV = n\bar{R}T,\; p_iV = n_i\bar{R}T \Rightarrow \frac{p_i}{p} = \frac{n_i}{n} = y_i$$

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Ideal gas mixture

$$G = H - TS = \sum_{i=1}^{C} n_i \bar{h}_i(T) - T \sum_{i=1}^{C} n_i \bar{s}_i(T, p_i)$$

$$= \sum_{i=1}^{C} n_i (\bar{h}_i(T) - T \bar{s}_i(T, p_i))$$

- We introduce the molar Gibbs function of component i as:

$$\bar{g}_i(T, p_i) = \bar{h}_i(T) - T \bar{s}_i(T, p_i)$$

Chemical potential of component i

$$\mu_i = \bar{g}_i(T, p_i) = \bar{h}_i(T) - T\bar{s}_i(T, p_i)$$

$$G = \sum_{i=1}^{C} n_i \bar{g}_i(T, p_i)$$

Chemical potential of component i

$$\mu_i = \bar{h}_i(T) - T\bar{s}_i(T,P)$$

$$= \bar{h}_i(T) - T(\bar{s}_i^0(T) - \bar{R}\ln\frac{y_i\, p}{p_{ref}})$$

$$= \bar{h}_i(T) - T\bar{s}_i^0(T) + \bar{R}T\ln\frac{y_i\, p}{p_{ref}}$$

$$= \bar{g}_i^0(T) + \bar{R}T\ln\frac{y_i\, p}{p_{ref}} (ideal\, gas\, only)$$

Chemical equilibrium

- Consider a simple chemical reaction at equilibrium:

$$1H_2 + \frac{1}{2}O_2 \rightleftharpoons 1H_2O$$

- Assume we have to start with 1 mole of H_2 and 1 mole of O_2. Lets assume that 2x moles of H_2 react with x moles of O_2 giving us 2x moles of H_2O. Thus at equilibrium, we have the following:

Chemical equilibrium

- At equilibrium:

$$1H_2 + \frac{1}{2}O_2 \rightleftharpoons 1H_2O$$

$$1-2x \quad 1-x \quad 2x$$

$$moles \quad moles \quad moles$$

- Thus the mole fraction at equilibrium is:

$$1H_2 + \frac{1}{2}O_2 \rightleftharpoons 1H_2O$$

$$\frac{1-2x}{2-x} \quad \frac{1-x}{2-x} \quad \frac{2x}{2-x}$$

$$\longrightarrow$$

$$dn_{H_2} = -dn_{H_2O},\; dn_{O_2} = -\frac{1}{2}dn_{H_2O}$$

$$\frac{-dn_{H_2}}{1} = \frac{-dn_{O_2}}{\frac{1}{2}} = \frac{dn_{H_2O}}{1}$$

Equation of reaction equilibrium

$$1H_2 + \frac{1}{2}O_2 \rightleftharpoons 1H_2O$$

$$\frac{1-2x}{2-x} \quad \frac{1-x}{2-x} \quad \frac{2x}{2-x}$$

$$\longrightarrow$$

$$dn_{H_2} = -dn_{H_2O},\ dn_{O_2} = -\frac{1}{2}dn_{H_2O}$$

$$\frac{-dn_{H_2}}{1} = \frac{-dn_{O_2}}{\frac{1}{2}} = \frac{dn_{H_2O}}{1}$$

Stoichiometric coefficients

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Equation of reaction equilibrium

$$1H_2 + \frac{1}{2}O_2 \rightleftharpoons 1H_2O \longrightarrow \frac{-dn_{H_2}}{1} = \frac{-dn_{O_2}}{\frac{1}{2}} = \frac{dn_{H_2O}}{1}$$

$$dG|_{T,P} = \mu_{H_2} dn_{H_2} + \mu_{O_2} dn_{O_2} + \mu_{H_2O} dn_{H_2O} \quad \Rightarrow$$

$$dG|_{T,P} = (-1\mu_{H_2} - \frac{1}{2}\mu_{O_2} + 1\mu_{H_2O}) dn_{H_2O}$$

At equilibrium: $dG|_{T,P} = 0$

$$-1\mu_{H_2} - \frac{1}{2}\mu_{O_2} + 1\mu_{H_2O} = 0$$

Consider a general reaction

- For a reaction given by:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

- The equation of reaction equilibrium is:

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D$$

The composition that would be present at equilibrium for a given T and P can be determined by solving this equation. The solution procedure is simplified through the equilibrium constant concept introduced next.

The equilibrium condition

Re-write the equilibrium condition in terms of the definition of g_i.

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D$$

$$\nu_A(\overline{g}_A^0 + \overline{R}T \ln \frac{y_A p}{p_{ref}}) + \nu_B(\overline{g}_B^0 + \overline{R}T \ln \frac{y_B p}{p_{ref}}) =$$

$$\nu_C(\overline{g}_C^0 + \overline{R}T \ln \frac{y_C p}{p_{ref}}) + \nu_D(\overline{g}_D^0 + \overline{R}T \ln \frac{y_D p}{p_{ref}})$$

$\overline{g}_i^0$ all of these terms are at temperature T and 1 atm.

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The equilibrium condition

Rearrange terms to obtain:

$$\nu_A(\bar{g}_A^0 + \bar{R}T \ln \frac{y_A p}{p_{ref}}) + \nu_B(\bar{g}_B^0 + \bar{R}T \ln \frac{y_B p}{p_{ref}}) =$$

$$\nu_C(\bar{g}_C^0 + \bar{R}T \ln \frac{y_C p}{p_{ref}}) + \nu_D(\bar{g}_D^0 + \bar{R}T \ln \frac{y_D p}{p_{ref}})$$

$$\downarrow$$

$$\nu_C \bar{g}_C^0 + \nu_D \bar{g}_D^0 - \nu_A \bar{g}_A^0 - \nu_B \bar{g}_B^0$$

$$= -\bar{R}T(\nu_C \ln \frac{y_C p}{p_{ref}} + \nu_D \ln \frac{y_D p}{p_{ref}} - \nu_A \ln \frac{y_A p}{p_{ref}} - \nu_B \ln \frac{y_B p}{p_{ref}})$$

The equilibrium condition

Define: $$\Delta G^0 = \nu_C \bar{g}_C^0 + \nu_D \bar{g}_D^0 - \nu_A \bar{g}_A^0 - \nu_B \bar{g}_B^0$$

$$(computed\ \ at\ T\ \ and\ 1\,atm)$$

$$-\frac{\Delta G^0}{\bar{R}T} = \nu_C \ln\frac{y_C p}{p_{ref}} + \nu_D \ln\frac{y_D p}{p_{ref}} - \nu_A \ln\frac{y_A p}{p_{ref}} - \nu_B \ln\frac{y_B p}{p_{ref}} =$$

$$= \ln\left[\frac{y_C^{\nu_C}\, y_D^{\nu_D}}{y_A^{\nu_A}\, y_B^{\nu_B}}\left(\frac{p}{p_{ref}}\right)^{\nu_C+\nu_D-\nu_A-\nu_B}\right]$$

The equilibrium condition

$$-\frac{\Delta G^0}{\overline{R}T} = \ln\left[\frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}}\left(\frac{p}{p_{ref}}\right)^{\nu_C+\nu_D-\nu_A-\nu_B}\right]$$

$$\downarrow$$

$$-\frac{\Delta G^0}{\overline{R}T} = \ln K(T)$$

Where the equilibrium constant K(T) is defined as

$$K(T) = \frac{y_C^{\nu_C} y_D^{\nu_D}}{y_A^{\nu_A} y_B^{\nu_B}}\left(\frac{p}{p_{ref}}\right)^{\nu_C+\nu_D-\nu_A-\nu_B}$$

$\log_{10}K$ values over a range of temperatures is provided in Table A-27

Example

Consider the gaseous reaction: $P_4 \rightarrow 2P_2$. For a system that has only gases P_4 and P_2 present, it is determined that at T = 1430K and P_{total} = 1 atm, the mole fraction of P_4 and P_2 are equal ($y_{P4} = y_{P2}$). Approximating the system as an ideal gas mixture, find the mole fractions of P_4 at the same temperature (T = 1430K) and at a total pressure P_{total} = 3/8 atm.

Example

- Consider the following gaseous reaction:

$$CO+H_2O \longleftrightarrow H_2+CO_2$$

- Initially we have 2 moles of H_2O and 1 mole of CO_2.
- How many moles of oxygen exist at equilibrium?
- If the reaction is carried out at a different pressure, how will the concentration of CO vary?

Example

- Write the reaction as a sum of 2 reactions!

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

$$CO + 1/2\ O_2 \longleftrightarrow CO_2$$

0 moles   0 moles   1 mole (initially)

2Y moles y moles   1-2Y (at equilibrium)

$$H_2O \longleftrightarrow ½\ O_2 + H_2$$

2 moles   0 moles   0 moles (initially)

2-2x moles   x moles   2x (at equilibrium)

Example

- Note the mole fractions in the mixture
  - CO: 2y/(3+x+y)
  - CO_2:(1-2y)/(3+x+y)
  - H_2:2x/(3+x+y)
  - O_2: (x+y)/(3+x+y)
  - H_2O: (2-2x)/(3+x+y)

$$
\begin{array}{lllll}
H_2O & \rightleftharpoons & \frac{1}{2}O_2 & + & H_2 & -\Delta\overline{G^{rxn}_{H_2O}} \\
CO & + & \frac{1}{2}O_2 & \rightleftharpoons & CO_2 & \Delta\overline{G^{rxn}_{CO_2}} \\
\hline
\end{array}
$$

$$
H_2O + CO \rightleftharpoons H_2 + CO_2 \quad \Delta\overline{G^{rxn}_{CO_2}} - \Delta\overline{G^{rxn}_{H_2O}}
$$

Solve for x and y

$$
\frac{\frac{1-2Y}{3+X+Y}}{\frac{2Y}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}} = e^{-\left(\frac{\Delta\overline{G^{rxn}_{CO_2}}}{RT}\right)}
$$

$$
\frac{\frac{2X}{3+X+Y}\left(\frac{X+Y}{3+X+Y}\right)^{1/2}}{\frac{2-2X}{3+X+Y}} = e^{-\left(\frac{-\Delta\overline{G^{rxn}_{H_2O}}}{RT}\right)}
$$