Equilibrium: the extent of a reaction

In stoichiometry we talk about theoretical yields, and there are many reasons actual yields may be lower.

Another critical reason actual yields may be lower is the reversibility of chemical reactions: some reactions may produce only 70% of the product.

Equilibrium looks at the *extent* of a chemical reaction.

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$$\Delta G_r = \Delta G_r^0 + RT \ln Q$$

Extent of reaction (ξ):

- The advantage of using ξ - unique rate of a given reaction.
- The major drawback: ξ is an extensive variable and is proportional to the mass of the system.
- The fractional conversion is an intensive measure of the progress of a reaction.

Extent of reaction (ξ):

$A \longrightarrow B$ $d\xi$ of moles of A is converted to B $dn_A = - d\xi$ $dn_B = d\xi$
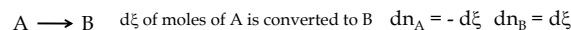
$$dG = -\mu_A d\xi + \mu_B d\xi \qquad \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$
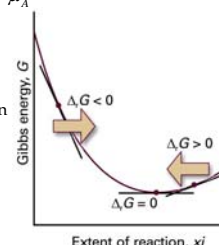
Reaction Gibbs energy

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} \qquad \xi = \text{extent of reaction}$$

$\Delta G_r < 0$ the forward reaction is spontaneous - exergonic

$\Delta G_r > 0$ the reverse reaction is spontaneous - endergonic

$\Delta G_r = 0$ the reaction is at equilibrium

Gibbs Free Energy

For a constant temperature and constant pressure process:

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\boxed{\Delta G = \Delta H_{sys} - T\Delta S_{sys}}$$

Gibbs free energy (ΔG) - Can be used to predict spontaneity.

$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$-\Delta G$ = -T($+\Delta S_{univ}$) $\Delta S_{univ} > 0$

$\Delta G > 0$ The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$+\Delta G$ = -T($-\Delta S_{univ}$) $\Delta S_{univ} < 0$

$\Delta G = 0$ The reaction is at equilibrium.

ΔG = -T(ΔS_{univ}) = 0 $\Delta S_{univ} = 0$

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Free Energy and Equilibrium

$$\Delta G° = -R\,T\,\ln K$$

R is constant so at a given temperature:

ΔG⁰(kJ)	K	Significance
200	9x10⁻³⁶	Essentially no forward reaction; reverse reaction goes to completion
100	3x10⁻¹⁸	
50	2x10⁻⁹	
10	2x10⁻²	
1	7x10⁻¹	Forward and reverse reactions proceed to same extent
0	1	
-1	1.5	
-10	5x10¹	
-50	6x10⁸	
-100	3x10¹⁷	Forward reaction goes to completion; essentially no reverse reaction
-200	1x10³⁵	

FORWARD REACTION   REVERSE REACTION

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Reaction Gibbs Energy ($\Delta_r G$)

$$A \rightleftharpoons B$$
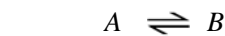
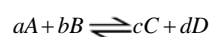| $t = 0$	1	0
$t = t$	$1 - d\xi$	$d\xi$
dn	$- d\xi$	$+ d\xi$

$d\xi$ is the extent of reaction

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

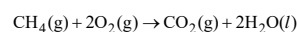$$\boxed{\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A}$$

The reaction Gibbs energy is the difference between the chemical potential of product and reactant at the *composition of the reaction mixture*

Reaction Gibbs Energy ($\Delta_r G$)

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

$$\boxed{\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_i v_i \mu_i}$$
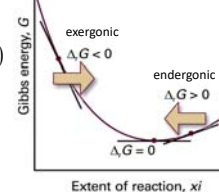
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r G = \left(2\mu_{H_2O(l)} + \mu_{CO_2(g)}\right) - \left(\mu_{CH_4(g)} + 2\mu_{O_2(g)}\right)$$

At equilibrium,

$$\boxed{\sum_i \mu_i v_i = 0}$$

exergonic
$\Delta G < 0$
endergonic
$\Delta G > 0$

Condition for chemical reaction equilibrium
At the reaction equilibrium, the chemical potentials of the product balance those of the reactants

Reaction Equilibrium $\quad \Delta_r G = \sum_i v_i \mu_i = \sum_i v_i [\mu_i^0(T) + RT \ln a_i]$

$$= \sum_i v_i \mu_i^0(T) + \sum_i RT \ln a_i^{v_i}$$

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln \prod_i a_i^{v_i} = \Delta_r G^0(T) + RT \ln Q$$

$$\boxed{Q = \prod_i a_i^{v_i}}$$

The reaction Quotient
(at any extent of the reaction)

At equilibrium,

$$\boxed{K = \left[\prod_i a_i^{v_i} \right]_{\text{at equilibrium}}}$$
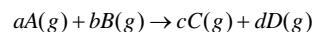
Thermodynamic equilibrium constant

$$\boxed{\Delta_r G^0 = -RT \ln K}$$

Can be used to calculate equilibrium constant for any reaction from tables of thermodynamic data

$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K$$

Practically a_i approximated by numerical values of molalities / by molar concentration / numerical values of partial pressures

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Reaction Equilibrium in an ideal gas reaction

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q$$

The reaction Quotient in terms of partial pressure(at any extent of reaction)
p^0 = 1 bar

$$\boxed{Q = \prod_i a_i^{v_i} = \prod_i \left(\frac{p_i}{p^0} \right)^{v_i}}$$

At equilibrium,

$$\boxed{K_p = \prod_i \left(\frac{p_i}{p^0} \right)^{v_i}_{\text{eqlm}}}$$

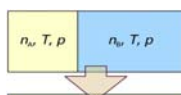$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K_p$$

$$\boxed{\Delta_r G^0 = -RT \ln K_p}$$

The Gibbs Energy of Mixing of Ideal Gases

$$\mu_i(T) = \mu_i^o(T) + RT \ln p_i \qquad p_i = \text{partial pressure of } i^{th} \text{ gas in bar.}$$

Before mixing:

$$G_{\text{before mixing}} = \sum_i n_i \left(\mu_i^o(T) + RT \ln p \right)$$

After mixing:

$$G_{\text{mixture}} = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^o(T) + RT \ln p_i \right)$$

$$= \sum_i n_i \left(\mu_i^o(T) + RT \ln x_i p \right)$$

Dalton's law of partial pressure, $p_i = x_i p$

$$\boxed{\Delta G_{mix} = nRT \sum_i x_i \ln x_i}$$

Gibbs free energy of mixing of ideal gases is always negative, and hence spontaneous

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The Enthalpy of Mixing of Ideal Gases

$$\Delta G_{mix} = nRT \sum_i x_i \ln x_i$$

$$\Delta S_{mix} = -\left(\frac{\partial (\Delta G_{mix})}{\partial T} \right)_{p,n} = -nR \sum_i x_i \ln x_i$$

$$\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0$$

Ideal gases show no intermolecular interactions and hence change in enthalpy is zero

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(isothermal) Pressure dependence of Chemical Potential

$$\left(\frac{\partial G}{\partial p} \right)_T = V \qquad \int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} V dp \qquad G_2 = G_1 + \int_{p_1}^{p_2} V dp$$

for one component system, $\qquad \mu_2(T) = \mu_1(T) + \int_{p_1}^{p_2} V_m dp$

Case 1: liquid or solid; V weakly dependent on p

$$\mu_2(T) = \mu_1(T) + V_m(p_2 - p_1) \qquad \text{for one component system}$$

Case 2: ideal gas; V is dependent on p,

$$\boxed{\mu_2(T) = \mu_1(T) + RT \ln \frac{p_2}{p_1}}$$

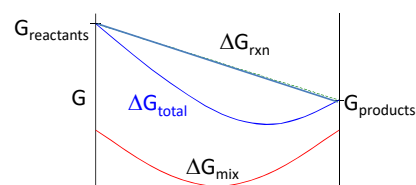$$\boxed{\mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}}$$

$$\boxed{\mu(T) = \mu^o(T) + RT \ln p}$$

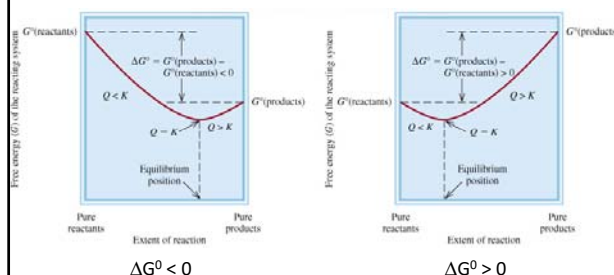μ^o = standard chemical potential, the chemical potential of the pure gas **at 1 bar** at temp T.

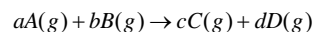p expressed in bar.

The Gibbs Energy of Mixing of Ideal Gases

Reaction Gibbs Energy ($\Delta_r G$ or ΔG_{rxn})

Free Energy Versus Extent of Reaction

$\Delta G^0 < 0$ $\Delta G^0 > 0$

Reaction Equilibrium in ideal gas reaction

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$

$$\Delta_r G(T) = \Delta_r G^0(T) + RT \ln Q$$

The reaction Quotient in terms of partial pressure(at any extent of reaction)
$p^0 = 1$ bar

$$Q = \prod_i a_i^{\nu_i} = \prod_i \left(\frac{p_i}{p^0} \right)^{\nu_i}$$

At equilibrium,

$$K_p = \prod_i \left(\frac{p_i}{p^0} \right)^{\nu_i}_{\text{eqlm}}$$

$$\Delta_r G(T) = 0 = \Delta_r G^0(T) + RT \ln K_p$$

$$\boxed{\Delta_r G^0 = -RT \ln K_p}$$

Temperature dependence of equilibrium constant

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$\boxed{\Delta G_r^0 = \sum_{\text{pdts}} \upsilon \Delta G_f^0 - \sum_{\text{reactants}} \upsilon \Delta G_f^0}$$

$$\Delta_r G^\circ = c\Delta_f G_C^\circ + d\Delta_f G_D^\circ - a\Delta_f G_A^\circ - b\Delta_f G_B^\circ$$

$$\Delta_r S^\circ = c\, S_C^\circ + d\, S_D^\circ - a\, S_A^\circ - b\, S_B^\circ.$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T}.$$

$$\left(\frac{\Delta_r G^\circ}{T} \right)_{T_2} = \left(\frac{\Delta_r G^\circ}{T} \right)_{T_1} + \Delta_r H^\circ \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Temperature dependence of equilibrium constant

$$\Delta_r G^0 = -RT \ln K$$

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d\left(\Delta_r G^0 / T\right)}{dT}$$

$$\frac{d\left(\Delta_r G^0 / T\right)}{dT} = -\frac{\Delta_r H^0}{T^2} \quad \text{(Gibbs Helmholtz Equation)}$$

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2}} \quad \textbf{van't Hoff equation}$$

For exothermic reactions, *K* decreases with increasing *T*

$$\boxed{\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Different types of equilibrium constants

$$K = \left[\prod_i a_i^{\nu_i} \right]_{equilibrium}$$
Thermodynamic equilibrium constant in terms of activity coefficients (a_i)

$$K_p = \left[\prod_i p_i^{\nu_i} \right]_{equilibriu\,m}$$
Standard equilibrium constant for gaseous reaction
p_i (in bar)

$$K_c = \left[\prod_i c_i^{\nu_i} \right]_{equilibriu\,m}$$
Standard concentration equilibrium constant
c_i in mol/L

$$K_x = \left[\prod_i x_i^{\nu_i} \right]_{equilibrium}$$
Mole-fraction equilibrium constant

Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

> **A change imposed on an equilibrium system is called a stress**
>
> **The equilibrium always responds in such a way so as to counteract the stress**

- Change in concentration of one or more reactants or products
- Change in temperature
- Change in pressure
- Addition of a catalyst

Le Châtelier's Principle

• Relation between K_p & K_c

• The van't Hoff eqn.; Dependence of equilibrium constant on T

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H_r^0}{R}$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta H_r^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

• Effect of pressure on K_p, K_c