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standard state of solvent: $x_A = 1$

In terms of molality, $\boxed{a_j = \gamma_j \frac{b_j}{b_j^{\ominus}}}$

Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^{\ominus}$	$a = \gamma b/b^{\ominus}$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

solute: it approaches ideal dilute solution as $x_B \longrightarrow 0$ (not 1).

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General expression: $\boxed{\mu = \mu^{\ominus} + RT\ln a = \mu^{\text{ideal}} + RT\ln\gamma}$

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two standard values differ by about 40 kJ mol^{-1}

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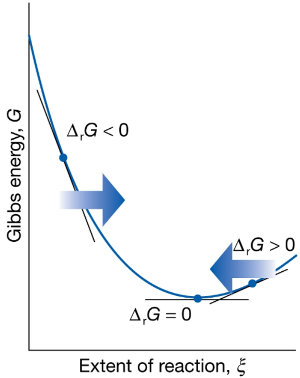
- reaction Gibbs energy : $\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,\,T}$; ξ measures extent of reaction
  - $\Delta_r G$ is a derivative

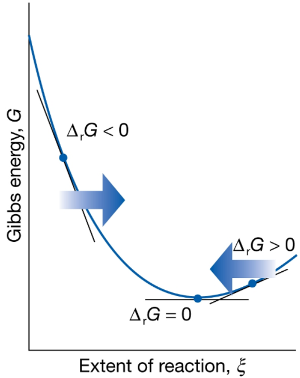
suppose the reaction advances by $d\xi$, suppose the reaction advances by $d\xi$,

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

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

$=$ difference between chemical potentials of reactants and products
at the composition of the reaction mixture


$\Delta_r G < 0$
$\Delta_r G > 0$
$\Delta_r G = 0$
Gibbs energy, G
Extent of reaction, ξ



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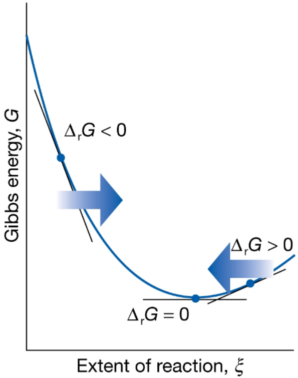

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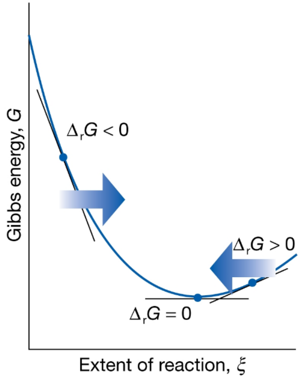

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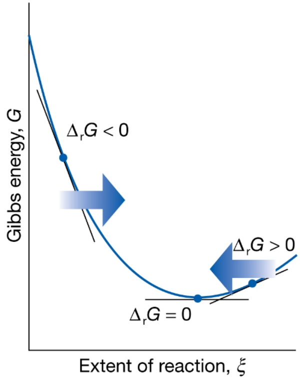

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  $\Delta_r G < 0 \implies$ forward reaction spontaneous
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  $\Delta_r G > 0 \implies$ reverse reaction spontaneous
- Equilibrium corresponds to zero slope
  $\Delta_r G = 0 \implies$ foot of the valley
  : reaction at equilibrium

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- coupled reaction :
  $C_6H_{12}O_6(aq) + 2\ NAD^+(aq) + 2\ ADP(aq) + 2\ P_i^-(aq) + 2\ H_2O(l)$
  $\longrightarrow 2\ CH_3COCO_2^-(aq) + 2\ NADH(aq) + 2\ ATP(aq) + 2\ H_3O^+(aq)$

$$\Delta_r G^\oplus = -147 - 2(-31) = -85\text{kJ mol}^{-1}$$

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- but biosynthesis occurs indirectly and is equivalent to consumption of 3 ATP molecules for each link

In moderately small protein like myoglobin, with about 150 peptide links, construction alone requires 450 ATP molecules

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When A and B are perfect gases

$$\Delta_r G = \mu_B - \mu_A = \left(\mu_B^\ominus + RT \ln p_B\right) - \left(\mu_A^\ominus + RT \ln p_A\right)$$

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At equilibrium, $\Delta_r G = 0 \implies \Delta_r G^{\ominus} + RT \ln K$ with $K = \left(\frac{p_B}{p_A}\right)_{\text{equilibr}}$

In general, for a reaction $\nu_A\mathrm{A}+\nu_B\mathrm{B} \leftrightarrows \nu_C\mathrm{C}+\nu_D\mathrm{D}$,

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$$Q = \frac{\text{activities of products raised to powers of stiochiometric coefficients}}{\text{activities of reactants raised to powers of stiochiometric coefficients}}$$

Writing νs for reactants as negative integers, $Q = \prod_j a_j^{\nu_j}$

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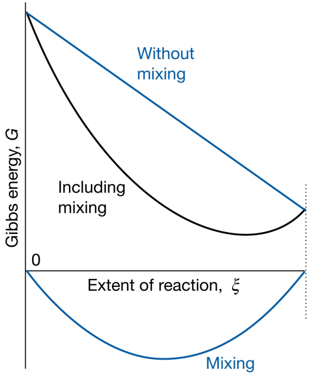

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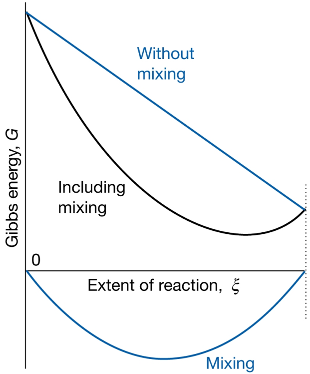

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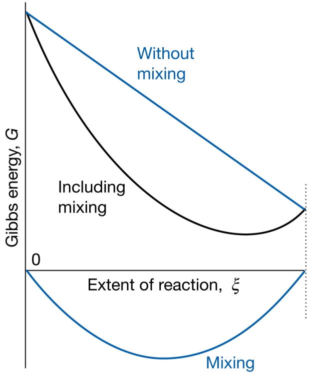

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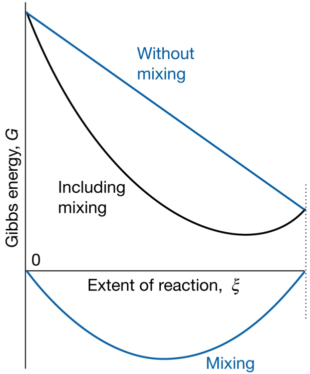

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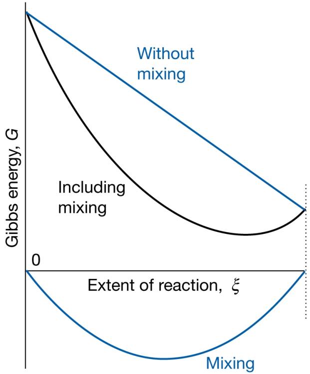

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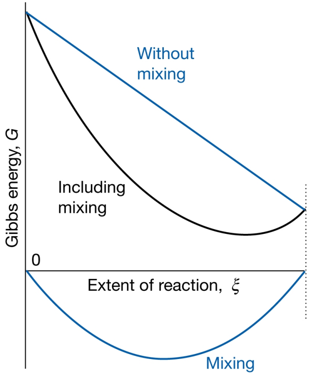

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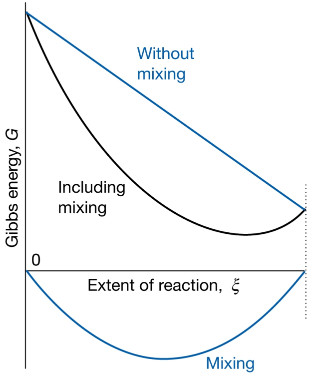

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  - corresponds to equilibrium composition

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$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,\,T} = \sum_j \nu_j \mu_j = \underbrace{\sum_j \nu_j \mu_j^{\ominus}}_{\Delta_r G^{\ominus}} + RT \sum_j \nu_j \ln a_j = \Delta_r G^{\ominus} + RT \ln \overbrace{\prod_j a_j^{\nu_j}}^{Q}$$

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Provided CO_2 can be treated as a perfect gas, $K = \frac{p_{CO_2(g)}}{p^{\ominus}} = p_{CO_2(g)}$

=numerical value of decomposition vapour pressure of calcium carbonate

$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, at 298 K

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$$\therefore \ln K = -\frac{2\times(-16.5\times10^3)}{8.3145\times298} = 6.1 \times 10^5$$

$$K = \frac{a_D^{\nu D}\, a_C^{\nu C}}{a_A^{\nu A}\, a_B^{\nu B}}$$

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$$\therefore \Delta_r G = \Delta_r G^\ominus + RT \ln \frac{a_P}{a_R} - \nu RT \ln 10 \log a_{H^+} = \Delta_r G^\ominus + RT \ln \frac{a_P}{a_R} + \nu RT \ln 10.\mathrm{pH}$$

with pH$= 7$, $\quad \Delta_r G^\oplus = \Delta_r G^\ominus + 7\nu RT \ln 10$

response of equilibria to the conditions

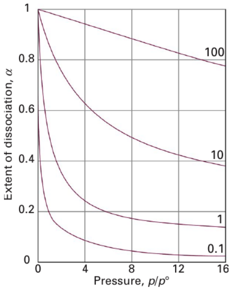
Le Chatelier's principle :

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance

How equilibria respond to changes of pressure

Consider reaction A$\rightleftharpoons$2B

$$\alpha = \sqrt{\frac{1}{1+\frac{4p}{Kp^{\ominus}}}}$$



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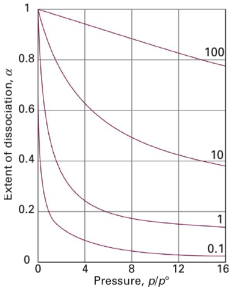

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even though K is independent of pressure
amounts of A and B do depend on pressure
as p is increased, α decreases
in accord with Le Chatelier's principle

effect of increase in pressure on ammonia synthesis

$$K = \frac{p_{NH_3}^2 \, p^{\ominus 2}}{p_{N_2} \, p_{H_2}^3} = \frac{x_{NH_3}^2 \, p^2 \, p^{\ominus 2}}{x_{N_2} \, x_{H_2}^3 \, p^4} = \frac{K_x \, p^{\ominus 2}}{p^2}$$

response of equilibria to changes of temperature

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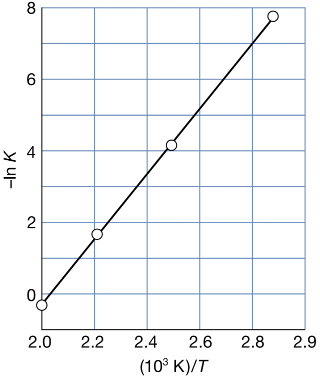
K vs. T(K)



or, $\frac{d\ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_r H^\ominus}{R}$

Example: $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$

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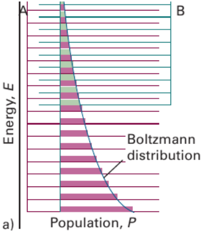
At a given temperature, there is a specific distribution of populations, and hence specific composition of reaction mixture



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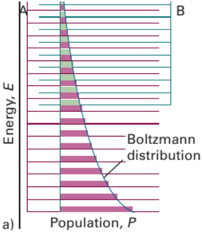

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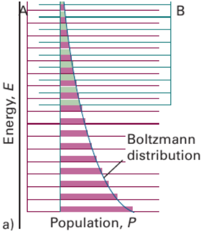

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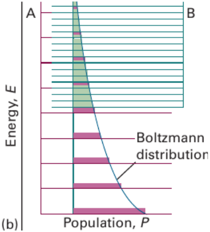
an endothermic reaction



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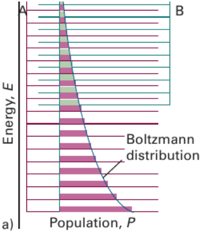

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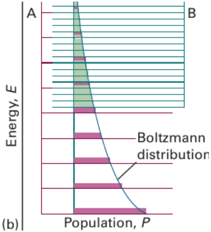

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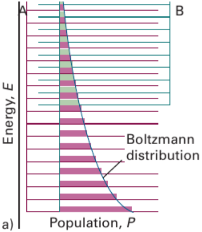

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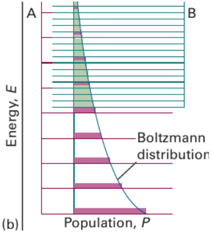

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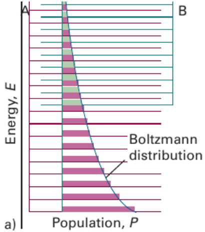

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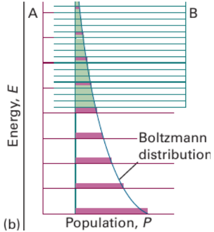

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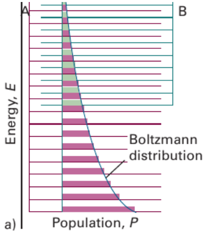

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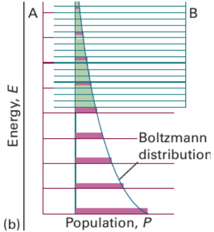

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