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$$\boxed{\mu_A = \mu_A^* + RT\ln x_A + RT\ln\gamma_A}$$

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	$a=p/p^*$, $a=\gamma x$	$\gamma \to 1$ as $x \to 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a=p/K$, $a=\gamma x$	$\gamma \to 1$ as $x \to 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a=\gamma b/b^\ominus$	$\gamma \to 1$ as $b \to 0$

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$b_B^\ominus = 1$ mol/kg

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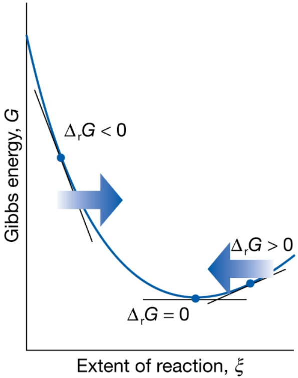
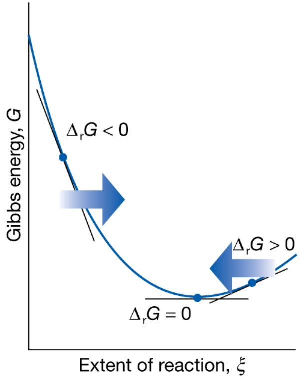
= difference between chemical potentials of reactants and products
at the composition of the reaction mixture


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



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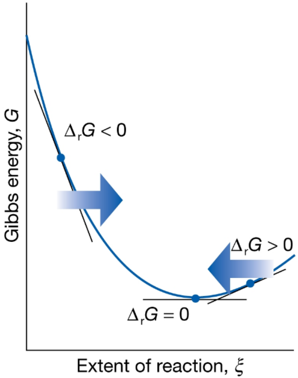

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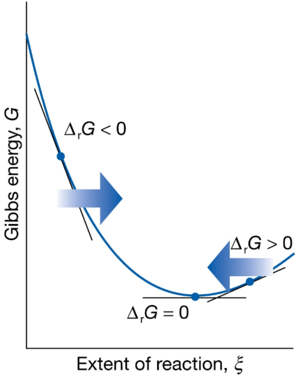

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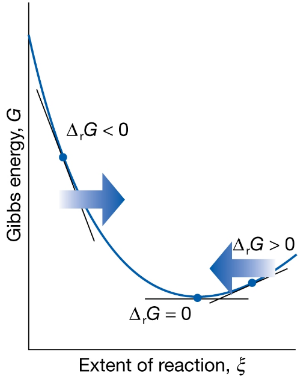

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- Equilibrium corresponds to zero slope
  $\Delta_r G = 0 \implies$ foot of the valley
  : reaction at equilibrium

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

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

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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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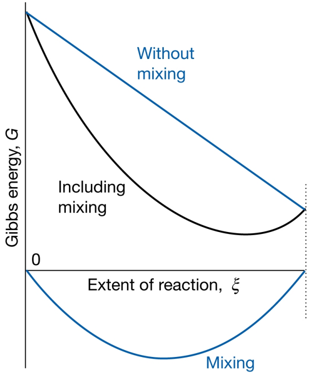

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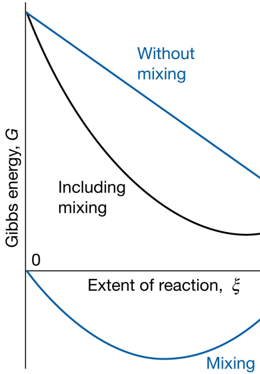

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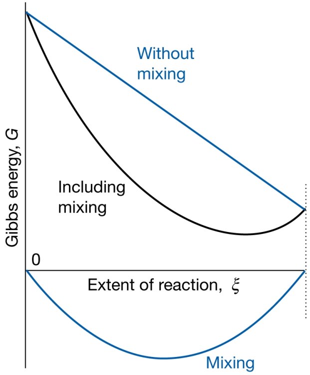

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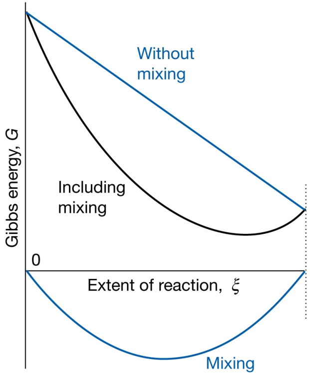

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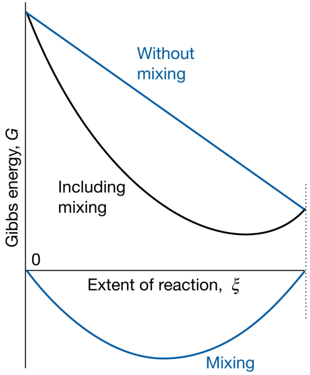

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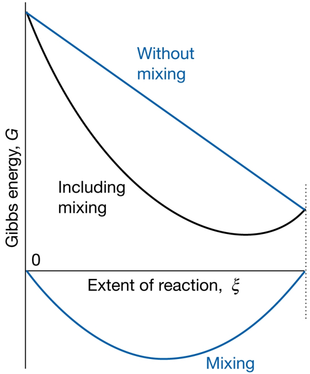

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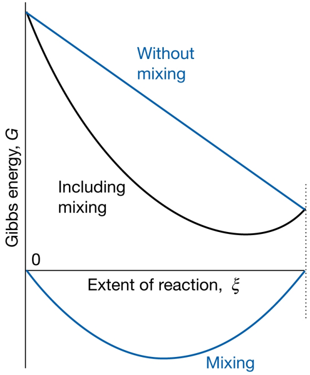

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Provided CO_2 can be treated as a perfect gas, $K = \frac{p_{CO_2(g)}}{p^{\ominus}} = p_{CO_2(g)}$

=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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$$= 2\Delta_f G^\ominus(NH_3,g) = 2 \times (-16.5)\ \text{kJ mol}^{-1}$$

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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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In the biological standard state, both P and R are at unit activity

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

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

response of equilibria to the conditions

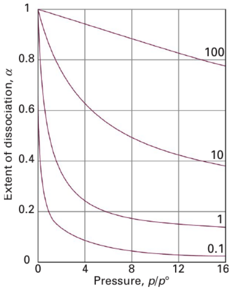
Le Chatelier's principle :

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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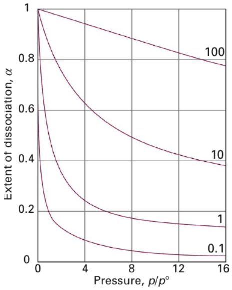

label : K

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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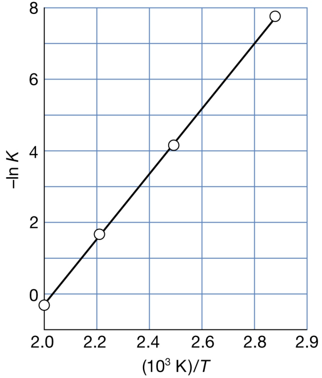
K vs. T(K)



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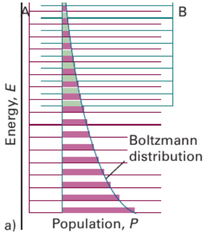
At a given temperature, there is a specific distribution of populations, and hence specific composition of reaction mixture



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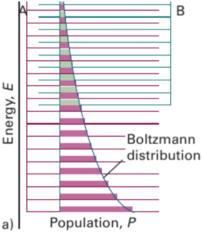

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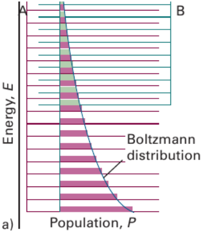

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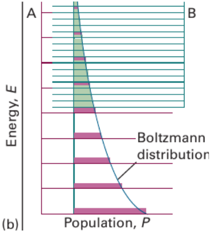
In a reaction, entropy plays a role as well as energy

an endothermic reaction



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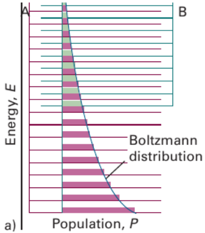

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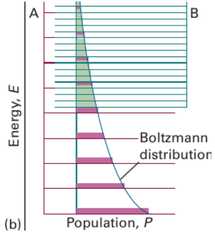

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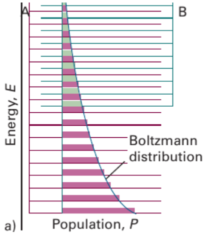

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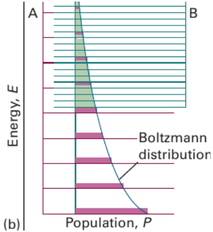

B energy levels lie higher than the A energy levels, but they are much more closely spaced $\Longrightarrow$ their total population may be considerable and B could even dominate in the reaction mixture at equilibrium

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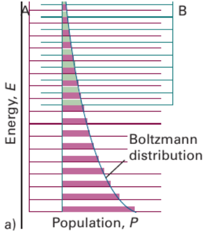

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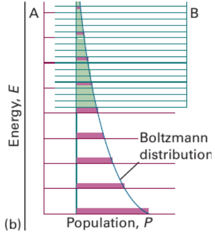
In a reaction, entropy plays a role as well as energy

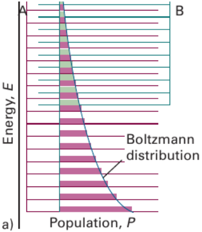
an endothermic reaction



B energy levels lie higher than the A energy levels, but they are much more closely spaced $\Longrightarrow$ their total population may be considerable and B could even dominate in the reaction mixture at equilibrium

Closely spaced energy levels correlate with high entropy, so entropy effects dominate

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



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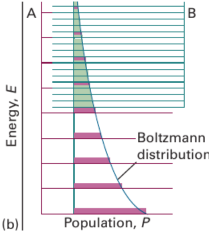

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$$K = e^{-\frac{\Delta_r H^\ominus}{RT}} e^{-\frac{\Delta_r S^\ominus}{R}}$$