Chemical equilibrium

Spontaneous chemical reactions

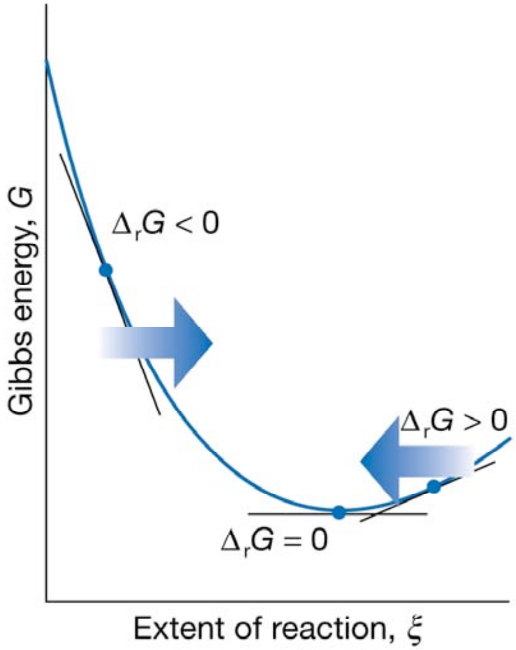
The direction of spontaneous change at constant temperature and pressure – towards lower values of the Gibbs energy. We locate the equilibrium composition of the reaction mixture by calculating its Gibbs energy and identifying the composition that corresponds to minimum G.

The reaction Gibbs energy

Consider the equilibrium $A \leftrightarrows B$. Suppose an infinitesimal amount $d\zeta$ of A turns into B:

$$dn_A = -d\zeta \qquad dn_B = +d\zeta$$

ζ - the **extent of reaction**, has the dimensions of amount of substance and is reported in moles. When the extent of reaction changes by a finite amount $\Delta\zeta$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\zeta$ and the amount of B changes from $n_{B,0}$ to $n_{B,0} + \Delta\zeta$.



The **reaction Gibbs energy**, $\Delta_r G$ – the slope of the graph of the Gibbs energy plotted against the extent of reaction:

$$\Delta_r G = \left(\frac{\partial G}{\partial \zeta}\right)_{p,T} \qquad dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\zeta + \mu_B d\zeta = (\mu_B - \mu_A)d\zeta$$

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

$\Delta_r G$ – can be interpreted as the difference between the chemical potentials of the reactants and products *at the composition of the reaction mixture.*

Because chemical potential varies with the composition, the slope of G changes as the reaction proceeds. Because the reaction runs in the direction of decreasing G (down the slope), the reaction A → B is spontaneous when $\mu_B < \mu_A$, whereas the reverse reaction is spontaneous $\mu_B > \mu_A$. The slope is zero and the reaction is spontaneous in neither direction when $\Delta_r G = 0$ and $\mu_B = \mu_A$. If we can find the composition of the reaction mixture that ensures $\mu_B = \mu_A$, then we can identify the composition of the reaction mixture at equilibrium.

Exergonic and endergonic reactions

At constant temperature and pressure:

If $\Delta_r G < 0$, the forward reaction is spontaneous – exergonic (work-producing).

If $\Delta_r G > 0$, the reverse reaction is spontaneous – endergonic (work-consuming).

If $\Delta_r G = 0$, the reaction is at equilibrium.

The description of equilibrium

Perfect gas equilibria

When A and B are perfect gases,

$$\Delta_r G = \mu_B - \mu_A = (\mu_B^{\varnothing} + RT \ln p_B) - (\mu_A^{\varnothing} + RT \ln p_A) = = \Delta_r G^{\varnothing} + RT \ln(p_B/p_A)$$

$$\Delta_r G = \Delta_r G^{\varnothing} + RT \ln(Q) \qquad Q = p_B/p_A$$

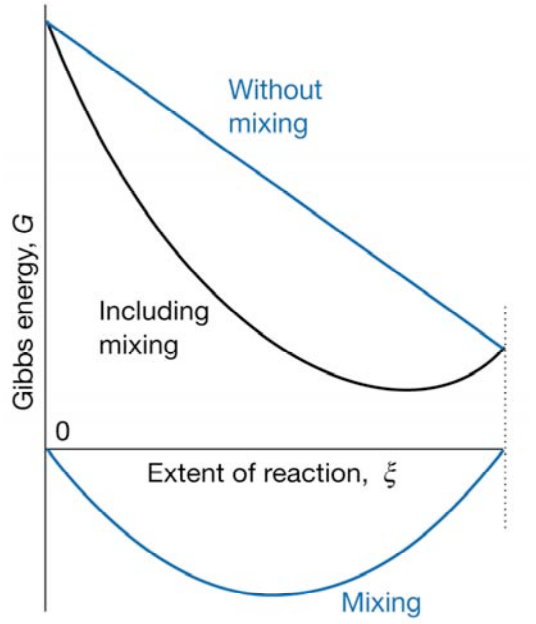
Q – a **reaction quotient**. The **standard reaction Gibbs energy** is defined as a difference in the standard Gibbs energies of formation, so in practice we calculate $\Delta_r G^{\varnothing}$ as

$$\Delta_r G^{\varnothing} = \Delta_f G^{\varnothing}(B) - \Delta_f G^{\varnothing}(A)$$

At equilibrium, $\Delta_r G = 0$ $\qquad 0 = \Delta_r G^{\varnothing} + RT \ln(K)$

$$RT \ln(K) = -\Delta_r G^{\varnothing} \qquad K = (p_B/p_A)_{\text{equilibrium}}$$

This is a link between tables of thermodynamic data and K.



In molecular terms, the minimum in the Gibbs energy, which corresponds to $\Delta_r G = 0$, stems from the Gibbs energy of mixing of the two gases. Consider a hypothetical reaction in which A molecules change into B molecules without mingling together. The Gibbs energy of the system changes from $G^\varnothing(\mathrm{A})$ to $G^\varnothing(\mathrm{B})$ in proportion to the amount of B that had been formed and the slope of the plot of G against the extent of reaction is a constant and equal to $\Delta_r G^\varnothing$ at all stages of the reaction. There is no minimum in the graph (except of pure B). However, in fact, the newly produced B molecules mix with the surviving A molecules:

$$\Delta_{\mathrm{mix}} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

This expression makes a U-shaped contribution to the total change in Gibbs energy and there is now a minimum in the Gibbs energy, and its position corresponds to the equilibrium composition of the reaction mixture.

When $\Delta_r G^\varnothing > 0$, the equilibrium constant $K < 1$. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favored at equilibrium. When $\Delta_r G^\varnothing < 0$, the equilibrium constant $K > 1$, so at equilibrium the partial pressure of B exceeds that of A – the product B is favored at equilibrium.

The general case of a reaction

Consider the reaction $2\text{ A} + \text{B} \rightarrow 3\text{ C} + \text{D}$

We can rewrite as $0 = 3\text{ C} + \text{D} - 2\text{ A} - \text{B}$ $\quad 0 = \sum_J \nu_J J$

ν_J – **stoichiometric numbers**: $\nu_A = -2$, $\nu_B = -1$, $\nu_C = 3$, $\nu_D = 1$

A stoichiometric number is positive for products and negative for reactants. We define ζ so that if it changes by $\Delta\zeta$, then the change in the amount of any species J is $\nu_J\Delta\zeta$.

To express the equation $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

we rearrange it to $0 = 2\ NH_3(g) - N_2(g) - 3\ H_2(g)$

$\nu(N_2) = -1$, $\nu(H_2) = -3$, $\nu(NH_3) = +2$

If initially there is 10 mol N_2 present, then when the extent of reaction changes from $\zeta = 0$ to $\zeta = 1$ ($\Delta\zeta = +1$ mol), the amount of N_2 changes from 10 mol to 9 mol. All the N_2 has been consumed when $\zeta = 10$. When $\Delta\zeta = +1$ mol, the amount of H_2 changes by $-3\times(1\text{ mol}) = -3$ mol and the amount of NH_3 changes by $+2\times(1\text{ mol}) = +2$ mol.

We will show that the Gibbs energy of reaction can always be written

$$\Delta_r G = \Delta_r G^{\varnothing} + RT\ln(Q)$$

with the standard Gibbs energy calculated from

$$\Delta_r G^{\Theta} = \sum_{\text{Products}} \nu\Delta_f G^{\Theta} - \sum_{\text{Reactants}} \nu\Delta_f G^{\Theta} \qquad \Delta_r G^{\Theta} = \sum_J \nu_J \Delta_f G^{\Theta}(J)$$

The quotient: Q = (activities of products)/(activities of reactants) $\quad Q = \prod_J a_J^{\nu_J}$

Because reactants have negative stoichiometric numbers, they automatically appear as the denominator. For pure solids and liquids, the activity is 1, so they make no contribution to Q even when they appear in the chemical equation.

Consider the reaction $2\,\mathrm{A} + 3\,\mathrm{B} \rightarrow \mathrm{C} + 2\,\mathrm{D}$

We can rewrite as $0 = 3\,\mathrm{C} + \mathrm{D} - 2\,\mathrm{A} - \mathrm{B}$ $\quad 0 = \sum_J \nu_J J$

$\nu_\mathrm{A} = -2,\ \nu_\mathrm{B} = -3,\ \nu_\mathrm{C} = +1,\ \nu_\mathrm{D} = +2$ $\qquad Q = \dfrac{a_C a_D^2}{a_A^2 a_B^3}$

Justification: When the reaction advances by $\mathrm{d}\zeta$, $\qquad \mathrm{d}n_\mathrm{J} = \nu_\mathrm{J}\mathrm{d}\zeta$

$$dG = \sum_J \mu_J dn_J = \left(\sum_J \nu_J \mu_J\right) d\zeta \qquad \Delta_r G = \left(\frac{\partial G}{\partial \zeta}\right)_{p,T} = \sum_J \nu_J \mu_J$$

$$\mu_\mathrm{J} = \mu_\mathrm{J}^{\emptyset} + RT \ln a_\mathrm{J} \quad \Delta_r G = \overbrace{\sum_J \nu_J \mu_J^{\Theta}}^{\Delta_r G^{\Theta}} + RT \sum_J \ln a_J^{\nu_J} = \Delta_r G^{\Theta} + RT \sum_J \ln a_J^{\nu_J}$$

$$= \Delta_r G^{\Theta} + RT \ln \overbrace{\prod_J a_J^{\nu_J}}^{Q} = \Delta_r G^{\Theta} + RT \ln Q$$

At equilibrium, the slope of G is zero, $\qquad \Delta_\mathrm{r} G = 0,\ K = \left(\prod_J a_J^{\nu_J}\right)_{equilibrium}$

For K we use the values of activities at equilibrium and for Q we use their values at the specific stage of reaction. An equilibrium constant K expressed in terms of activities (or fugacities for gases) – a **thermodynamic equilibrium constant**. Because activities are dimensionless numbers, the thermodynamic equilibrium constant is also dimensionless. In elementary applications, the activities are often replaced by the numerical values of molalities or molar concentrations, and fugacities are replaced by partial pressures. In either case, the resulting expressions are only approximations. The approximation is particularly severe for electrolyte solutions – in them the activity coefficients differ from 1 even in very dilute solutions.

$\Delta_r G = 0$: $\boldsymbol{RT\ln K = -\Delta_r G^{\varnothing}}$ – an exact and highly important thermodynamic relation, enables us to predict the equilibrium constant of any reaction from tables of thermodynamic data and to predict the equilibrium composition of the reaction mixture.

Example 1. Calculating an equilibrium constant

Calculate the equilibrium constant for the ammonia synthesis reaction,

$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$

at 298 K and show how K is related to the partial pressures of the species at equilibrium when the overall pressure is low enough for the gases to be treated as perfect.

We calculate the standard Gibbs energy and convert it to the equilibrium constant. Because the gases are perfect, we replace each fugacity by a partial pressure.

$-\Delta_r G^{\varnothing} = 2\Delta_f G^{\varnothing}(NH_3,g) - \{\Delta_f G^{\varnothing}(N_2,g) + 3\Delta_f G^{\varnothing}(H_2,g)\} = 2\Delta_f G^{\varnothing}(NH_3,g) = 2 \times (-16.5\ \text{kJ mol}^{-1})$

$\ln K = -2 \times (-16.5\ \text{kJ mol}^{-1}) / \{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})$

$K = 6.1\times10^5$

the thermodynamically exact result

$$K = \frac{a_{NH_3}^2}{a_{N_2}a_{H_2}^3} = \frac{\left(f_{NH_3}/p^{\Theta}\right)^2}{\left(f_{N_2}/p^{\Theta}\right)\left(f_{H_2}/p^{\Theta}\right)^3} = \frac{f_{NH_3}^2 p^{\Theta 2}}{f_{N_2} f_{H_2}^3} \approx \frac{p_{NH_3}^2 p^{\Theta 2}}{p_{N_2} p_{H_2}^3}$$

Example 2. Estimating the degree of dissociation at equilibrium

The standard Gibbs energy of reaction for the decomposition $H_2O(g) \rightarrow H_2(g) + 1/2\ O_2(g)$ is +118.0 kJ mol^{-1} at 2300 K. What is the degree of dissociation of H_2O at 2300 K and 1.00 bar.

The equilibrium constant is obtained from the standard Gibbs energy of reaction, so the task is to relate the degree of dissociation, α, to K and then find its numerical value. We proceed by expressing the equilibrium composition in terms of α and solve for α in terms of K. As the standard Gibbs energy of reaction is large and positive, we expect K and α to be small.

$\ln K = (+118.0\times10^3 \text{ J mol}^{-1}) /\{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\times(2300 \text{ K})$ $\qquad K = 2.08\times10^{-3}$

The equilibrium composition can be expressed in terms of α by drawing up the following table:

	H_2O	H_2	O_2	equilibrium table
Initial amount	n	0	0	The equilibrium constant
Change to reach equilibrium	$-\alpha n$	$+\alpha n$	$+(1/2)\alpha n$	is therefore
Amount at equilibrium	$(1 - \alpha)n$	αn	$(1/2)\alpha n$	
Mole fraction	$\frac{1-\alpha}{1+(1/2)\alpha}$	$\frac{\alpha}{1+(1/2)\alpha}$	$\frac{(1/2)\alpha}{1+(1/2)\alpha}$	$K = \frac{p_{H_2}p_{O_2}^{1/2}}{p_{H_2O}}$
Partial pressure	$\frac{(1-\alpha)p}{1+(1/2)\alpha}$	$\frac{\alpha p}{1+(1/2)\alpha}$	$\frac{(1/2)\alpha p}{1+(1/2)\alpha}$	$= \frac{\alpha^{3/2}p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

For $\alpha \ll 1$, $\quad K \approx \frac{\alpha^{3/2}p^{1/2}}{2^{1/2}} \qquad \alpha \approx \left(2^{1/2}K\right)^{2/3} = 0.0205$

About 2% of water has decomposed.

The relation between equilibrium constants

We need to express the thermodynamic equilibrium constant in terms of the mole fractions, x_J, or molalities, b_J, of the species. For that, we need to know the activity coefficients and then use $a_J = \gamma_j x_J$ or $a_J = \gamma_j b_J / b^{\varnothing}$

For an equilibrium $A + B \leftrightarrows C + D$

$$K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{b_C b_D}{b_A b_B} = K_\gamma K_b$$

The activity coefficients must be evaluated at the equilibrium composition, which may involve a complicated calculation, because the latter is known only if the equilibrium composition is already known.

In elementary applications, and to begin the iterative calculation of the concentrations in a real example, we can assume that the activity coefficients are all close to 1, $K_\gamma = 1$. Then $K \approx K_b$ and equilibria are discussed in terms of molalities (or molar concentrations).

Equilibria in biological systems

For biological systems it is appropriate the biological standard state, pH = 7. The relation between the thermodynamic and biological standard Gibbs energies of reaction for the reaction

$A + \nu\, H^+(aq) \rightarrow P$ is $\Delta_r G^{\oplus} = \Delta_r G^{\varnothing} + 7\nu RT \ln 10$

There is no difference between the two standard values if hydrogen ions are not involved in the reaction.

Consider the reaction $NADH(aq) + H^+(aq) \rightarrow NAD^+(aq) + H_2(g)$ at 37°C, for which $\Delta_r G^{\varnothing} = -21.8$ mol^{-1}. NADH is the reduced form of nicotinamide adenine dinucleotide and NAD^+ is its oxidized the molecules play an important role in the later stages of the respiratory process.

$7 \ln 10 = 16.1$ $\Delta_r G^{\oplus} = -21.8\ kJ\ mol^{-1} + 16.1 \times (8.3145 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1})(310\ K) = +19.7\ kJ\ mol^{-1}$

Here, the biological standard value is opposite in sign to the thermodynamic standard value.

The response of equilibria to the conditions

Equilibria respond to changes in pressure, temperature, and concentrations of reactants and products. The equilibrium constant is not affected by the presence of a catalyst or an enzyme. Catalysts increase the rate at which equilibrium is attained but do not affect its position.

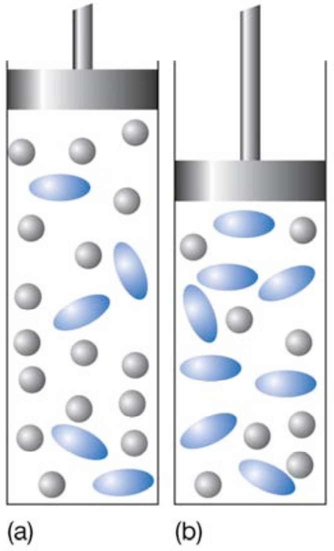
How equilibria respond to pressure

The equilibrium constant depends on the value of $\Delta_r G^{\varnothing}$, which is defined at a single, standard pressure. Therefore, the value of $\Delta_r G^{\varnothing}$ and hence K is independent of the pressure at which the equilibrium is actually established: $\left(\partial K/\partial p\right)_T = 0$

This does not necessarily mean that the equilibrium composition is independent of pressure. We distinguish between two ways to apply pressure:

1) The pressure within a reaction vessel can be increased by injecting an inert gas into it. However, so long as the gases are perfect, the addition of gas leaves all the partial pressures of the reacting gases unchanged. The addition of an inert gas leaves the molar concentrations of the original gases unchanged, as they continue to occupy the same volume – no effect on the equilibrium composition of the system.

2) The pressure may be increased by confining the gases to a smaller volume. Then the partial pressures are changed. The equilibrium constant itself is independent of pressure. However, compression can adjust the individual partial pressures of the reactants and products in such a way that, although each one changes, their ratio (as it appears in the equilibrium constant) remains the same.

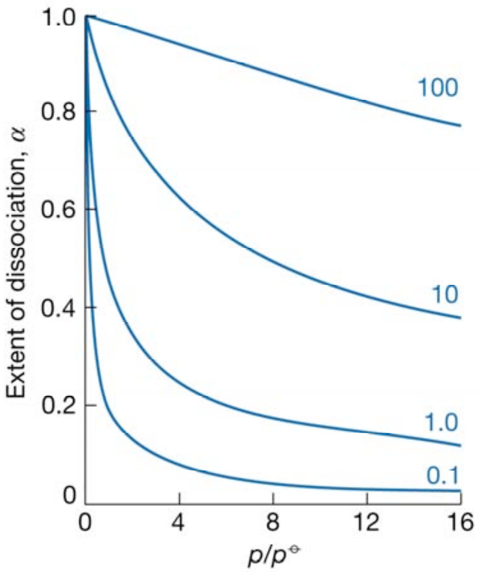


Consider the perfect gas equilibrium A $\leftrightarrows$ 2 B, $K = \dfrac{p_B^2}{p_A p^\Theta}$ – remains constant only if an increase in p_A cancels and increase in the square of p_B. This relative steep increase in p_A compared to p_B will occur if the equilibrium composition shifts in favor of A at the expense of B. The number of A molecules will increase as the volume of the container decreases.

The increase in the number of molecules A and the corresponding decrease in the number of B molecules due to compression – a special case of the

Le Chatelier's principle:

When a system at equilibrium is subjected to a disturbance, the composition of the system adjusts so as to minimize the effect of the disturbance.



If a system at equilibrium is compressed, then the reaction will adjust so as to minimize the increase in pressure. This it can do by a reduction in the number of molecules in the gas phase, which implies a shift A $\leftarrow$ 2 B. The quantitative treatment of this effect shows that the extent of dissociation, α, of A into B is

$$\alpha = \left(\frac{1}{1+4p/K}\right)^{1/2}$$

Here p is to be understood as $p/p^{\varnothing}$.

Suppose that there is an amount n of A present initially (and no B). At equilibrium the amount of A is $(1 - \alpha)n$ and the amount of B is $2\alpha n$. The mole fractions present at equilibrium are

$$x_A = \frac{(1-\alpha)n}{(1-\alpha)n+2\alpha n} = \frac{1-\alpha}{1+\alpha} \qquad x_B = \frac{2\alpha}{1+\alpha} \qquad K = \frac{p_B^2}{p_A} = \frac{x_B^2 p^2}{x_A p} = \frac{4\alpha^2 p}{1-\alpha^2}$$

The result shows that, even though K is independent of pressure, the amount of A and B do depend on pressure. As p is increased, α decreases, in accord with Le Chatelier's principle.

To predict the effect of an increase in pressure on the composition of the ammonia synthesis at equilibrium, note that the number of gas molecules decreases from 4 to 2 – an increase in pressure will favor the product.

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

K_x – the part of the equilibrium constant that contains the equili-brium mole fractions of reactants and products. Doubling the pressure must increase K_x by a factor of 4 to preserve the value of K.

The effect of temperature

The equilibrium constant of a reaction changes when the temperature is changed. According to Le Chatelier's principle, we can expect a reaction to respond to a lowering of temperature by releasing heat and to respond to an increase of temperature by absorbing heat.

The equilibrium constant of an endothermic reaction increases with temperature: increased temperature favors the products.

The equilibrium constant of an exothermic reaction decreases with temperature: increased temperature favors the reactants.

The van't Hoff equation *(the van't Hoff isochore)*

$$\text{(a)}\ \frac{d\ln K}{dT}=\frac{\Delta_r H^\Theta}{RT^2}\qquad\qquad \text{(b)}\ \frac{d\ln K}{d(1/T)}=-\frac{\Delta_r H^\Theta}{R}$$

Derivation: (a): $\ln K=-\frac{\Delta_r G^\Theta}{RT}$ $\qquad$ $\frac{d\ln K}{dT}=-\frac{1}{R}\frac{d\left(\Delta_r G^\Theta/T\right)}{dT}=-\frac{1}{R}\left(-\frac{\Delta_r H^\Theta}{T^2}\right)=\frac{\Delta_r H^\Theta}{RT^2}$

We differentiated ln K and use the Gibbs-Helmholtz equation here.

(b): $\frac{d(1/T)}{dT}=-\frac{1}{T^2}$ $\qquad$ $dT=-T^2d(1/T)$ $\qquad$ $\frac{d\ln K}{d(1/T)}=-\frac{\Delta_r H^\Theta}{R}$

The equation shows that d ln$K$ / dT < 0 (and dK/dT < 0) for exothermic reaction under standard conditions ($\Delta_r H^\varnothing < 0$).

A negative slope means that ln K (and K itself) decreases as T rises – the equilibrium shifts away from products. The opposite occurs in the case of endothermic reactions.

$\Delta_r G^\varnothing = \Delta_r H^\varnothing - T\Delta_r S^\varnothing$ $\qquad$ $-\Delta_r G^\varnothing/T = -\Delta_r H^\varnothing/T + \Delta_r S^\varnothing$

When the reaction is exothermic, $-\Delta_r H^\varnothing/T$ corresponds to a positive change of entropy in the surroundings and favors the formation of products. When the temperature is raised, $-\Delta_r H^\varnothing/T$ decreases, and the increasing entropy of the surroundings has a less important role – the equilibrium lies less to the right. When the reaction is endothermic, the principal factor is the increasing entropy of the reaction system. The importance of the unfavorable change of entropy of the surroundings is reduced if the temperature is raised and the reaction is able to shift towards products.

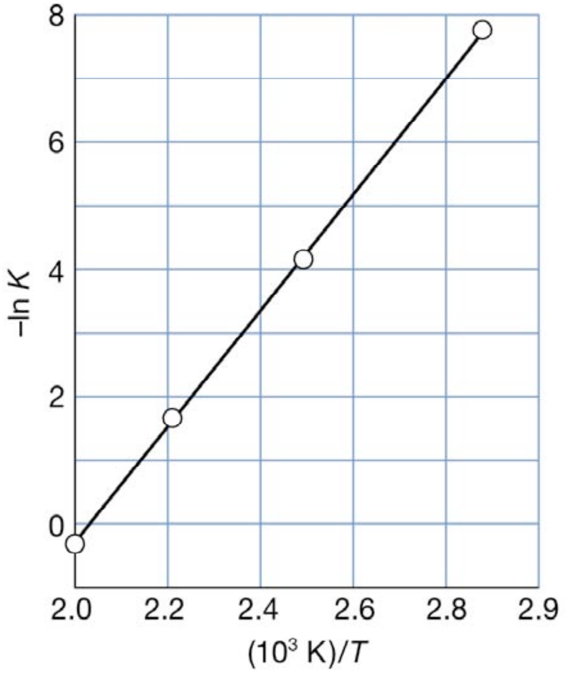
Example 3. Measuring a reaction enthalpy

The data below show the temperature dependence of the equilibrium constant of the reaction

$$\mathrm{Ag_2CO_3(s)} \leftrightarrows \mathrm{Ag_2O(s)} + \mathrm{CO_3(g)}$$

Calculate the standard reaction enthalpy of decomposition.

T/K	350	400	450	500
K	3.98×10^{-4}	1.41×10^{-2}	1.86×10^{-1}	1.48



Provided the reaction enthalpy can be assumed to be independent of temperature, a plot of –ln K against $1/T$ should be a straight line of slope $\Delta_\mathrm{r}H^{\varnothing}/R$.

T/K	350	400	450	500
(10^3 K)/T	2.86	2.50	2.22	2.0
-ln K	7.83	4.26	1.68	-0.39

The slope of the graph is $+9.6\times10^3$, so

$\Delta_\mathrm{r}H^{\varnothing} = 9.6\times10^3 \times R = +80\ \mathrm{kJ\ mol^{-1}}$

This is a noncalometric method to get $\Delta_\mathrm{r}H^{\varnothing}$.

The value of *K* at different temperatures

To find the value of the equilibrium constant at a temperature T_2 in terms of its value K_1 at another temperature T_1, we integrate the equation between these two temperatures:

$$\ln K_2 - \ln K_1 = -\frac{1}{R}\int_{1/T_1}^{1/T_2} \Delta_r H^\Theta d(1/T)$$

If we suppose that $\Delta_r H^\varnothing$ varies only slightly with temperature, $\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\Theta}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

To estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K (6.1×10^5) we use the standard reaction enthalpy: $\Delta_r H^\varnothing = 2\Delta_f H^\varnothing(\mathrm{NH_3,g})$ and assume that its value is constant over the range of temperatures:

$\ln K_2 = \ln(6.1\times10^5) - (-92.2\times10^3\ \mathrm{J\ mol^{-1}} / 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times\{1/(500\ \mathrm{K}) - 1/(298\ \mathrm{K})\}$
$= -1.71$ $K_2 = 0.18$

Knowledge of the temperature dependence of the equilibrium constant for a reaction can be useful in the design of laboratory and industrial processes: synthetic chemists can improve the yield of a reaction by changing the temperature of the reaction mixture, etc.