Chem Factsheet

www.curriculum-press.co.uk Number 246

Chemical Stability

Studying chemistry requires an understanding of the stability of substances. A perusal of everyday materials reveals they have a range of different properties. There are some chemicals, for example fuels, where society depends on its property to combust and release energy, but of equal importance is that the fuel can be stored and transported safely. That is, it is stable until its needs to be used.

Understanding chemical stability means realising that spontaneous change occurs when there is a natural tendency for it to occur. For example, adding a teaspoon of table salt to water will cause the salt to spontaneously dissolve. In isolation, table salt is a stable substance, but adding it to water makes it unstable.

In thermochemistry a **system** consists of all the substances directly involved in a chemical reaction. The **surroundings** consists of everything else in the Universe with the exception of the system.

Internal energy, U, is the energy contained within a system. This internal energy is difficult to measure as it is the sum of kinetic energies and potential energies of all particles in the system. A system will be thermodynamically stable when that system is in its lowest energy state. A chemical system will also be thermodynamically stable if it is in chemical equilibrium with the surroundings. This will continue indefinitely unless the system is changed. For example, when adding table salt to water, the state of the system spontaneously changes to form a solution, moving to a more stable state from a less stable one.

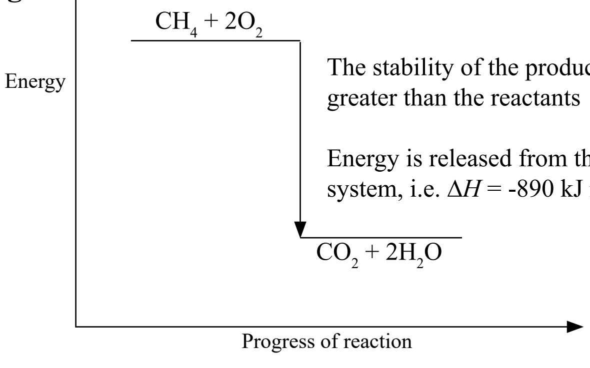
Chemical reactions and energy

Enthalpy, H, describes the heat content of a system measured at constant pressure. Its actual value cannot be measured, but the enthalpy change during a reaction ΔH, can be measured and is defined as the heat change of the system measured at constant pressure.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

The energetic stability of a substance depends on the relative energetic stability of its potential products. Consider a simple fuel such as methane, CH_4, which combusts to form carbon dioxide, CO_2, and water, H_2O. Plotting their relative stabilities on an energy diagram, the combined stability of carbon dioxide and water is greater than that of methane and oxygen as represented in Fig. 1.

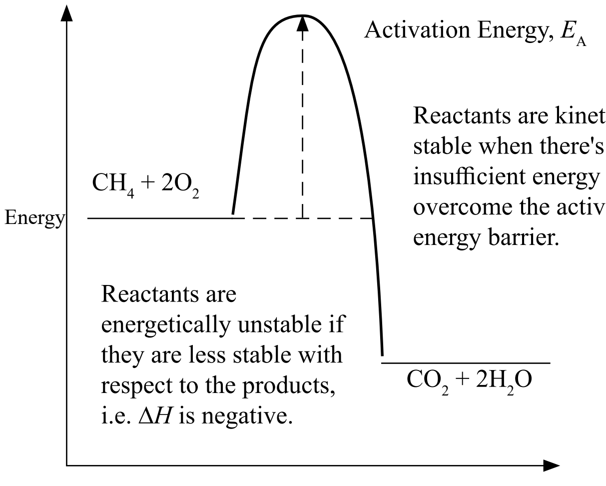
Fig. 1



During a chemical reaction, chemical bonds are broken. This requires energy. Energy is then released when new chemical bonds are formed. If more energy is released than is required, then the products will be energetically more stable than the reactants.

As methane is energetically unstable with respect to carbon dioxide and water, it might be expected that methane would immediately oxidise in oxygen. This does not happen. In order for methane to combust, energy is required to initiate the reaction. This is achieved by igniting the gas using a spark or a flame. This is because a minimum amount of energy, the activation energy, E_A, is needed before a reaction can start. If there is insufficient energy available through the natural collisions of the particles involved, then the system is described as being kinetically stable as represented in Fig. 2. Fuels are examples of substances that are described as being energetically unstable, but kinetically stable. This is an important chemical property for a fuel as they need to be stored and transported safely.

Fig. 2



Substances that are **energetically unstable** but do not change spontaneously are said to be **kinetically stable** because the activation energy barrier for the reaction is too high.

Energtic stablility and entropy

As sodium chloride (table salt) is soluble in water, it is a reasonable assumption that dissolving sodium chloride to form a solution is an exothermic process. In fact, sodium chloride has an endothermic enthalpy of solution and therefore, based on enthalpy changes, sodium chloride should not dissolve spontaneously in water.

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H^\ominus_{sol} = +3.87$ kJmol^{-1} (at 25°C)

Considering spontaneous change in terms of just decreases in enthalpy (H) is not sufficient. An examination of the chemical equation clearly shows a change in the state of the system. A solid, ordered lattice has changed into dissociated ions that have spread out to form a more disordered state.

Spontaneous change involves an **increase in disorder**, whether it is energy or matter that is becoming more disordered / more spread out.

Entropy, S, is a measure of the disorder of a system. The total entropy change for any process is determined as the entropy change of the system plus the entropy change of the surroundings and can be described as follows:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$
$$= \Delta S_{system} - \frac{\Delta H}{T}$$

since $\Delta S_{surroundings} = -\Delta H/T$

For a spontaneous change to occur, $\mathbf{\Delta S_{total} > 0}$. i.e., the total entropy of the Universe (system + surroundings) always tends to increase. This observation is expressed as the second law of thermodynamics.

When there is a small enthalpy change, as with sodium chloride dissolving, the process will occur spontaneously because the increase in entropy of the system (positive ΔS_{system}) outweighs the negative $-\Delta H/T$ making $\Delta S_{total} > 0$. Sodium chloride dissolves because its particles can spread out into the solution, instead of being maintained in an ordered solid structure.

When completing thermodynamic calculations; enthalpy change data, ΔH, is usually provided in kJ mol^{-1}, but entropy change data, ΔS, is provided in JK^{-1}mol^{-1}, and appropriate conversions are required. Note that temperature is always calculated in Kelvin, K.

Energetic stability and Gibbs free energy

Understanding the stability of a system depends on knowing the entropy change, ΔS, the enthalpy change, ΔH, and the temperature, T. Their relationship is best considered via the standard Gibbs free energy change ($\Delta G^{\ominus}$) which is derived from the previous relationship

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H}{T}$$

Multiply both sides by -T

$$-T\Delta S_{total} = -T\Delta S_{system} + \Delta H$$

If ΔG is defined as $-T\Delta S_{total}$

then $\Delta G = \Delta H - T\Delta S$ where all 3 changes refer to the sysytem

Under standard conditions this becomes: $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Hence, **the** criterion for spontaneous change is that $\mathbf{\Delta G^{\ominus} < 0}$.

ΔG is similar in magnitude to ΔH with $T\Delta S$ being less significant. Hence ΔG is usually expressed in kJ mol^{-1} like ΔH. This means ΔS values need to be converted from JK^{-1} mol^{-1} to kJK^{-1} mol^{-1} by dividing by 1000.

Example 1

Methane combusts at room temperature, 25°C. Explain the chemical stability of methane in terms of its thermodynamic properties.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

	$\Delta H^{\ominus}_f$ (kJ mol^{-1})	**$S^{\ominus}$ (JK^{-1} mol^{-1})**
$CH_4(g)$	- 74.8	186.2
$O_2(g)$	0	102.5
$CO_2(g)$	- 393.5	69.9
$H_2O(l)$	- 285.8	213.6

$\Delta H = \Sigma\Delta H^{\ominus}_f$(products) - $\Sigma\Delta H^{\ominus}_f$(reactants)
$= (-393.5 + (2 \times -285.8)) - (-74.8) = -890.3$ kJ mol^{-1}

The reaction is exothermic, releasing 802.3 kJ mol^{-1} of heat into the surroundings.

$\Delta S^{\ominus} = \Sigma S^{\ominus}$(products) - $\Sigma S^{\ominus}$(reactants)
$= 213.6 + (2 \times 69.9) – (186.2 + (2 \times 102.5)) = -37.8$ JK^{-1}mol^{-1}

There is a decrease in disorder, due to a decrease in the number of gas particles in the system.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = (-890.3) – (298 \times -0.0378) = -879.0$ kJ mol^{-1}

$\Delta G^{\ominus} < 0$, therefore this reaction is thermodynamically spontaneous.

Energetic stability and chemical equilibrium

In a closed system, chemical reactions will achieve an equilibrium state, a mixture of reactants and products where the rate of the forward and backward reactions are equal. The position of this equilibrium is described by the equilibrium constant, K. Calculating standard Gibbs free energy changes refers to the formation of pure products from pure reactants. In a chemical reaction there will be a mixture of substances, reactants and products, which will increase the entropy of the system. This entropy of mixing is greatest when the substances are in equal proportions.

Fig. 3

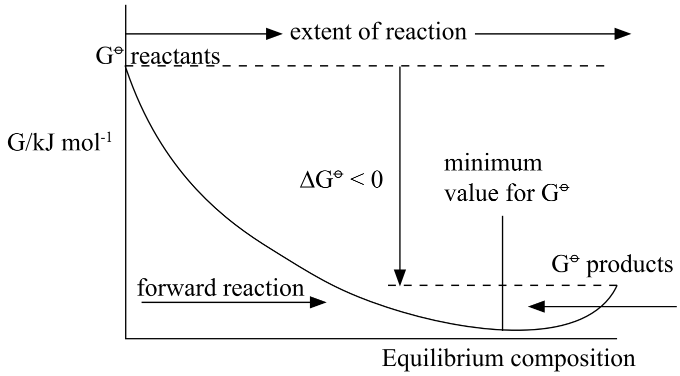


Fig. 3 describes a reaction occupying a single phase (gas or solution), where the Gibbs free energy of the reactants is greater than the Gibbs energy of the products, that is, $\Delta G^{\ominus} < 0$. The reaction takes place spontaneously. As the reaction proceeds, ΔG reaches its minimum at equilibrium and as further progress towards the products would mean ΔG increasing, this is not allowed and the composition of the system remains at its equilibrium value.

For any spontaneous reaction, the composition of a reaction mixture will change spontaneously in the direction of decreasing Gibbs free energy until the Gibbs free energy reaches its **minimum** value.

The standard Gibbs free energy change is linked to the equilibrium constant by the expression: $\Delta G^{\theta} = -RT \ln K$
where R is the gas constant, 8.31 JK^{-1} mol^{-1}.

The significance of this relationship in terms of energetic stability is summarised below:

Standard Gibbs energy change $\Delta G^{\ominus}$ / kJmol^{-1}	**Equilibrium Constant, K**	**Equilibrium Position**
More negative than -35	Greater than 10^6	Reaction effectively complete
Between -35 and 0	Between 10^6 and 1	Products predominate
Between 0 and +35	Between 1 and 10^{-6}	Reactants predominate
More positive than +35	Smaller than 10^{-6}	Effectively no reaction

Note: Gibbs free energy change of mixing is significant for ΔG^{θ} values between +35 kJmol^{-1} and -35 kJmol^{-1}.

Kinetic Stablity

Thermodynamics allow chemists to predict the stability of a chemical reaction based on the equilibrium conditions of the products after the reaction has taken place. However it cannot explain the rate of the reaction, i.e. whether the reaction is fast, slow or does not occur. This depends on the kinetic stability of a given reaction, which is related to the rate constant, k. The rate constant is associated with the activation energy, E_A, the minimum energy required when reactants collide for the reaction to proceed. Refer to Fig. 2.

Fig. 4

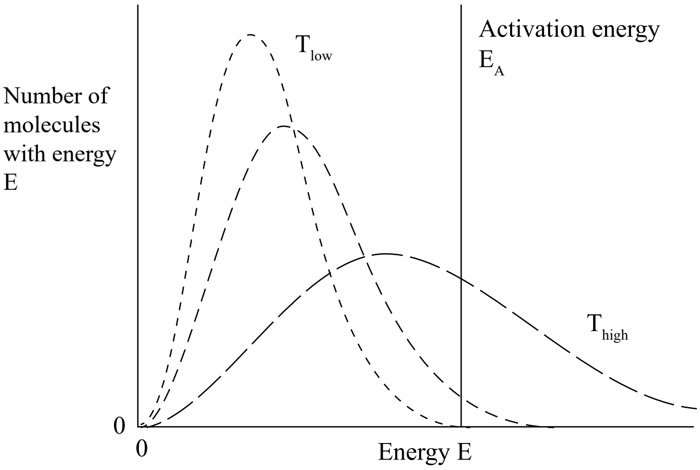


Fig. 4, illustrates the Maxwell-Boltzmann distribution of molecular energies in a system. The activation energy, E_A, is represented by a vertical line. This identifies the minimum energy required for successful collisions. The distribution of molecular energies shifts at different temperatures. At higher temperatures, there are more energetic particles and the likelihood of successful collisions is increased. The distribution T_{low} represents a reaction that is kinetically stable, i.e. the rate of reaction is very low. In contrast, the distribution T_{high}, represents a reaction that is kinetically unstable, i.e. it has a high rate of reaction.

The Arrhenius equation predicts that the rate constant, k, is related to the activation energy and is temperature dependent.

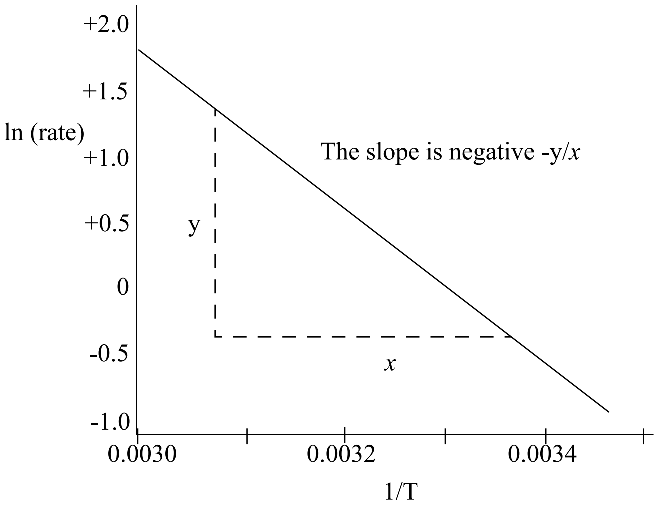
$$\ln k \;=\; \ln A - \frac{E_A}{RT} \quad \text{or} \quad k = Ae^{-EA/RT}$$

A plot of Lnk against 1/T is called an Arrhenius plot, where InA is the intercept, the gradient equals $-E_A/R$ and R is the gas constant, 8.31 JK^{-1} mol^{-1}. The value for A can be taken as a constant over small temperature ranges. By this means the activation energy, E_A, can be found for a given reaction.

Example 2

The reaction rate for a given reaction is investigated and the activation energy determined by plotting Ln(rate) against 1/T and measuring the slope of the graph, see Fig. 5.

Fig. 5



The analysis of the graph involves determining the slope. $-E_A/R$, which is measured at -6020 K.

Therefore, $-E_A = -6020 \times 8.31$, and $E_A = +50000$ Jmol^{-1} or +50 kJmol^{-1}.

Even an activation energy of +50kJmol^{-1} will have a significant effect on the rate of reaction and therefore the kinetic stability of the reactants. Adding energy to the reaction (e.g. increasing the temperature) will increase the number of energetic particles, i.e. those with energies equal to or greater than the activation energy. This has the effect of decreasing the kinetic stability of the reactants allowing the reaction proceed, or proceed at a faster rate.

Questions

1. For each of the following examples, comment on the feasibility of the reactions described, giving your reasoning.
   (a) $A(l) \rightarrow B(l) + C(g)$ ΔH = -180 kJmol^{-1}
   (b) $2A(s) + 2B(g) \rightarrow C(g)$ ΔH = +100 kJmol^{-1}
   (c) $A(s) \rightarrow B(s) + C(g)$ ΔH = +220 kJmol^{-1}
   (d) $2A(g) + B(g) \rightarrow 2C(g)$ ΔH = -90 kJmol^{-1}

2. Methane is heated with steam in the presence of a nickel catalyst to produce hydrogen, $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$.
   Using the following thermodynamic data, determine the minimum temperature required for this reaction to be feasible.

	$CH_4(g)$	$H_2O(g)$	$CO(g)$	$3H_2(g)$.
$\Delta H^{\ominus}_{f}$ / kJmol^{-1}	-75	-242	-111	0
$S^{\ominus}$ / JK^{-1}mol^{-1}	186.2	188.7	197.6	130.6

3. The equation, $\Delta G = \Delta H - T\Delta S$, compares with the equation for a straight line graph, i.e. $y = mx + c$.
   Values for ΔG for a chemical reaction were determined at different temperatures, K. Plot a graph of ΔG against T and use it to find:
   (a) ΔH, (b) ΔS and (c) the temperature at which the reaction becomes energetically feasible.

T / K	250	500	750	1000	1250
ΔG / kJmol^{-1}	+375	+150	-75	-300	-525

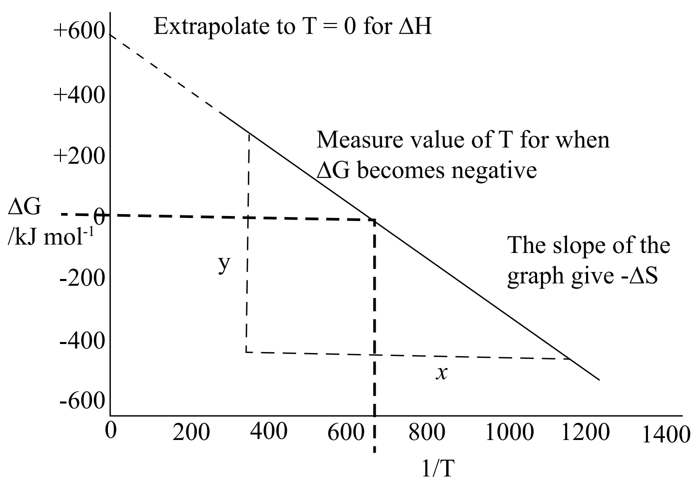
4. The Haber process is the industrial production of ammonia. Increasing the temperature used in the process will increases the reaction rate. Using the thermodynamic data provided, show how increasing the temperature affects the thermodynamic stability of the reaction. Comment on the chemical stability of the reaction in terms of reactants and products involved.
   For the reaction, $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$ ΔH = -92.4 kJmol^{-1} ΔS = -198.7 JK^{-1}mol^{-1}

Answers

1. (a) Reaction is feasible at all temperatures; ΔS is positive (a gas is produced), → $-T\Delta S$ is negative. ΔH is negative.
   Therefore ΔG is negative at all temperatures.
   (b) Reaction is not feasible at any temperature; ΔS is negative (fewer gas products) → $-T\Delta S$ is positive. ΔH is positive.
   Therefore ΔG is positive at all temperatures.
   (c) The reaction is feasible at high temperatures, but not at low temperatures; ΔS is positive (a gas is produced) → $-T\Delta S$ is negative.
   At low temperatures ΔG is positive because ΔH is positive.
   At higher temperature the negative $-T\Delta S$ outweighs ΔH and $\Delta H - T\Delta S$ becomes negative.
   (d) The reaction is feasible at low temperatures, but not at high temperatures; ΔS is negative (fewer gas products) → $-T\Delta S$ is positive. At low temperatures ΔG is negative because ΔH is negative. At higher temperatures the positive $-T\Delta S$ outweighs ΔH and $\Delta H - T\Delta S$ becomes positive.

2. $\Delta H = (111) - (-75 + -242) = +206$ kJmol^{-1}
   $\Delta S = (+589.4) - (+374.9) = +214.5$ JK^{-1}mol^{-1}
   To be feasible $\Delta G < 0$
   $\therefore \Delta H - T\Delta S < 0$ or $\Delta H < T\Delta S$
   Remember to convert ΔS into kJK^{-1}mol^{-1}
   $+206 < +0.2145T$
   $T > 960K$

3.



   (a) When T = 0, $\Delta G = \Delta H$. Extrapolating the plotted line to T = 0 should give a value for ΔH around +600 kJmol^{-1}.
   (b) The slope of the graph, determined by measuring x and y, gives a negative slope, –y/x. From the equation, the slope, $-\Delta S$, gives a value for ΔS of +0.900 kJK^{-1}mol^{-1}, or +900 JK^{-1}mol^{-1}.
   (c) The reaction becomes feasible at the temperature when ΔG becomes less than 0. From the graph, this should occur at 667K.

4. Using, $\Delta G = \Delta H - T\Delta S$, the limit of feasibility for the Haber process is when $\Delta G = 0$.
   If $\Delta G = 0$, then $\Delta H = T\Delta S$
   Remember to convert ΔS into kJK^{-1}mol^{-1}
   $-92.4 = -0.1987T$
   $T = 465K$
   But, as ΔH is negative and ΔS is negative in the forward direction (products), the reaction is feasible to the products at temperatures below 465K. At temperatures above 465K the reaction is feasible towards the reactants.

Acknowledgements: *This Factsheet was researched and written by* ***Gareth Riley. Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. Chemistry Factsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***