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CHEMICAL REACTIONS

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Chemical reactions

The evolution of thermodynamic systems takes place by the interaction amongst the particles composing it and between those and the surrounding ones. We may call ‘particle collision’ this short-range interaction, in general (not only for a gas, but for condense matter, and even for matter-radiation interaction). Usually the collision is not very energetic, and we say that it is of thermal type (corresponding to mechanical dissipation and heat transfer), but sometimes it is so energetic that molecules break and form new bonds, and we say that the interaction is of chemical type (usually manifested by heat release, gas production, solution precipitation, or colour change). It might even happen that the interactions be so energetic that the nucleus of atoms break apart or get together, and we call them of nuclear type. Sometimes, nuclear changes take place by atom exchange, without major energy changes, as when HDO molecules are formed by mixing normal water (H_2O) with heavy water (D_2O), where D stands for deuterium).

When a chemical bond is broken, energy is absorbed, and when a chemical bond forms, energy is given off; thence, to initiate a reaction, some energy input is required (activation energy), and the exothermic or endothermic character of a reaction depends on the relative strength of broken bonds and formed bonds.

Thermodynamic analysis is required to study chemical reactions, not only because chemical yield exponentially grows with temperature, but because the extent of a reaction at equilibrium and the energies involved are governed by genuine thermodynamic variables as enthalpy and entropy. Physico-chemical evolution in a system surrounded by a large environment at constant T and p , always drives towards minimising its energy (enthalpy, really) while maximising its entropy, or, more precisely, by minimising its Gibbs function $G=H-TS$, what corresponds to the maximisation of entropy in an isolated system. Thermodynamics, however, does not teach what kind of products will form or at what speed, both things being dependent on catalysts; that is why it is so important in Thermodynamics to always refer to a concrete given reaction (not just to the reactives).

The study here focuses on chemical equilibrium, sometimes named Chemical Thermodynamics or Thermochemistry. The kinetic problem (reaction rates), of paramount importance in practice, can only be tackled after its equilibrium Thermodynamics has been settled.

From the many different types of chemical reactions, we later analyse in detail the [combustion process](#), leaving aside acid-base reactions, and organic and inorganic synthesis reactions. We also leave aside electrical effects in electrolytes (ionic systems), electrodes (in solution, or in gas), and plasmas (ionised gases).

Stoichiometry

A chemical reaction process is specified by a so-called stoichiometric equation for a given reaction:

$$\sum_{i=1}^{C_{\text{reactants}}} \nu_i' M_i = \sum_{i=1}^{C_{\text{product}}} \nu_i'' M_i \quad \text{or} \quad 0 = \sum_{i=1}^C \nu_i M_i \quad (9.1)$$

(e.g. $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$, or $0 = \text{H}_2\text{O} - \text{H}_2 - \frac{1}{2}\text{O}_2$), where the first form is preferred for kinetic studies when a direction in the process is implicit, i.e. initial reactants (left) converting into products (right), whereas the last form is more simple for equilibrium studies where no direction is privileged. Notice that microscopically the reaction is always on both directions, to the right and to the left in (9.1), the rates being balanced when at equilibrium.

A stoichiometric equation specifies what chemical species transform (the M_i ; there may be others that are needed, as the catalysts, but do not transform, globally), and in what proportions they transform (the ν_i , are called stoichiometric coefficients). The same reactants may react differently to give other products under different conditions (e.g. $\text{H}_2 + \text{O}_2 = 2\text{OH}$ or $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$), and even the same reaction may be written with different stoichiometric coefficients (e.g. $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ or $\text{H}_2 + (1/2)\text{O}_2 = \text{H}_2\text{O}$), so it is imperative to refer to a concrete reaction and not just to the reactants. But a given stoichiometric reaction as (9.1) is not just a label; it is the mass conservation equation if M_i is the molar mass of species i , and may be the set of elementary conservation equations when the molecular form of M_i is considered (e.g. for $0 = \text{H}_2 + (1/2)\text{O}_2 - \text{H}_2\text{O}$, $\nu = [1, 1/2, -1]$; mass conservation is $0 = \sum \nu_i M_i = 1 \cdot 2 + (1/2) \cdot 32 - 18$ with $M_i = [2, 32, 18]$ g/mol; conservation of elements are: $0 = \sum \nu_i M_i = 1 \cdot 2 + (1/2) \cdot 0 - 2$ for hydrogen atoms, and $0 = \sum \nu_i M_i = 1 \cdot 0 + (1/2) \cdot 2 - 1$ for oxygen atoms.

The state of equilibrium of an isolated system, be it reactive or not, is the one that maximises the entropy of the system, and for a system in contact with an infinite atmosphere at T and p constant it is the one that minimises its Gibbs potential; nothing new, but we have to introduce new variables and new reference states, to deal with the state of a reactive system.

Extent of reaction and affinity

When a mixture with initial composition n_{i0} reacts within a closed system (control mass), the degree of advancement at any later time, or extent of the reaction, ξ , is defined as::

$$\xi \equiv \frac{n_i - n_{i0}}{\nu_i} \quad \text{for a given} \quad 0 = \sum \nu_i M_i \quad (9.2)$$

i.e., it is a reduced amount-of-substance that is independent of the particular species considered (the state variable of chemical progress). The variation of extent with time is the reaction rate:

$$\dot{\xi} \equiv \frac{d\xi}{dt} \quad (9.3)$$

but this is not a thermodynamic variable of equilibrium, and depends not only on the state of the system but on the presence of catalysts.

To simplify the analysis of equilibrium states ($G=G_{\min}$ for a system at T and p constant), we introduce the chemical affinity, A , defined as:

$$A \equiv -\sum_{i=1}^c \nu_i \mu_i \quad \text{such that} \quad dG = -SdT + Vdp + \sum_{i=1}^c \mu_i dn_i = -SdT + Vdp - Ad\xi \quad (9.4)$$

i.e., at T and p constant, $dG = -Ad\xi$, a positive affinity ($A > 0$) makes the system to evolve to the right of (9.1) and to advance the extent of the reaction ($\xi > 0$, such as $dG = -Ad\xi < 0$). We see that affinity is the combination of chemical potentials that has the same role in reactions as the individual chemical potentials in mixtures: to mark the natural tendency to evolve.

Notice that a single isolated chemical reaction can only proceed if its affinity is positive, $A > 0$ (at a rate dictated by its kinetics). But, if $A < 0$, it may run uphill if external exergy is applied, e.g. forced by solar radiation (ozone formation, photosynthesis), by electricity (electrolysis), or by more than one reaction taking place at the same time; in this case, Thermodynamics only forces that $dG = -\sum A_r d\xi_r < 0$, so that reactions with negative affinity may proceed coupled to other reaction of positive affinity and at a rate such that $\dot{G} = -\sum A_r \dot{\xi}_r < 0$, what is actually the rule in biological reactions. In all these cases of forcing a reaction uphill against its affinity, it is necessary that the activation energy for the reverse downhill reaction be high, to avoid immediate decomposition.

[Exercise 1. Affinity dependence on extent of reaction](#)

Enthalpy of formation and absolute entropy

Energy was defined only as increments ($\Delta E \equiv W|_{Q=0}$, [Chapter 1](#)) and a reference state had to be assigned for the system (e.g. specific internal energy u , or enthalpy h , equal to 0 or other fixed value, at a given state: liquid at the triple point, or any other); in [Chapter 7 \(Mixtures\)](#) we adopted an energy reference state for each of the conservative components in a mixture, but this is no longer possible in reactive systems, since chemical species are not conservative. However, atomic species are conservative in chemical reactive systems, so that only references for chemical elements can be arbitrarily chosen. Accordingly, we choose as reference for enthalpy the most stable natural form of the chemical elements at standard temperature and pressure (in Chemistry traditionally taken as $T^\oplus = 298.15$ K (25 °C) and $p^\oplus = 100$ kPa). Notice that the

traditional superscript symbol for standard state is the load line sign, \ominus , proposed by S. Plimsoll in mid-19th century to mark midway between the bow and the stern vessel waterline at nominal load (we use the symbol \oplus for typographical reasons).

Thus, for instance, we adopt $h^{\oplus}=h(T^{\oplus},p^{\oplus})=0$ for diatomic hydrogen as obtained from water (^1H with 115 ppm of ^2H), $h(T^{\oplus},p^{\oplus})=0$ for monatomic helium from natural gas (^4He with 1.4 ppm of ^3He), $h^{\oplus}=0$ for metallic lithium, ..., $h^{\oplus}=0$ for carbon in the form of graphite (not as diamond or fullerenes, with 98.9 % of ^{12}C and 1.1 % of ^{13}C), etc.

Standard-state enthalpies for non-elementary species are called enthalpies of formation, $h_f^{\oplus}=h(T^{\oplus},p^{\oplus})\neq 0$, and can be evaluated in the simplest case by calorimetric measurement of the reaction of formation of the compound from its elements, $h_r^{\oplus} = \sum_{i=1}^C \nu_i h_{f_i}^{\oplus}$, or in many cases indirectly evaluated by Hess rule (see below); the most accurate results are obtained by electrochemical measurements in redox systems. A tabulation of [standard enthalpies of formation is presented aside](#), including the chemical elements, for which the surname 'formation' added to the standard enthalpy is irrelevant: $h_f^{\oplus}=h^{\oplus}=h(T^{\oplus},p^{\oplus})=0$. Notice that standard enthalpies of formation are usually negative because the formation reaction is usually exothermic (use as a mnemonic the case of water, which formation reaction coincides with the combustion reaction $\text{H}_2+\frac{1}{2}\text{O}_2=\text{H}_2\text{O}$ and $h_f^{\oplus}=-286$ kJ/mol); for alkanes, for instance, they are all negative with absolute values increasing with molecular size: -75 kJ/mol for CH_4 , -126 kJ/mol for $n\text{-C}_4\text{H}_{10}$, -250 kJ/mol for $n\text{-C}_8\text{H}_{18}$, etc. The value for the enthalpy of formation of a liquid is always algebraically smaller than that of its vapour state, the difference being the vaporization enthalpy, $h_f^{\oplus}(\text{g})-h_f^{\oplus}(\text{l})=h_{LV}^{\oplus}$ (e.g. $h_f^{\oplus}(\text{C}_8\text{H}_{18}(\text{l}))=-250$ kJ/mol against $h_f^{\oplus}(\text{C}_8\text{H}_{18}(\text{g}))=-208$ kJ/mol); you may use as mnemonic the values for water: $h_f^{\oplus}(\text{H}_2\text{O}(\text{l}))=-286$ kJ/mol and $h_f^{\oplus}(\text{H}_2\text{O}(\text{g}))=-242$ kJ/mol ($h_{LV}^{\oplus}(\text{H}_2\text{O})=2442$ kJ/kg=44 kJ/mol).

Notice that sometimes it is postulated that enthalpies of formation are zero for the chemical elements at *any* temperature, a fact that can be easily demonstrated after (9.11) without any assumption since for the trivial reaction $M_E=M_E \quad \partial h_r/\partial T=c_{p,ME}(T)-c_{p,ME}(T)=0$.

We also adopted an entropy reference state for the working substance (Chapter 2) or for each of the conservative components in a mixture (Chapter 7), and we could proceed now similarly as for enthalpies and adopt an entropy reference for the conservative entities (elementary species); but there is an experimental fact, explained by the information-measuring entropy in (2.1), that makes another choice preferable: entropies at 0 K may be taken equal to zero not only for elementary species but for any perfect crystalline compound (on the basis that all quantum states are at the singly-defined ground level). This conclusion is so important, that it is known as the Third Principle or Third Law of Thermodynamics: $S=0$ at $T=0$, or better $S\rightarrow 0$ when $T\rightarrow 0$, since $T=0$ is an asymptotic limit.

Entropies referred to this universal reference state are known as absolute entropies, and are computed from the general expression $ds=(c_p/T)dT-\alpha v dp$ (4.8) by means of thermal capacities and phase-transition enthalpies, beginning with an extrapolation of the Debye model for solids at cryogenic temperatures (thermal capacities tend to zero at $T=0$ K as $c_v=(12\pi^4/5)R(T/T_D)^3$, where T_D is Debye's temperature), in the way:

$$s(T, p) = \int_0^{T_b} \frac{c_1 T^3 + c_2 T}{T} dT + \int_{T_b}^{T_i} \frac{c_p(T, p)}{T} dT + \frac{\Delta h_i}{T_i} + \int_{T_i}^T \frac{c_p(T, p)}{T} dT \quad (9.5)$$

A tabulation of [absolute entropies at standard conditions is presented aside](#). Notice that standard absolute entropies are always positive because all terms in (9.5) are positive, values increasing with molecular size in a similar way as molar c_p increases with molecular size (more energy levels available). However, when thermochemical data of ions are included, negative values for s^\oplus may appear because the reference taken for ions is $s(\text{H}^+, \text{aq. } 1 \text{ mol/litre, } T^\oplus, p^\oplus)=0$.

It is customary to include in the thermochemical tabulation not only h_f^\oplus and s^\oplus , but also the standard Gibbs function of formation, g_f^\oplus , although it is redundant since:

$$g_f^\oplus \equiv h_f^\oplus - T^\oplus \sum_{i=1}^C \nu_i s_i^\oplus \text{ for the reaction of formation of a compound from its elements} \quad (9.6)$$

Notice that in the case of the chemical elements, the reaction of formation ($M=M$) implies $\sum \nu_i s_i^\oplus=0$ and hence $h_f^\oplus=0 \rightarrow g_f^\oplus=0$, but our initial choice of $h^\oplus=0$ for elements does not imply $g^\oplus=0$; instead, from definition ($G=H-TS$), $g^\oplus=h^\oplus - T^\oplus s^\oplus = -T^\oplus s^\oplus \neq 0$, but it is the standard Gibbs' function for the reaction of formation, g_f^\oplus , what matters in reactive systems.

The Third Principle of Thermodynamics states that entropy changes tend to zero at very low temperatures, $ds|_{T \rightarrow 0} \rightarrow 0$, a law of Nature first found by Walther Hermann Nernst in 1911 from experiments with vapours at higher temperature, solids at low temperature, and galvanic cells. A corollary of it is that $\alpha|_{T \rightarrow 0} \rightarrow 0$, since $\alpha \equiv (1/V) \partial V / \partial T|_p = -(1/V) \partial S / \partial p|_T$ and $ds|_{T \rightarrow 0} \rightarrow 0$. Notice that the ideal gas model does not satisfies the Third Principle (for them, $\alpha = 1/T \rightarrow \infty$ as $T \rightarrow 0$).

Additionally, one may consider states of a system at 0 K different from the perfectly ordered crystalline structure, e.g. molecular dipoles oriented at random back and forth, instead of ordered one way, in which case a [residual entropy](#) $s = -k \sum p_i \ln p_i = R \ln 2 = 8.3 \cdot 0.69 = 5.8 \text{ J/(mol} \cdot \text{K)}$ should be assigned to the reference state at $T=0$; in the case of H_2O a residual entropy $s = R \ln(3/2) = 8.3 \cdot 0.4 = 3.4 \text{ J/(mol} \cdot \text{K)}$ at $T=0$ is added to account for the [proton disorder](#) possible around oxygen atoms (each O-atom is surrounded by four H-atoms in a near tetrahedral shape, with the two of them belonging to the water molecule being closer than the two others, forming the H-bonds).

Enthalpy of reaction

Chemical reactions give way to vigorous transfers between the potential energy associated to the position of the atoms and the kinetic energy associated to the microscopic velocities of the molecules (translation, rotation, and vibration), thus producing a macroscopic heating or cooling (temperature change; the most common case being for reactions to be exothermic, i.e. to give off heat when maintained at constant temperature). Several new equilibrium variables are defined to analyse reactive systems (e.g. the enthalpy of reaction, h_r).

Let a given chemical reaction ($0=\sum \nu_i M_i$) be at equilibrium with a generic extent ξ (with a Gibbs function $G(T,p,\xi)$) in a control mass system. Notice that for this reaction to be at equilibrium for any generic ξ , some other constrain must act on the system, as in electrochemical reactors. We define, in this neighbourhood of equilibrium the volume of reaction, v_r , the internal energy of reaction, u_r , the enthalpy of reaction, h_r , the entropy of reaction, s_r , the Gibbs function of reaction, g_r , and so on, as:

$$v_r \equiv \left. \frac{\partial V}{\partial \xi} \right|_{T,p}, \quad u_r \equiv \left. \frac{\partial U}{\partial \xi} \right|_{T,p}, \quad h_r \equiv \left. \frac{\partial H}{\partial \xi} \right|_{T,p}, \quad s_r \equiv \left. \frac{\partial S}{\partial \xi} \right|_{T,p}, \quad g_r \equiv \left. \frac{\partial G}{\partial \xi} \right|_{T,p} \quad (9.7)$$

For instance, the volume of reaction, v_r , is the variation of the volume of the control mass when the reaction proceeds one extent of reaction (when one mole of reactive with stoichiometric coefficient equal to unity is processed). Not to be confused with the molar volume $v=V/n$, or the change in volume by total amount of substance; by the way, the total amount of substance is not conservative and an amount of substance of reaction, n_r , can be defined similarly to (9.7):

$$n_r \equiv \left. \frac{\partial n}{\partial \xi} \right|_{T,p} = \sum_{i=1}^c \nu_i \quad (9.8)$$

for instance, for $H_2 + \frac{1}{2}O_2 = H_2O$ $n_r=1-1-0.5=-0.5$, i.e. for every mole of hydrogen processed, half a mole of mixture is lost.

For reactions in a gas phase (it is valid even with some condensed phase because its volume is usually negligible), the volume of reaction is, with the perfect gas model:

$$v_r = \left. \frac{\partial(nRT/p)}{\partial \xi} \right|_{T,p} = \frac{RT}{p} \sum_{i=1}^c \nu_i \quad (9.9)$$

The internal energy of reaction can be deduced from the enthalpy of reaction, a more usual variable, as follows:

$$u_r = h_r - pv_r = h_r - RT \sum_{i=1}^c \nu_i \quad (9.10)$$

The enthalpy of reaction usually has a small variation with temperature since:

$$\left. \frac{\partial h_r}{\partial T} \right|_{p,\xi} = \left. \frac{\partial^2 H}{\partial \xi \partial T} \right| = \left. \frac{\partial^2 H}{\partial T \partial \xi} \right| = \sum_{i=1}^c \nu_i c_{p_i} \quad (9.11)$$

and all c_p being of the same order of magnitude and the ν_i of alternating signs, the sum nearly cancels.

The entropy of reaction is related to the enthalpy of reaction and the Gibbs function of reaction as always:

$$g_r = h_r - Ts_r \quad (9.12)$$

and from $dG = -SdT + Vdp - Ad\xi$ with (9.7) and the Maxwell relation $dA/dT = dS/d\xi = -s_r$ one gets:

$$g_r = -A = h_r - T \left. \frac{\partial A}{\partial T} \right|_{p,\xi} \Rightarrow \left. \frac{\partial g_r}{\partial \frac{1}{T}} \right|_{p,\xi} = h_r = - \left. \frac{\partial A}{\partial \frac{1}{T}} \right|_{p,\xi} \quad (9.13)$$

that is known as Gibbs-Helmholtz equation, or van't Hoff equation, and that will be used below to compute equilibrium constants based in the above-mentioned fact that h_r is nearly a constant.

Standard enthalpies, entropies and Gibbs functions of reactions are computed from the corresponding [tabulated values](#) in the form:

$$h_r^\oplus = \sum_{i=1}^C \nu_i h_{f_i}^\oplus, \quad g_r^\oplus = \sum_{i=1}^C \nu_i g_{f_i}^\oplus, \quad s_r^\oplus = \sum_{i=1}^C \nu_i s_i^\oplus \quad (9.14)$$

[Exercise 2. Redundancy in thermochemical data](#)

Measurement of the equilibrium variables (9.7) is difficult (may be done in electrochemical cells), and the usual way to measure e.g. the enthalpy of reaction is by calorimetry in a steady-state control volume. But, in order to have common reference states for reactions, actual values are corrected to correspond to a standard reactor interfaces (Fig. 9.1), with as many inputs as reactants (that are assumed to enter separately), and as many outputs as products (that are assumed to exit separately in spite of the fact that actual reactors usually have a common exit). The corrections for energy functions are small (only mixing and demixing heats), but for entropy and Gibbs function the corrections may be important.

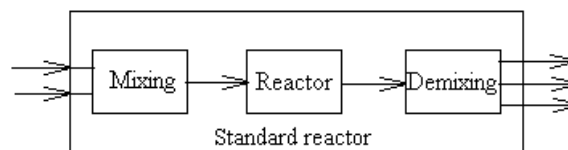


Fig. 9.1. In a standard reactor, each reactive and each product is assumed to enter/exit pure by a separate duct.

Enthalpy of reaction (as the other variables in (9.7)) being a state variable, its value for a given reaction is independent of any reaction sequence thought. This additivity of h_r is known as Hess rule (after G.H. Hess, a Swiss-born professor of chemistry at St. Petersburg who empirically discovered it in 1840); e.g. $h_r^\oplus = -393.5$ kJ/mol for $C + O_2 = CO_2$, $h_r^\oplus = -110.5$ kJ/mol for $C + (1/2)O_2 = CO$, $h_r^\oplus = -283$ kJ/mol for $CO + (1/2)O_2 = CO_2$, and $(-110.5) + (-283) = (-393.5)$.

Sometimes the term 'heat of reaction' is employed to define the heat exchange with the environment. If the reaction is at constant pressure (be it in a control mass or a steady control volume) the heat of reaction

is equal to the enthalpy of reaction, and if the volume is kept constant in a control mass system, the heat of reaction is equal to the internal energy of reaction (see (9.10)). In combustion reactions, the heat of reaction is ascribed to the fuel (the oxidiser assumed to be freely available as oxygen in the air), and the term 'heating value' is defined as the negative of the heat of reaction (to have positive values).

Exercise 3. Enthalpy of formation from heat of combustion

Exergy of reaction and exergy of reactants

Exergy ([Chapter 3](#)) is a state function (of the system plus the atmosphere) and the balance equations ([7.13-14](#)) apply for any process, inclusive of chemical reactions. The novelty here is that we want to know the exergy of substances not existing in the reference atmosphere, and thus we need chemical reactions to synthesise them. The analysis is based in the fact that, for a process at constant T and p , exergy-change equals Gibbs'-function-change, $\Delta\Phi|_{T,p}=\Delta G$ ([Chapter 4](#)); for a steady flow system, the minimum useful work to advance its extent ξ by one mole (or the maximum useful work obtained) is thus its Gibbs function of reaction: $w_{u,\min}=dG/d\xi|_{T,p}=g_r=\psi_r$.

We want to know the minimum work to get a pure chemical component from a reference environment. For a substance in the reference atmosphere ([Table 3.3](#)), equation ([7.15](#)), $\psi_i=-R_uT^\oplus\ln x_{i0}$, directly gives their molar exergy of separation, shown in Table 9.1 (e.g. $\psi_{Ar}=-R_uT^\oplus\ln x_{Ar}=-8.3\cdot 298\cdot\ln 0.0095=11.5$ kJ/mol), except for water vapour, where ([7.16](#)) must be used: $\psi_{H_2O}=-R_uT^\oplus\ln(x_{H_2O}p^\oplus/p^*(T^\oplus))=-R_uT^\oplus\ln\phi=-8.3\cdot 298\cdot\ln 0.6=1.26$ kJ/mol.

Table 9.1. Molar exergy of separation of species in the reference atmosphere at 100 kPa.

Component	At 288 K and 60 % RH		At 298 K and 60 % RH	
	Molar fraction x_i	Molar exergy ψ_i	Molar fraction x_i	Molar exergy ψ_i
N ₂	0.7720	0.62 kJ/mol _{N2}	0.7651	0.66 kJ/mol _{N2}
O ₂	0.2080	3.8 kJ/mol _{O2}	0.2062	3.9 kJ/mol _{O2}
H ₂ O	0.0102	1.2 kJ/mol _{H2O}	0.0190	1.3 kJ/mol _{H2O}
Ar	0.0095	11 kJ/mol _{Ar}	0.0094	12 kJ/mol _{Ar}
CO ₂	0.0003	20 kJ/mol _{CO2}	0.0003	20 kJ/mol _{CO2}

For a substance not in the reference atmosphere, e.g. CO, a chemical reaction must be set to produce it from the existing ones, e.g. $CO_2=CO+(1/2)O_2$, and the process arranged as in Fig. 9.2.

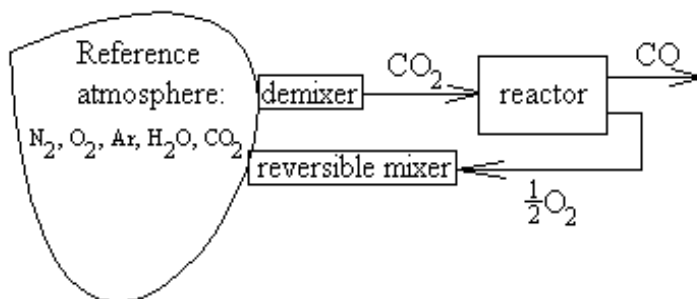


Fig. 9.2. Example of synthesising a substance out of the reference atmosphere.

Assuming everything is done at the standard temperature and pressure, the exergy of demixing CO₂ (minimum work required from a mechanical reservoir) is 20 kJ/mol_{CO₂} (Table 9.1). The exergy to produce the reaction CO₂=CO+(1/2)O₂ at standard conditions is its Gibbs function:

$$\psi_r^\oplus = g_r^\oplus = \sum_{i=1}^C \nu_i g_{f_i}^\oplus \quad (9.15)$$

e.g. for CO₂=CO+(1/2)O₂ $\psi_r^\oplus = g_{f,CO}^\oplus + (1/2)g_{f,O_2}^\oplus - g_{f,CO_2}^\oplus = (-137)+0-(-394)=257$ kJ/mol_{CO₂}=257 kJ/mol_{CO} Finally in the mixer one may get an exergy (maximum obtainable work) contrary to the one for demixing, i.e. (1/2)·3.9 kJ/mol_{CO}. Thus, to produce CO from the atmosphere one has to spend a minimum work of 20+257-2=275 kJ/mol_{CO₂} that is thence the exergy of CO. In general, the exergy of synthesising a component M₁ from species M_i in the atmosphere is:

$$\psi_{M_1}^\oplus = \psi_r^\oplus - \sum_{i=2}^C \nu_i \psi_{M_i}^\oplus = g_{f,M_1}^\oplus + \sum_{i=2}^C \nu_i (g_{f,M_i}^\oplus - \psi_{M_i}^\oplus) \quad \text{for } 0=M_1 + \sum_{i=2}^C \nu_i M_i \quad (9.16)$$

Notice the difference between exergy of a substance and exergy of reaction, because it is sometimes confused in combustion reactions. For instance, when one carelessly says the 'available energy of a fuel', one usually refers to the exergy of reaction with pure oxygen and not really to fuel exergy, similarly as when one says carelessly 'the heating power of a fuel', one usually refers to the heating power of the combustion reaction of that fuel with oxygen, pure or in a mixture.

Take methane for instance; its standard enthalpy for the reaction of combustion, after (9.14), is $h_r^\oplus = h_{f,CO_2}^\oplus + 2h_{f,H_2O}^\oplus - h_{f,CH_4}^\oplus - 2h_{f,O_2}^\oplus = -393.52 - 2 \cdot 285.93 - (-74.85) - 2 \cdot 0 = -890.3$ kJ/mol_{CH₄} (also known, changed of sign, as its higher heating value). The exergy of methane, however, after (9.16) is $\psi_{CH_4}^\oplus = \psi_{CO_2}^\oplus + 2\psi_{H_2O}^\oplus + \psi_r^\oplus - 2\psi_{O_2}^\oplus = 20 + 2 \cdot 1.3 + 818 - 2 \cdot 3.9 = 831$ kJ/mol_{CH₄} and the exergy of the combustion reaction is, after (9.15), $\psi_r^\oplus = g_r^\oplus = g_{CO_2}^\oplus + 2g_{H_2O}^\oplus - g_{CH_4}^\oplus - 2g_{O_2}^\oplus = -394.38 - 2 \cdot 237.18 - (-50.79) - 2 \cdot 0 = -818.0$ kJ/mol_{CH₄}. If we had only the standard atmosphere (and not natural gas wells), obtaining pure methane would cost at least 831 kJ/mol_{CH₄} of work; now, with this methane, we could burn it and get 890 kJ/mol_{CH₄} of heat and no work (afterwards, we could run a typical thermal engine with this heat and get some 300 kJ/mol_{CH₄} of work; 30 % of 890); or we could perform the same chemical reaction in an electrochemical cell and obtain at most 818 kJ/mol_{CH₄} of work (the additional 12 kJ/mol_{CH₄} of work might be obtained by reversible mixing of the exhaust gases with the atmosphere), although with present-day fuel-cell technology one could produce some 450 kJ/mol_{CH₄} of work (50 % of 890), more than with the thermal engine. Notice that the 818 kJ/mol_{CH₄} of maximum work obtainable refers to the standard conditions of pure CH₄ with pure O₂; the maximum work obtainable from methane and air in an ideal fuel cell would be that, minus the work required to obtain the oxygen from the air, i.e. 818-2·3.9=810 kJ/mol. A summary on [Chemical exergy](#) is available aside.

[Exercise 4. Fuel cell car](#)

Equilibrium composition

A chemical reaction will proceed, in the presence of an atmosphere, until $G(T,p,x_i)=\min$, i.e. until $A(T,p,x_i)=0$, thus establishing a relation between T and p and the composition x_i at equilibrium, what we intend to elaborate more, here. First, we separate the affinity dependence on temperature and give it a new name (we only deal with ideal gaseous mixtures):

$$A(T, p, x_i) = -\sum v_i \mu_i(T, p, x_i) \stackrel{\text{PGM}}{=} -\sum v_i \mu_i^\oplus(T, p^\oplus) - \sum v_i RT \ln \frac{x_i p}{p^\oplus} \quad (9.17)$$

introducing the standard affinity, $A(T, p^\oplus)$ (i.e. the affinity for pure substances at p^\oplus), and the so called equilibrium constant, K , (it is not a constant because it depends on temperature, but it is non-dimensional), in the way:

$$A(T, p^\oplus) \equiv -\sum v_i \mu_i^\oplus(T, p^\oplus) \equiv RT \ln K(T, p^\oplus) \quad (9.18)$$

such that at equilibrium ($A=0$), from (9.17) one gets:

$$\ln K(T, p^\oplus) \stackrel{\text{equilibrium}}{=} \sum v_i \ln \frac{x_i p}{p^\oplus} \quad \text{or} \quad \prod_{i=1}^C \left(\frac{x_i p}{p^\oplus} \right)^{v_i} = K(T, p^\oplus) \quad (9.19)$$

But, from van't Hoff equation, (9.13), and assuming $h_r = \text{constant} = h_r^\oplus$ as reasoned in (9.11), $\ln K$ can be approximated as $\ln K = C_1 + C_2/T$, where C_1 is obtained from $\ln K(T, p^\oplus) = (A^\oplus)/(RT) = -g_r^\oplus/(RT)$, and C_2 from van't Hoff equation, $d \ln K/d(1/T) = -h_r^\oplus/R$, what yields $\ln K = -g_r^\oplus/(RT^\oplus) + (h_r^\oplus/(RT^\oplus))(1 - T^\oplus/T)$, which can also be set as $\ln K = -s_r^\oplus/R + h_r^\oplus/(RT)$. The desired relation between equilibrium composition x_i , and T and p , for a given reaction $0 = \sum v_i M_i$ is then:

$$\prod_{i=1}^C x_i^{v_i} = \left(\frac{p}{p^\oplus} \right)^{-\sum v_i} K(T, p^\oplus) = \left(\frac{p}{p^\oplus} \right)^{-\sum v_i} \exp \left[-\frac{g_r^\oplus}{RT^\oplus} + \frac{h_r^\oplus}{RT^\oplus} \left(1 - \frac{T^\oplus}{T} \right) \right] \quad (9.20)$$

where the constants are computed from the standard enthalpies and Gibbs functions of formation (9.14). For more precise work, experimental values of $K(T)$ are tabulated for important reactions (or, most often, the related variable 'pK', $pK = -\log_{10} K$ is tabulated, because of the exponential character of K).

Notice that the equilibrium equation (9.20) and its equilibrium constant, K , all refer to a single reaction in an ideal gas mixture. Condensed pure species participating in the reaction (like carbon; reactions in solution have not been considered here), must not be included in the $\prod x_i$, not in the pressure summation, because pressure has a negligible contribution to the chemical potential of condensed matter. On the other hand, there can be (and usually there are) several chemical reactions, R , to consider in a problem. How many? The answer is that as many as chemical components intervening, C , minus the number of atomic species, E , involved; i.e. $R = C - E$. Notice that, if electrically-charged components are involved, one must add electrical neutrality an additional equilibrium constrain. The variance V (number of degrees of

freedom) of a reactive system in equilibrium with P phases is then $V=2+C-P-R=2+E-P$, what is an extension of the traditional Gibbs phase rule analysed in detail in [Chapter 2: Entropy](#). Mind that sometimes F (for freedom) is used instead of V (variance), and Φ instead of P for phases.

[Exercise 5. Equilibrium composition](#)

Stability of the equilibrium. Principle of Le Châtelier

We saw in [Chapter 4](#) that for an equilibrium state to be stable ($d^2S < 0$ if isolated, $d^2G > 0$ if in contact with the atmosphere), it has to be thermally stable (implies positive isobaric thermal capacity), it has to be mechanically stable (implies positive isothermal compressibility), and it has to be chemically stable, what implies, as above, that, if perturbed, the system evolves trying to counteract the perturbation, meaning that:

- If T increases in an exothermic reaction, the extent of reaction decreases (to produce less energy), and the contrary for an endothermic reaction. The demonstration is based on van't Hoff equation, $\partial(A/T)/\partial(1/T)|_p = -h_r$.
- If p increases in a reaction with $n_r > 0$ (that generate amount of substance), the extent decreases (to produce less moles), and the contrary for a $n_r < 0$ reaction. The demonstration is based on $\partial A/\partial p|_T = -v_r$, that for gas reactions reduces to $\partial(A/T)/\partial(\ln p)|_T = -R \sum \nu_i$.
- If one reactive or product n_i increases (adding a little), the extent changes so that this substance is (partially) consumed. For ideal mixtures, $\partial(A/T)/\partial(\ln n_i)|_{T,p} = -R(\nu_i + \sum \nu_j x_j)$.

The first statement of this general stability criterion is due to H. Le Châtelier, who in 1884 proposed it for precisely these changes in chemical reactions. The most general idea is that stable systems are stable because they resist an imposed stress (i.e. they respond with an opposing strain); unstable systems disappear.

[Exercise 6. Town gas manufacture](#)

The importance of these qualitative-prediction arguments should not be underestimated; they yield most-valuable information with minimum effort, as may be appreciated in the following example.

Consider for instance the oxidation by oxygen of an elementary material M (e.g. hydrogen, aluminium, carbon). We can put in general that reaction as $M+O_2=MO_2$, and it might correspond to a quick combustion process, a slow oxidation, or a controlled electrochemical process. The following questions can be answered based exclusively on the standard thermochemical data.

Question 1. Is $M+O_2=MO_2$ a natural or an artificial process? Answer: it only depends on g_r (or $A=-g_r$); $A > 0$ means it can take place spontaneously, i.e. without exergy input, whereas if $A < 0$ it can only happen when aided. For instance, for carbon, $C+O_2=CO_2$ is a natural process at usual T - p -conditions, that takes place slowly if left alone, or quickly if properly triggered, but does not demands exergy, as can be deduced from $A=-g_r=-\sum \nu_i g_{f,i} = -(-393.52+0+0)$ kJ/mol. The same happens for $2H_2+O_2=2H_2O$, but not for $(1/2)N_2+O_2=NO_2$, since in the latter case $A=-g_r=-\sum \nu_i g_{f,i} = -(33.18+0+0)$ kJ/mol. It might be argued that

there are several other nitrogen oxides that could be formed, but all of them require an exergy source to be formed. The problem of the well-known NO_x -pollution is another question: once they are formed at high temperatures inside combustion devices, their dissociation rate is too slow to our convenience, towards the innocuous equilibrium state.

Question 2. What effect may a catalyst have? Answer: adding a catalyst makes absolutely no difference to the equilibrium state, thus, a reaction with $A > 0$ can naturally progress, and if $A < 0$ it requires assistance, independently of the catalyst. However, catalysts can widely change the reaction rate. For instance, a suitable catalyst may accelerate the slow dissociation rate of NO_2 (urea is being tried on diesel engines), and platinum catalyses the slow oxidation of hydrogen to yield a rapid combustion, but catalysts cannot change the direction, only the speed (both, the forward and backward speeds of the dynamic process, since their ratio is the equilibrium constant, that is not changed).

Question 3. What is the effect of pressure on the decomposition $\text{N}_2\text{O}_4 = 2\text{NO}_2$? Answer: pressure shifts the equilibrium to the left, towards the smaller amount of substance, since $\partial(A/T)/\partial(\ln p)|_T = -R \sum \nu_i = -R(2-1) < 0$ (more pressure, less affinity). The synthesis of ammonia, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$, is performed at high pressure (>10 MPa) for the same reason, whereas it is better e.g. to carry out natural gas reforming: $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$ at low pressure.

Question 4. What is the effect of an inert gas on the chemical equilibrium? Answer: it depends on whether the inert gas is added at constant volume (increasing the pressure) or at constant pressure (increasing the volume): at constant volume there is no effect because concentrations of the reactants, $c_i = n_i/V$, remain the same (both n_i and V), whereas at constant pressure the equilibrium will shift towards increasing the amount of substance, since the effect is equivalent to a decrease in pressure for the reactant species considered alone (without the inert one); thence, for instance, adding argon to an isobaric reactor where $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$ is taking place, would yield less ammonia.

Question 5. What is the effect of temperature on the voltage of an electric battery? Answer: batteries and fuel cells yield more electricity (higher voltage) the lower the temperature, because they are exothermic processes, and thus, $\partial(A/T)/\partial(1/T)|_p = -h_r > 0$ and $\partial A/\partial T|_p < 0$. However, other effects like mass transport and ionic conduction are faster at higher temperatures and this may more than offset the drop in open-circuit voltage. Recall that we only analyse equilibrium states and not reaction rates. For the same reason, the synthesis of ammonia, $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$, that is also exothermic and thus would yield more at low temperatures ($d\xi/dT < 0$), is actually performed at some 650 K to increase the rate ($d\xi/dT > 0$).

Question 6. Why iron ore is reduced with coal and aluminium ore is not? Answer: because a plot of affinities versus temperature shows that aluminium affinity for oxygen is greater than that of carbon, which is greater than that of iron, and thus, carbon can get hold of the oxygen in iron oxide but not in aluminium oxide (Fig. 9.3). It may be interesting to have a closer look at such a plot, which is known as Ellingham diagram. First of all, what is plotted is $A(T, p^\ominus)$, defined by (9.18) and computed with the model developed in (9.20), i.e.:

$$A(T, p^\oplus) = RT \ln K(T, p^\oplus) = RT \left[-\frac{g_r^\oplus}{RT^\oplus} + \frac{h_r^\oplus}{RT^\oplus} \left(1 - \frac{T^\oplus}{T} \right) \right] = -h_r^\oplus + Ts_r^\oplus \quad (9.21)$$

showing that plots are straight lines with a slope equal to s_r^\oplus and the ordinate at the origin equal to $-h_r^\oplus$, both values easily found for each reaction from the standard thermochemical values.

Let us begin with a trivial case: the ‘reaction’ of liquid water to produce vapour water (line 6 in Fig. 9.3), for which $-h_r^\oplus = [h_f^\oplus(\text{H}_2\text{O}, \text{g}) - h_f^\oplus(\text{H}_2\text{O}, \text{l})] = -(-241.82 + 285.83) = -44$ kJ/mol, and $s_r^\oplus = s^\oplus(\text{H}_2\text{O}, \text{g}) - s^\oplus(\text{H}_2\text{O}, \text{l}) = (188.72 - 69.95) = 119$ J/mol. Liquid and vapour are at equilibrium when $A=0$, corresponding to the well-known boiling-point, $T_b = 373$ K ($T_b = h_r^\oplus / s_r^\oplus = 44000 / 119 = 370$ K with this approximate model).

As for the oxides, it is evident from Fig. 9.3 (line 7) that NO_2 is unstable (at any temperature, it requires an exergy supply to be formed) whereas the others are stable, i.e. materials have positive affinities for their oxides. But the affinity decreases with temperature (because entropy decreases by fixing oxygen gas into a solid compound), and copper oxide becomes unstable above 1750 K.

To see why iron ore can be reduced with coal, i.e. to analyse the reaction $2\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) = 4\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$, it is enough to plot the basic reaction $(4/3)\text{Fe} + \text{O}_2 = (2/3)\text{Fe}_2\text{O}_3$ and $\text{C} + \text{O}_2 = \text{CO}_2$ (taking care to arrange the stoichiometric coefficients to allow for the same amount of oxygen) and subtract, i.e. look at the relative affinities: for $T > 950$ K carbon has more affinity than iron (for oxygen), and this is the principle of operation for the blast furnace.

Notice, by the way, that hydrogen would work similarly as reducer of iron ore, and that aluminium ore cannot be reduced by either, within a practical temperature range; availability of charcoal since the Stone Age, replaced by coal since the 17th c., is what has dictated the preference of carbon as the metallurgist's reducer of choice. It is apparent from Fig. 9.3 that aluminium would be a better reducer of iron oxide than carbon, what is demonstrated in the thermite reaction $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$, but aluminium is expensive to get (in spite of Al being 8 % by mass of Earth crust, against 5 % Fe or 0.02 % C). Commercial production of aluminium was started by H. Deville in 1854 by reduction of aluminium chloride (produced by carbo-chlorination of alumina) with sodium metal (produced by reduction of sodium carbonate with carbon), an ingenious example of achieving a desired result by multiple steps where the direct process (carbon reduction of alumina) is not feasible.

Notice also that we have only considered one of the iron oxide (hematite, Fe_2O_3) and only one of the carbon oxides (carbon dioxide, CO_2), amongst other simplifications (e.g. we have extrapolated beyond the phase changes, as above the melting point of CuO at 1500 K, or below the condensation point of water at 373 K).

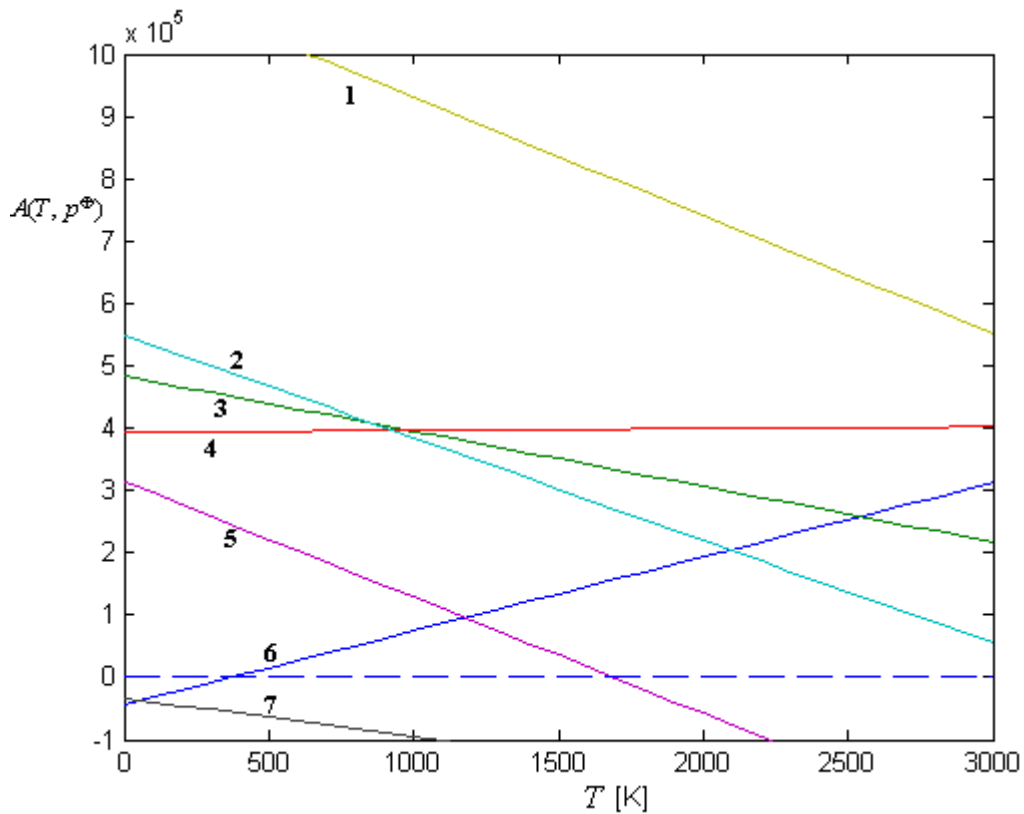


Fig. 9.3. Some examples of affinity variation with temperature:

- | | |
|---|---|
| 1 | $\frac{4}{3} \text{Al(s)} + \text{O}_2(\text{g}) = \frac{2}{3} \text{Al}_2\text{O}_3(\text{s})$ |
| 2 | $\frac{4}{3} \text{Fe(s)} + \text{O}_2(\text{g}) = \frac{2}{3} \text{Fe}_2\text{O}_3(\text{s})$ |
| 3 | $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{H}_2\text{O}(\text{g})$ |
| 4 | $\text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$ |
| 5 | $2\text{Cu(s)} + \text{O}_2(\text{g}) = 2\text{CuO(s)}$ |
| 6 | $\text{H}_2\text{O(l)} = \text{H}_2\text{O(g)}$ |
| 7 | $\frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) = \text{NO}_2(\text{g})$ |

Electrochemical systems. Fuel cells

We have only considered chemical reactions in absence of external force fields. Gravitational forces do not introduce new chemical behaviour except at the huge intensities inside stars, but electrical forces may have a profound influence on chemical reactions, particularly when ions are involved.

A fuel cell is an open-system electrochemical reactor, fed with a fuel and an oxidiser, and given off electricity, heat and reaction products. Figure 9.4 shows the concept of a fuel cell in comparison with a normal chemical reactor.

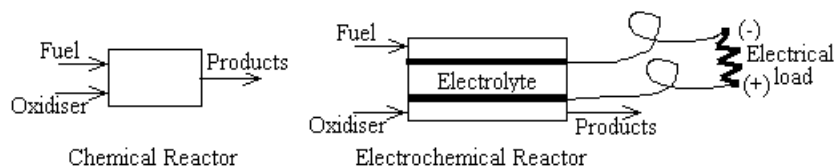


Fig. 9.4. A chemical reactor and a fuel cell (an electrochemical reactor, with an electrolyte sandwiched between two porous electrodes).

Taking as example the reaction of hydrogen (the fuel most used to study fuel cells, because of its fast kinetics) with the oxygen in the air (the most ready oxidiser), in a normal reactor (a combustor in this case), the reaction (started for instance by a spark) globally corresponds to $H_2+(1/2)O_2=H_2O$ and develops violently (may explode), greatly rising the temperature of the system. However, in the electrochemical reactor (a fuel cell), the gradient of electrochemical potential at the electrodes forces the diffusion and ionisation of the substances: in the anode (a porous conducting catalyst), the fuel decomposes as $H_2=2H^++2e^-$ until an equilibrium concentration would be reached for a given temperature and pressure, but the electrons are left to flow through a conductor to an electrical load and finally to a cathode, and the ions are left to diffuse through an electrolyte to the cathode. At the cathode (a porous conducting catalyst), the oxidiser is reduced by the electrons as $O_2+4e^-=2O^{2-}$, and the ions combine to yield $2H^++O^{2-}=H_2O$, although the combined reaction $O_2+4e^-+4H^+=2H_2O$ is preferred to represent this process because the O^{2-} ion is not found alone, contrary to the H^+ ion that travels alone through the electrolyte.

Globally, the reaction is $H_2+(1/2)O_2=H_2O$ in both cases (for the combustor and for the fuel cell), and thus they have the same enthalpy (-286 kJ/mol) and exergy (-237 kJ/mol) of reaction, but in the typical combustor all the chemical energy goes to thermal energy whereas in a fuel cell part of the chemical energy already goes to electrical work, and only the rest goes to the products, or as output heat for non-adiabatic reactors in any case (i.e. for reactions at 25 °C and 100 kPa, the combustor output is $q=286$ kJ/mol and $w=0$, whereas the fuel cell output is $w<w_{max}=237$ kJ/mol and $q>49$ kJ/mol), at 25 °C and 100 kPa. Notice that the enthalpy of reaction varies only a little with temperature, but the exergy of reaction (the Gibbs function of reaction) diminish roughly linearly with increasing temperatures, $-g_r=-h_r^\oplus+Ts_r^\oplus=-h_r^\oplus-(g_r^\oplus-h_r^\oplus)(T/T^\oplus)$, as shown in Fig. 9.5 where the electrical efficiency, η_e , defined as the work-output at a given temperature divided by the heat-output at standard conditions (higher heating value) is presented for a hydrogen fuel cell.

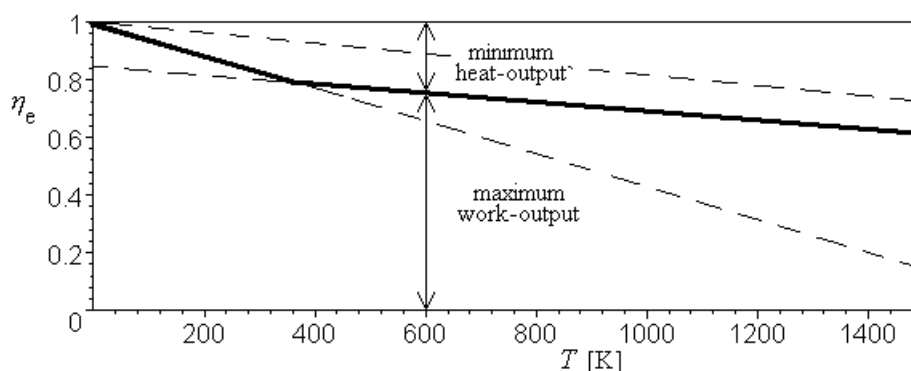


Fig. 9.5. Thermodynamic limit to the electrical efficiency of a hydrogen-oxygen fuel cell at 100 kPa (solid line; dash lines correspond to other possible definition of this efficiency).

Each electrochemical reaction has its own electromotive voltage, ε , that at equilibrium must satisfy $g_r=-zF\varepsilon$, where z is the number of electrons involved in the reaction equation, and F the Faraday constant ($F=96485$ C/mol). For instance, for the hydrogen-oxygen reaction $\varepsilon=1.23$ V at 298 K and 100 kPa (or 1.03 V at 1000 K); that is why fuel cells are usually packed in stacks to reach the desired voltage.

The variation of voltage with temperature, $d\varepsilon/dT$ can be deduced as follows. From $g_r=h_r-Ts_r$ and Maxwell relation $s_r=-\partial A/\partial T=\partial g_r/\partial T$, we get $g_r=h_r-T(dg_r/dT)$ and $dg_r/dT=(h_r-g_r)/T$, and this variation can be

approximated by its value at the standard state, as follows: $dg_r/dT = d(-zF\varepsilon)/dT = (h_r - g_r)/T \approx (h_r^\ominus - g_r^\ominus)/T^\ominus = (h_r^\ominus + zF\varepsilon)/T^\ominus$, i.e. $d\varepsilon/dT = -(h_r^\ominus/(zF) + \varepsilon)/T^\ominus$, that is negative in this case (the sign can be more easily deduced from $dg_r/dT = -s_r \approx -s_r^\ominus$ and knowing that the entropy of reaction is negative for the oxidation of hydrogen, or simply from Le Châtelier's principle: if temperature is increased in an exothermic reaction, the change is as to yield less energy; i.e. the open-circuit voltage output decreases with increasing temperature and fuel cells are more efficient at low temperatures (theoretically, at least, because other effects like mass transport and ionic conduction are faster at higher temperatures and this may more than offset the drop in open-circuit voltage)).

The fuel cell was invented in 1839 by William Grove as the reverse process to water electrolysis, but only started to be used in the 1960s aboard the Gemini space vehicles, and only entered the market in the 1990s with small powers plants (up to 200 kW). The majority of fuel cells use hydrogen (sometimes very pure) as fuel, some fuel cells work off methane, and a few use liquid fuels such as methanol (notice the chronological evolution in fuels used by mankind: wood, coal, oil, natural gas, hydrogen?).

There are several types of fuel cells, mainly characterised by the electrolyte used, but we classify them according to their operating temperature as:

- about 350 K (80 °C, low temperature or PEMFC type). PEMFC stands for Proton Exchange Membrane Fuel Cell (also Polymer Electrolyte Membrane). They have graphite electrodes and a solid electrolyte of perfluorosulfonic acid polymer (Nafion™ by DuPont), a membrane presently selling at more than 500 \$/m²). PEM fuel cells seem to be the most promising from the thermodynamic and handling points-of-view. Up to 33 kW single-stacks have been built, with electrical efficiencies of 54 %, but require high-purity hydrogen (<10 ppm CO). Alkaline fuel cells (AFC, the ones used in space applications with electrical efficiencies of 70 %), also work in this temperature range, but they cannot tolerate carbon dioxide even at atmospheric concentrations; their electrolyte is KOH in an asbestos matrix, and, although the reaction is the same as in PEMFC, the ions are OH⁻ instead of H⁺.
- about 500 K (200 °C, medium temperature or PAFC type). PAFC stands for Phosphoric Acid Fuel Cell. The electrolyte is a concentrated aqueous solution of H₃PO₄ embedded in a silicon carbide ceramic matrix, and the moving ions are H⁺. It is presently the most developed type, yielding up to 200 kW with electrical efficiencies of 40 %, but the electrodes require a lot of platinum catalyst, and the electrolyte must be kept warm (>45 °C) even when not in use, to avoid expansion stresses on solidification.
- about 900 K (650 °C, high temperature or MCFC type). MCFC stands for Molten Carbonates Fuel Cell. The electrolyte is a mixture of molten carbonates, mainly calcium carbonate), and the moving ions are CO₃²⁻. The electrodes require a lot of platinum catalyst.
- about 1300 K (1000 °C, very-high temperature or SOFC type). SOFC stands for Solid Oxide Fuel Cell. The electrolyte is a solid oxide ceramic through which O²⁻ ions flow.

In summary, the basic working of a fuel cell is to produce electrons from the fuel (basically hydrogen), and to capture electrons with an oxidiser (basically oxygen from the air), but channelling the electrons

through a solid conductor (instead of directly as in combustion), what requires an additional path for the ions to balance the charge. The present solutions are:

- To produce electrons from the fuel at the anode ($\text{H}_2 \rightarrow \text{e}^-$):
 - $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ and an acid electrolyte that allows protons, H^+ , to flow to the cathode (PEMFC and PAFC).
 - $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ and an alkaline electrolyte that allows hydroxide ions, OH^- , to flow to the anode (AFC).
 - $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ and an electrolyte that allows carbonate ions, CO_3^{2-} , to flow to the anode (MCFC).
 - $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ and an electrolyte that allows oxygen ions, O^{2-} , to flow to the anode (SOFC).
- To capture electrons with oxygen at the cathode ($\text{O}_2 + \text{e}^- \rightarrow$):
 - $(1/2)\text{O}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$ (PEMFC and PAFC).
 - $(1/2)\text{O}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$ (AFC).
 - $(1/2)\text{O}_2 + 2\text{e}^- + \text{CO}_2 \rightarrow \text{CO}_3^{2-}$ (MCFC).
 - $(1/2)\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$ (SOFC).

Type of problems

Besides housekeeping problems of how to deduce one particular equation from others, and checking the redundancy of thermochemical data, the types of problems in this chapter are:

1. Find thermochemical values for new compounds from other reactions (notably combustion).
2. Find the convenient temperature and pressure to carry out a reaction in the desired direction.
3. Find the energy exchanges in a reaction.
4. Find the exergy (maximum obtainable work) of a fuel and of a reaction.
5. Find the composition at equilibrium, and its variation with T and p .

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