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COMBUSTION THERMODYNAMICS

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COMBUSTION THERMODYNAMICS

COMBUSTION

Combustion is a self-propagating exothermic oxidative chemical reaction, mostly in gas phase, producing light, heat and smoke in a nearly-adiabatic flame front. The overall process in combustion is analogous to those taking place in fuel cells and living-matter respiration, so that the same overall results apply in all three cases, in spite of their details being so different; combustion is characterised by the very high temperatures reached.

The practical goal in combustion study is the prediction of its performance, for a safe, efficient and clean design and operation of fire-making devices, in terms of the multiple physico-chemical phenomena involved; it is thence a prerequisite to analysis the latter. Those phenomena may be split in two groups: equilibrium behaviour (what we need and what we get), and kinetics (how we get it; at what rate). Combustion Thermodynamics focuses on the former physico-chemical phenomena: fuel/air ratios, heating values, maximum work obtainable, exhaust composition, etc., whereas [Combustion kinetics](#) focuses on mixing process, flame geometry, ignition, extinction, propagation, stability, etc.

The study of combustion is based on the more general subject of [Thermodynamics of Chemical Reactions](#), usually called Thermochemistry. We shall deal here only with the peculiarities of the combustion reaction, i.e. with focus on the thermodynamics of a fuel-and-air gas-phase reaction.

It may be helpful to have in mind a concrete instance of a combustion process, and we proposed the idealised burner sketched in Fig. 1, a steady-state combustor burning natural gas (here idealised as pure methane) in air, with some heat output (as in a domestic water heater). This model already emphasises the black-box approach typical of thermodynamic analysis (it does not look into the internal details of how

the fuel and air mix, the geometry of the flame, or any other gradient or discontinuity within), and assumes the combustor is large enough for the exhaust to be in equilibrium (no longer reacting, no gradients).

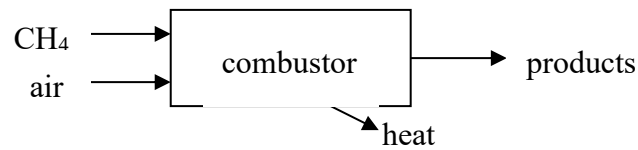


Fig. 1. A simplified model of a natural-gas combustor.

A detailed description of fuels, oxidisers, their mixing, the ignition process and the kinetics of its propagation, can be found [elsewhere](#). A succinct description of the process in Fig. 1 may be as follows. As it will be shown below, at least 9.5 m^3 of air are required for the complete combustion of 1 m^3 of methane at same p - T conditions (the molar stoichiometric air/fuel ratio is $A_0=9.5$), with a maximum heat output of $55 \text{ MJ/kg}_{\text{CH}_4}$ (or $37 \text{ MJ/m}^3_{\text{CH}_4}$, the higher heating value of methane) that would decrease as the exhaust temperature increase until a maximum when no heat is exchanged, some 2200 K (the adiabatic combustion temperature for the stoichiometric mixture). The exhaust composition for stoichiometric mixture consists of 71% by volume of N_2 , 19% H_2O , 9% CO_2 , and much less than 1% of undesirable gases called ‘emissions’, that are noxious to the health: CO , NO , NO_2 , aromatic-hydrocarbon vapours and maybe soot. Those figures already show that thermodynamic properties of exhaust gases can be approximated by those of air for a crude analysis (as air properties can be approximated by those of nitrogen); similarly, they show the importance of water as the only condensable gas in the exhaust, and the small proportion of contaminant emissions, although the massive use of combustion renders their effects very obvious. Nowadays, even the inert gas CO_2 is considered an undesirable emission, since it contributes to the menacing global warming and its associated climate changes.

[Exercise 1. Combustion emissions.](#)

THERMODYNAMICS FUNDAMENTALS

Perhaps a rough summary of Thermodynamics Fundamentals seems appropriate at the beginning of a new application of the general theory, instead of the recourse to ‘as you may know’. We should only consider systems such that their equilibrium states are just characterised by its energy E , volume V and amount of each chemical species n_i . For such a system in such states, the traditional formulation of Thermodynamics is based on these principles:

- Zero Law: there exists an state-function named temperature, $T(E, V, n_i)$, indicating the thermal level of the system, such that if two systems having different temperatures are put in contact, their energy varies, flowing from the hotter to the colder one until both reached the same value (equilibrium).
- First Law: there exists a path-function named heat, Q , measuring the thermal energy exchanged by the system, such that when two control-mass systems having different temperatures exchange energy, the heat flow at the frontier is just the change in stored energy minus the work received by the system; i.e. $Q=\Delta E-W$.

- Second Law: there exists a state-function named entropy, $S(E, V, n_i)$, measuring the distribution of thermal energy within the system, such that for any process in a control-mass system, its variation is lower-bounded to $\Delta S \geq \int dQ/T$, with the equality holding only for the limit case of a non-dissipating process.
- Third Law: there exists a singular value for the state-function entropy, such that all entropy variations tend to die for any processes at that limit $T=0$ K, i.e. $\Delta S|_{T \rightarrow 0 \text{ K}} \rightarrow 0$.

These basic general principles and other particular assumptions on the behaviour of some type of substances, give way to a formulation that is actually applied when solving problems, and that is here briefly refreshed, following our [Thermodynamics Lectures](#).

Details on the concept of energy, an additive and conservative function of kinetic and potential terms, can be found [aside](#), but the energy balance of a control mass system (one that cannot exchange mass with the surroundings), and the perfect substance model for stored thermal energy, should be kept in mind:

$$\Delta E = Q + W \quad (\text{energy balance of a control mass}) \quad (1)$$

$$\Delta E = mc_v \Delta T \quad (\text{stored thermal energy model for a perfect substance}) \quad (2)$$

Details on the concept of entropy, an additive non-conservative function measuring the internal distribution of energy and other conservative properties, can be found [aside](#), but its basic expression as a function of other variables, and its particularisation for a perfect gas, should be retained:

$$\Delta S = \int \frac{dU + pdV}{T} = \int \frac{dQ + dE_{mdf}}{T} \quad (\text{general expressions for entropy change}) \quad (3)$$

$$\Delta S^{\text{PGM}} = mc_p \ln \frac{T_2}{T_1} - mR \ln \frac{p_2}{p_1} \quad (\text{entropy change in a perfect gas model}) \quad (4)$$

The combination of energy and entropy called exergy, measuring the maximum work obtainable from a system, or the minimum work required to reach a global non-equilibrium state, is, for a control mass:

$$\Delta \Phi \equiv W_{u_{\min}} = W_u|_{\Delta S_{\text{univ}}=0} = \Delta E + p_0 \Delta V - T_0 \Delta S \quad (5)$$

Many thermodynamic variables (some extensive, others intensive) are used to simplify the analysis of systems, amongst which enthalpy, thermal capacities, dilation and compressibility can be distinguished:

$$H \equiv U + pV, \quad c_p \equiv T \left. \frac{\partial s}{\partial T} \right|_p = \left. \frac{\partial h}{\partial T} \right|_p, \quad c_v \equiv T \left. \frac{\partial s}{\partial T} \right|_v = \left. \frac{\partial u}{\partial T} \right|_v, \quad \alpha \equiv \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p, \quad \kappa \equiv \frac{-1}{V} \left. \frac{\partial V}{\partial p} \right|_T \quad (6)$$

But it must be remembered that, for pure substances, there are only two independent state variables, and all others can be obtained by a combination of this two. In particular, the ideal gas equation of state is omnipresent in all combustion studies:

$$pV=nRT \quad \text{with } R=8.314 \text{ J/(mol}\cdot\text{K)}, \text{ or in the form } \rho = \frac{p}{RT} \quad \text{or} \quad v = \frac{RT}{p} \quad (7)$$

where the same symbol is used for the universal gas constant, $R_u=8.3 \text{ J/(mol}\cdot\text{K)}$, and the particular gas constant, $R \equiv R_u/M$, for a gas of molar mass M . Most combustion processes take place within a control volume, the combustor, and thus the equations developed in [Control Volume](#) analysis must be known, particularly the omni-present steady-state mass and energy balances:

$$0 = \sum^{\text{openings}} \dot{m}_e \quad \text{with} \quad \dot{m} \equiv \rho v A \quad (8)$$

$$0 = \dot{Q} + \dot{W} + \sum^{\text{openings}} \dot{m}_e h_{t_e} \quad (9)$$

\dot{W} being the shaft work input, \dot{Q} the heat received, and h_{t_e} the total specific enthalpy for each entrance (or exit) with mass flow rate \dot{m}_e . There are few combustion problems where equations (7-9) are not involved.

Phase changes in pure substances are needed in combustion only to deal with pure liquid fuels, and it may be enough to recall the equation for the vapour pressure curve, i.e. Clapeyron's equation, more usually used in the form of Antoine's fitting:

$$\left. \frac{dp}{dT} \right|_{\text{sat}} = \frac{h_{lv}}{T v_{lv}} \quad \rightarrow \quad \ln \frac{p}{p_0} = \frac{-h_{lv}}{RT} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad \rightarrow \quad \ln \frac{p}{p_0} = A - \frac{B}{T/T_{\text{unit}} + C} \quad (10)$$

The Thermodynamics of mixtures is so important to combustion, that a more detailed summary is here included.

THERMODYNAMICS OF MIXTURES

Combustion always involve a mixture, at least of a fuel and an oxidiser (usually air, another mixture itself!), and the exhaust is always a mixture of burnt gases (except in the two ideal cases $\text{C}+\text{O}_2=\text{CO}_2$ and $\text{H}_2+(1/2)\text{O}_2=\text{H}_2\text{O}$). The general theory of [Thermodynamics of Mixtures](#) is developed aside, but the important points to combustion are summarised here.

EQUILIBRIUM

An isolated mixture with conservative amounts of substance n_i tends to reach an equilibrium state defined by its entropy $S(U, V, n_i)$ being a maximum, what implies, in absence of external fields, that the temperature $T=\partial U/\partial S$, pressure $p=T\partial S/\partial V$, and chemical potential for each conservative species $\mu_i=-T\partial S/\partial n_i$, are uniform at equilibrium (in absence of external forces). [Multi-phasic mixtures](#), and [mixture segregation](#) due to external force fields, can be found aside.

CHEMICAL POTENTIAL EXPRESSIONS

The chemical potential, μ_i , measures the tendency for an species to migrate, i.e. the escaping tendency of chemical energy, in a similar way as temperature measures the escaping tendency of thermal energy, and

pressure the escaping tendency of compression energy. For a mixture in contact with an infinite environment at $T=\text{constant}$ and $p=\text{constant}$, as the ambient atmosphere, it is better to work with the Gibbs function for the system $G(T,p,n_i)\equiv U+pV-TS=H-TS$, instead of with the entropy of an isolated system. It can be deduced, from Gibbs equation and Euler theorem for homogeneous functions, that $G=\sum\mu_i n_i$; i.e.:

$$G \equiv U + pV - TS = H - TS = \sum_{i=1}^c n_i \mu_i \quad (11)$$

The differential form of the Gibbs function is used a lot in thermochemistry:

$$dG = -SdT + Vdp + \sum \mu_i dn_i \quad (12)$$

Several useful relations can be derived from it. First, the Gibbs-Duhem equation, subtracting (12) to the total differential of (11), i.e.:

$$0 = SdT - Vdp + \sum n_i d\mu_i \quad (13)$$

Second, the general dependence of $\mu_i(T)$ and $\mu_i(p)$; the former comes from the equality of the crossed second derivatives $\partial^2 G / (\partial T \partial n_i) = -s_i = \partial^2 G / (\partial n_i \partial T) = \partial \mu_i / \partial T$ and from $g_i = h_i - Ts_i$, what yields:

$$\left. \frac{\partial \frac{\mu_i}{T}}{\partial \frac{1}{T}} \right|_{p, n_i} = h_i \quad (14)$$

known as van't Hoff equation; on the other hand, $\mu_i(p)$ comes directly from the equality of the crossed second derivatives $\partial^2 G / (\partial p \partial n_i) = -v_i = \partial^2 G / (\partial n_i \partial p) = \partial \mu_i / \partial p$; i.e.:

$$\left. \frac{\partial \mu_i}{\partial p} \right|_{T, n_i} = v_i \quad (15)$$

For an ideal gaseous mixture, IGM, the chemical potential for an species i takes the form:

$$\mu_i(T, p, x_i)_{\text{IGM}} = \mu_i(T, p^\ominus, 1) + RT \ln(p/p^\ominus) + RT \ln x_i \quad (16)$$

indicating that the chemical potential varies with temperature according to the enthalpy function (13), and varies with pressure logarithmically according to (12) and $v_i = RT/p$, and varies with the molar fraction x_i also logarithmically.

THERMAL CAPACITY AVERAGING

The perfect gas model, besides the ideal gas equation of state (7), assumes constant thermal capacities c_p , simplifying the computations a lot; but a good averaged value of c_p must be taken in combustion studies, since c_p varies considerably: e.g. for air at 300 K $c_p = 1000 \text{ J}/(\text{kg}\cdot\text{K}) = 29 \text{ J}/(\text{mol}\cdot\text{K})$, but at 3000 K $c_p = 1240 \text{ J}/(\text{kg}\cdot\text{K}) = 36 \text{ J}/(\text{mol}\cdot\text{K})$, and for water-vapour at 300 K $c_p = 1900 \text{ J}/(\text{kg}\cdot\text{K}) = 34 \text{ J}/(\text{mol}\cdot\text{K})$, but at 3000 K $c_p = 3100 \text{ J}/(\text{kg}\cdot\text{K}) = 56 \text{ J}/(\text{mol}\cdot\text{K})$. Figure 2 gives a plot of $c_p(T)$ for the most important combustion gases; from that, averaged values that may be used for preliminary computations are presented in Table 1.

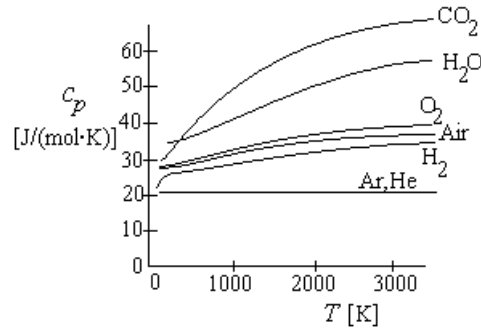


Fig. 2. Variation of thermal capacity with temperature for gases of interest in combustion. For preliminary computations, the usual averaged values are presented in Table 1.

Table 1. Mean values used for constant-thermal-capacity models in combustion.

Gas	c_p [J/(mol·K)]
Diatomic molecules: N ₂ , O ₂ , CO, NO, H ₂ , OH...	34
Water vapour: H ₂ O	47
Carbon dioxide: CO ₂	54
Monoatomic molecules: Ar, He, H, O, N ...	21

For a more crude manual analysis, the drastic simplification of assuming an averaged thermal capacity for the exhaust mixture of say $c_p=36$ J/(mol·K) may be cost effective. On the other hand, for high-precision computations, temperature correlations for thermal capacities must be used, as the traditional JANAF tables, or other [polynomial fitting](#).

WATER VAPOUR CONDENSATION

Except in a few theoretical cases ($C+O_2=CO_2$, $CO+(1/2)O_2=CO_2$, $S+O_2=SO_2$, etc., that really take place also with some water vapour), water is a genuine combustion product. Leaving aside the important problem of acid rain formation in the combustion of sulfur-containing fuels, water is the only condensable component in the products, being produced in such sizeable amounts (typically $x_{H_2O} \approx 10\%$) that its detailed account on mass and energy balances is of paramount importance).

Gaseous mixtures with a condensable component are dealt with in detail for the case of [humid air aside](#). Here we are concerned mostly with humid flue gases, but the approximation of non-condensable products by air may be good enough; if not, the only modification is in the thermal capacity of non-condensable gases, that should be changed from $c_p=1000$ J/(kg·K)=29 J/(mol·K) for air at about 15 °C to $c_p=1100$ J/(kg·K)=32 J/(mol·K) for a typical exhaust mixture at about 50 °C; the molar mass changes even less because the increase due to the formation of carbon dioxide practically compensates with the decrease due to water formation.

Recalling that liquid-vapour equilibrium, for ideal two-phase mixtures, implies uniform chemical potential for each species i , one arrives at Raoult's law (see [Mixtures](#)):

$$x_{i,vap}/x_{i,liq}=p_i^*(T)/p \quad (17)$$

i.e. the molar fraction of species i in the vapour phase, divided by the molar fraction in the liquid phase, is equal to the vapour pressure for the pure i -component at that temperature, p_i^* (obtained from Clapeyron's

equation or Antoine's correlation), divided by the pressure of the mixture, p . It often helps to think of the pressure of the mixture as the summation of partial pressures attributed to each i -component, $p_i = x_{i,\text{vap}} p$, so that at liquid-vapour equilibrium $p_i = x_{i,\text{liq}} p^*(T)$.

For the case of one condensing species (water), the important equations are:

- Maximum water-vapour fraction, x_{vap} (notice that 'vap' now refers to the substance and not only to the phase) dissolved in a given flue gas at given pressure p , and temperature T :

$$x_{\text{vap}} = p_i^*(T)/p \quad (18)$$

- Dew point, i.e. condensing temperature, T_{dew} , for a given pressure p , and water molar fraction $x_{i,\text{vap}}$, it is solved from:

$$x_{i,\text{vap}} = p_i^*(T_{\text{dew}})/p \quad (19)$$

- Total pressure, p , for the two-phase system at equilibrium (humid exhaust plus condensate) at temperature T :

$$p = \sum p_{i,\text{non-cond}} + p_{\text{water}}^*(T) \quad (20)$$

THERMOCHEMISTRY

A detailed thermodynamic treatment of generic reacting systems can be found [aside](#). We will focus here just in combustion reactions of simple fuels: hydrogen, carbon, and pure hydrocarbons (commercial fuels are complex mixtures of hydrocarbons; see [Fuel properties](#)).

STOICHIOMETRY, EXTENT AND AFFINITY

A combustion process involves a set $\{M_i, i=1..C\}$ of chemical species i , identified by their molecular formula M_i (M_i is also used for their molar mass), undergoing a simultaneous set of chemical reactions $\{R_i, i=1..R\}$, each one specified by its so-called stoichiometric equation:

$$\sum_{i=1}^C \nu_{ir}' M_i = \sum_{i=1}^C \nu_{ir}'' M_i \quad \text{or} \quad 0 = \sum_{i=1}^C \nu_{ir} M_i \quad \text{for } r=1..R \quad (\text{e.g. } \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}) \quad (21)$$

where the first form is preferred for kinetic studies when a direction in the process is implicit (it is said to occur from reactants (left) converting into products (right), and sometimes an arrow is used instead of the equal sign), whereas the last form is more simple for equilibrium studies where no direction is privileged. In any case, (21) serves as the mass conservation equation if M_i is the molar mass of species i , and serves to build the set of elementary conservation equations when the molecular form of M_i is considered. The ν_i are called stoichiometric coefficients for that reaction. Notice that the stoichiometric coefficients change if one writes $0=2\text{H}_2+\text{O}_2-2\text{H}_2\text{O}$, or $0=\text{H}_2+(1/2)\text{O}_2-\text{H}_2\text{O}$, or $0=\text{H}_2\text{O}-\text{H}_2-(1/2)\text{O}_2$.

Most commercial fuels are hydrocarbons (chemical notation should be briefly refreshed, e.g. to distinguish between n-octane and iso-octane). According to the stoichiometric ratio for full oxidation of a fuel, air/fuel mixtures fed to a combustor are classified as:

- Lean mixtures (little fuel content, excess of air).
- Stoichiometric mixtures (with the precise or theoretical amount of fuel as established in a given reaction as (21)).
- Rich mixtures (more fuel than needed, but excess fuel will pyrolyse to small-molecule fuels, and only small molecules appear at the exhaust).

The ratio air-to-fuel in molar base is $A_n \equiv n_{\text{air}}/n_{\text{fuel}}$, and in massic base $A_m \equiv n_{\text{air}}/n_{\text{fuel}}$, although it is often stated simply as A (but notice the values are different, though non-dimensional; e.g. theoretical air ratio for methane, $\text{CH}_4 + 2 \cdot (\text{O}_2 + 3.76 \cdot \text{N}_2) = \text{CO}_2 + 2 \cdot \text{H}_2\text{O} + 7.52 \cdot \text{N}_2$, is $A_n = 2 \cdot (1 + 3.76)/1 = 9.5$, and $A_m = A_n M_a / M_f = 9.5 \cdot 0.029 / 0.016 = 17$, sometimes written as $A = 9.5 \text{ mol}_a / \text{mol}_f = 17 \text{ kg}_a / \text{kg}_f$). The relative air-to-fuel ratio λ is with respect to the stoichiometric air-to-fuel ratio A_0 ; i.e. $\lambda \equiv A/A_0$ (now independent of the molar or massic base). In the USA, the inverse of these functions are often used, namely the fuel-to-air ratio, $f = 1/A$ (either in molar or massic base, as above), and the equivalence ratio $\phi = 1/\lambda$.

As for the products of combustion, the molar fractions are always used (also said 'volume fractions' since they are the same with the ideal-gas mixture model predominant in combustion exhaust). Notice, however, that, to avoid condensation of water inside the instruments, measurements of exhaust gases are taken on a dry mixture that is obtained by passing the exhaust gases through desiccants (an ice bath is often good enough, since most water is condensed and left behind).

When a control-mass mixture with initial composition n_{i0} reacts, the extent of the reaction at any later time, ξ (Greek letter xi, also called progress or degree of advancement of a reaction, a convenient normalised mole-account system) is defined as:

$$\xi \equiv \frac{n_i - n_{i0}}{\nu_i} \quad \text{for a given } i = \sum \nu_i M_i \quad (22)$$

The extent of a reaction marks the state of progress; to measure the tendency to progress, the chemical affinity, A , is defined:

$$A \equiv - \sum_{i=1}^C \nu_i \mu_i \quad (23)$$

such that Gibbs function variations are:

$$dG = -SdT + Vdp + \sum_{i=1}^C \mu_i dn_i = -SdT + Vdp - Ad\xi \quad (24)$$

the minus sign being introduced in the definition of A to ensure that natural evolution (entropy increase in an isolated system, or Gibbs-function decrease in a system at T and p constant) corresponds to a positive affinity, i.e. $dG = -Ad\xi \leq 0 \rightarrow$ progress, i.e. $d\xi/dt > 0$, only if $A > 0$. It is important to notice that reactions with

negative affinities can naturally progress only at the expense of other reactions with positive and larger affinities, since the real limit, at T and p constant, is $dG = -\sum A d\xi \leq 0$ for the whole set of reactions.

Although both, affinity and extent, are thermodynamic state functions, the reaction rate $d\xi/dt$ is not, similarly to heat transfer. Reaction rates depend a lot on the presence of catalysts, that have no influence on reaction equilibrium.

ENTHALPY OF FORMATION AND ABSOLUTE ENTROPY

Compounds are not conserved-entities in combustion, but atoms are. Thus, energy and entropy reference states for each atom must be agreed in reacting systems, instead of the energy and entropy reference state for each compound used in non-reacting systems. References are free to choose by the observer, but they must necessarily be consistently related. The best references are:

- Enthalpy reference: zero enthalpy is assigned to the most stable natural form of each chemical elements at standard temperature and pressure ($T^\ominus = 25^\circ\text{C} = 298.15\text{ K}$ and $p^\ominus = 100\text{ kPa}$). Enthalpies for non-elementary species at standard temperature and pressure, called standard enthalpies of formation, h_f^\ominus , are experimentally measured (usually by calorimetry, most of the times indirectly) and tabulated. Enthalpy of an species at other temperature and pressure are computed from the general relation $dh = c_p dT + (1 - \alpha T) v dp$, according to the model used (e.g. for perfect gases $h = h_f^\ominus + c_p(T - T^\ominus)$).
- Entropy reference: zero entropy is assigned to each species (not just to each elementary species but compounds too) at 0 K and any pressure, since it is an experimental fact explained by information theory that entropy changes in the limit $T \rightarrow 0$ also tend to zero. Entropy values at the standard state ($T^\ominus = 298\text{ K}$ and $p^\ominus = 100\text{ kPa}$), known as absolute standard entropies, s^\ominus , are computed by integration of experimentally measured (usually by spectrometry) thermal capacity data, according to $ds = (c_p/T)dT - \alpha v dp$, and tabulated. Standard entropy, s_i^\ominus , should not be confused with standard formation entropy, $s_f^\ominus = \sum_{i=1}^C \nu_i s_i^\ominus$.

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

$$g_f^\ominus \equiv h_f^\ominus - T^\ominus \sum_{i=1}^C \nu_i s_i^\ominus \quad \text{for the reaction of formation of the compound: } 0 = \sum \nu_i M_i. \quad (25)$$

HEATING VALUE

The standard practical heating value (PHV, also called practical calorific value, PCV) of a fuel is defined as the heat transfer to cooling water in a Junkers-type calorimeter, i.e. a flow calorimeter with inputs (fuel and air mixture, and cooling water) and output approaching standard conditions (298 K and 100 kPa), i.e. the specific combustion enthalpy, h_{PHV} (or its molar value). The fuel is burnt with excess air for complete combustion, since the heating value is independent of excess air, while the cooling flow-rate is traded off for best resolution (least uncertainty in $\dot{Q} = \dot{m}_w c_w \Delta T_w = \dot{m}_f h_{\text{PHV}}$).

However, in order to provide a common reference to allow direct combination of heating values for several reactions, a theoretical standard is defined by assuming that inlet and outlet flows run through

separated pipes for each pure chemical species. Thus, a so called standard higher heating value (HHV or h_{HHV} , sometimes known as high calorific value HCV) is defined as the heat release to the ambient when fuel, oxidiser and products flow at 298 K, 100 kPa and species-separated), and computed by adding the latent heat of the water-vapour (exiting the calorimeter above-mentioned), to the PHV. For instance, the HHV for methane is (from the [Combustion Data Table](#)) $h_{\text{HHV}}=890$ kJ/mol ($h_{\text{HHV}}=55$ MJ/kg), meaning that if a steady flow of methane is made to burn with air (or oxygen) at 100 kPa, both inlets (methane and air) being at 298 K, and the outlet is cooled to 298 K, and only CO_2 and H_2O were produced and all the water in the exhaust were condensed, 890 kJ by mole of methane will be released to the ambient (55 MJ by kg of methane). In practice, there will be just one tail-pipe and at 25 °C the water will be some 95% condensed (forming a mist of micrometric droplets) and some 5% dissolved in the gas stream, and some traces of unburnt hydrocarbons and possibly soot will also show up in the exhaust, and the measured heating value would be slightly smaller.

However, for applications where the exhaust gases are above their dew point (a very common situation since the exhaust dew point is typically below 60 °C), it is advantageous for the calculations to establish a different standard, called lower heating value (LHV or h_{LHV}), that assumes all water exits at 100 kPa and 25 °C but in the gaseous state (a virtual state not possible in practice for pure water); thus, the LHV is equal to the HHV minus the vaporisation enthalpy of the exhaust water at 25 °C (2.44 MJ/kg or 44 kJ/mol of water produced). For instance, for methane, its combustion being $\text{CH}_4+2\text{O}_2=\text{CO}_2+2\text{H}_2\text{O}$, the LHV is $h_{\text{LHV}}=890-2\times 44=802$ kJ/mol. Care is needed when using tabulated heating values, to know if they are HHV or LHV.

Notice that the heating value of a fuel depends on input and output conditions and the path followed; heat is a path variable, not a state function; HHV and LHV are defined as state functions, the negative of the reaction enthalpy ($h_{\text{LHV}}=-h_{\text{r,comb}}$), being for a given constant-pressure process. Fortunately for combustion reactions, the heat release is practically independent on pressure, and depends very little with temperature; even the difference between burning at constant pressure or at constant volume is not significant. Notice also that the heating value of a fuel must be understood as the heat released in its combustion with air (or any inert mixture with oxygen). Finally, recall that it has no sense to talk about the 'energy content' of a fuel or of any other system, since energy is only defined between two states of a closed system, by $\Delta E \equiv W|_{Q=0}$; similarly, heat is only defined as energy transfer through an impermeable boundary, by $Q \equiv \Delta E - W$.

For combustion at constant pressure, be it in a flow system (the most usual case) or in a control mass (e.g. in an ideal Diesel cycle), the energy balance is:

$$Q = \Delta H = -n_{\text{fuel}} h_{\text{HHV}} \quad (26)$$

assuming all water is in condensed form. For combustion at constant volume of a control mass (e.g. in an ideal Otto cycle), the energy balance is $Q = \Delta E = \Delta U$, but since the available data are enthalpies, $Q = \Delta(H - pV) = \Delta H - V\Delta p$. If there is no condensed matter, i.e. for initial and final gaseous states, $pV = \sum nRT$ and $Q = \Delta H - V\Delta p = \Delta H - (\sum n_{\text{final}} - \sum n_{\text{initial}})RT$; for instance, if 1 mol of CO is burnt at constant pressure in air

at 298 K and 100 kPa, the heat release is $h_{\text{HHV}}=h_{\text{LHV}}=283$ kJ/mol, whereas if the initial state is the same but the burning is inside a rigid vessel at constant volume, the heat release may range from 283 kJ/mol for a very diluted mixture to $283 \cdot 10^3 + (1-1.5) \times 8.3 \times 298 = 282$ kJ/mol for an stoichiometric CO/O₂ mixture. If there is some condensed matter, either initially or at the end, a more involved analysis is required, although, if the saturation pressure of the condense matter at the standard temperature is small, the same equation as for gaseous mixtures may be applied just considering the non-condensed species; for instance, if 1 mol of H₂ is burnt at constant pressure in air at 298 K and 100 kPa, the heat release would be $h_{\text{HHV}}=286$ kJ/mol if the exhaust water were fully condensed, $h_{\text{LHV}}=242$ kJ/mol if all the exhaust water were in its vapour state, or a value close to the HHV in the practical case, whereas if the initial state is the same but the burning is inside a rigid vessel at constant volume, the heat release may range from 242 kJ/mol for a very diluted gaseous mixture, to $286 \cdot 10^3 + (0-1.5) \times 8.3 \times 298 = 284$ kJ/mol for an stoichiometric H₂/O₂ mixture, that would produce near-zero gaseous moles. In summary, the heat release slightly varies from constant pressure to constant volume combustion, the larger variation being with the physical state of water at the end: for long-chain hydrocarbons the LHV is 6.5% lower than the HHV, the difference increasing with decreasing carbon content (6.9% for C₈H₁₈, 9.1% for CH₄ and 15.4% for H₂).

All the above-defined heating values are global values for a non-equilibrium combustion process between the initial and the final states quoted, but no difference is found if the instantaneous equilibrium changes are introduced and the heating value is defined as the enthalpy of reaction (changed of sign because the assumed direction for the heat release), i.e.

$$h_{\text{HHV}} = -h_r^\oplus \equiv -\left. \frac{\partial H}{\partial \xi} \right|_{p,T} = -\sum_{i=1}^C \nu_i h_i^\oplus = -\sum_{i=1}^C \frac{\dot{n}_i h_i^\oplus}{\dot{n}_{\text{fuel,in}}} \quad \text{and} \quad h_{\text{LHV}} = h_{\text{HHV}} - \nu_{\text{H}_2\text{O}} h_{\text{lv}}^\oplus \quad (27)$$

i.e. the ratio of the change of the enthalpy of a reacting system at equilibrium to the change in the extent of reaction when an infinitesimal advance in the extent of the combustion reaction (scaled per unit of amount of fuel) takes place. Similarly, the heat release at constant volume can be identified with the internal energy of reaction at constant volume, or with the internal energy of reaction at constant pressure for the case: $\partial U / \partial \xi|_{V,T} = \partial U / \partial \xi|_{p,T} + \partial U / \partial p|_{\xi,T} \partial p / \partial \xi|_{V,T}$. The value for the molar enthalpy of water, for the liquid-to-vapour phase change at $T^\oplus=298$ K is $h_{\text{lv}}^\oplus=44.0$ kJ/mol=2442 kJ/kg.

MAXIMUM WORK

A combustion process may exchange both heat and work with the surroundings, only heat, only work, or nothing of the two. The energy balance of the combustor relates the heat and work flows with the entrance and exit temperatures.

The work obtainable from the combustion of a fuel depends on the actual process (as does the heat release); if the combustion is performed in a rigid open chamber (as in a gas-turbine), no work will be produced (at the combustion chamber), but if it is performed in a chamber with moving parts (as in a reciprocating engine), some work will be produced. The maximum obtainable work, or the minimum required work to reverse the process, for a steady process in the presence of an environment at temperature T_0 is the change in flow-exergy from inlet to outlet, $\Delta \psi = \Delta h_i - T_0 \Delta s$, that for standard conditions is:

$$w_{\min}^{\oplus} = \Delta\psi^{\oplus} = g_r^{\oplus} - h_r^{\oplus} - T^{\oplus} s_r^{\oplus} = \sum \nu_i h_{f,i}^{\oplus} - T^{\oplus} \sum \nu_i s_i^{\oplus} \quad \text{for a given } 0 = \sum \nu_i M_i \quad (28)$$

where $h_{f,i}^{\oplus}$ are standard enthalpies of formation of the participating compounds $i=1..C$, and s_i^{\oplus} their absolute standard entropies. For instance, for the theoretical combustion of methane with oxygen, $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$, $\Delta\psi^{\oplus} = g_r^{\oplus} - h_r^{\oplus} - T^{\oplus} \sum \nu_i s_i^{\oplus} = -890 \cdot 10^3 - 298 \times (214 + 2 \times 70 - 186 - 2 \times 205) = -817 \cdot 10^3$ J/mol, i.e. 817 kJ/mol of work might be produced (the remainder to the heating value being evacuated as heat, on account of the energy balance $q+w=\Delta h_t$). Similarly, for $\text{H}_2 + (1/2)\text{O}_2 = \text{H}_2\text{O}$ a maximum of $\Delta\psi^{\oplus} = -286 \cdot 10^3 - 298 \times (70 - 131 - 0.5 \times 205) = -237 \cdot 10^3$ J/mol, i.e. as much as 237 kJ/mol of work might be generated. If an energy efficiency is defined as the quotient between work produced and heating value, the maximum efficiency would be 0.92 for methane and 0.83 for hydrogen (but mind that it would be 1.002 for carbon).

Recall here that there is a small difference between the maximum work obtainable from combustion and the maximum work obtainable from the fuel (in spite of ambient-air having no exergy), because the streams (to be considered separate components, since the thermochemical values refer to separate streams) have some chemical exergy relative to the atmosphere, even when at T^{\oplus} and p^{\oplus} . For instance, the maximum work obtainable from methane is $\psi^{\oplus}_{\text{CH}_4} = 831$ kJ/mol (against the 817 kJ/mol above), computed by adding the exergy of one mole of carbon dioxide, $\psi^{\oplus}_{\text{CO}_2} = 20$ kJ/mol, and two moles of water, $\psi^{\oplus}_{\text{H}_2\text{O}} = 1.3$ kJ/mol, and subtracting the exergy of two moles of oxygen, $\psi^{\oplus}_{\text{O}_2} = 3.9$ kJ/mol, to the exergy of the $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ reaction, $|\psi^{\oplus}_r| = 817$ J/mol. Similarly, the exergy of hydrogen at the standard state is $\psi^{\oplus}_{\text{H}_2} = 236$ kJ/mol, to be compared with the exergy from $\text{H}_2 + (1/2)\text{O}_2 = \text{H}_2\text{O}$, $|\psi^{\oplus}_r| = 237$ J/mol.

Although an indirect realisation of the same global reaction can approach that maximum work, as in fuel cells, direct combustion processes cannot approach those values. To begin with, if a constant-pressure combustion process (the difference with a constant-volume process being small) were very slow, the heat release would just dissipate to the environment without any possible work, i.e. all the exergy of the reaction would be lost by entropy generation inside. If the process is rapid, as most combustions really are, it may be assumed adiabatic to a first approximation, the heating value being spent in heating the exhaust gases themselves instead of in heat transfer to another medium; no work is actually produced, but some work may be obtained afterwards, since the exhaust is hotter than the environment.

To evaluate the maximum work obtainable from the adiabatically burnt gases, its exergy, one must compute the flow exergy, $\Delta\psi = \Delta h_t - T_0 \Delta s$, of the hot exhaust stream relative to the atmosphere. It is good enough to retain just the thermomechanical exergy, since the chemical exergy of dilution into the atmosphere is much smaller. For hydrogen at standard conditions, for instance, the maximum obtainable work (236 kJ/mol in an ideal fuel cell) is reduced to some 170 kJ/mol in the adiabatic exhaust at 100 kPa and 2480 K after isobaric combustion of hydrogen with stoichiometric air, or to some 180 kJ/mol in the adiabatic products at 870 kPa and 2950 K after isochoric combustion with stoichiometric air, due to the unavoidable entropy generation inherent to the combustion process (entropy increase without entropy flow).

Burning with pure oxygen increases the temperature of the adiabatic exhaust and thus its exergy. For instance, in the case of H₂/O₂, some 190 kJ/mol of exergy per mole of hydrogen may be obtained from the very hot adiabatic exhaust at some 4000 K and 100 kPa (difficult to compute because of dissociations). In spite of this advantage of higher temperatures (already discovered by Carnot in the most general case), practical combustion is most of the times with common air, even in some excess to further decrease the temperature achieved, since common materials cannot withstand such high temperatures.

ADIABATIC COMBUSTION TEMPERATURE

The adiabatic model very accurately predicts homogeneous combustion temperatures in gas phase, because of the very poor thermal conductivity of gases and the low speed (<0.5 m/s laminar burning speed for ordinary hydrocarbon/air mixtures). The adiabatic model, however, overestimates the temperature in the case of high radiation emission in non-premixed flames, and for high speeds flows relative to solids (as in afterburner heat-exchangers).

The adiabatic temperature is a thermodynamic state variable that results from the conversion of internal chemical energy to internal thermal energy after the combustion process takes place, and depends on the actual fuel and oxidiser (e.g. CH₄/air), their ratio (e.g. lean, stoichiometric or rich mixtures), their initial thermodynamic state (e.g. premixed gases at 298 K and 100 kPa, although energies associated to mixing and pressure are negligible), and the type and proportions of the compounds formed. It can be measured at the exhaust of an adiabatic combustor, or just after a flame, but the practical difficulties in ensuring minimal heat losses, particularly from the thermometer probe, render a theoretical computation more precise than the actual measurement.

The problem with the computation is that the type and proportions of the compounds formed must be known, what is partially solved assuming a set of compounds dictated by experience, and assuming that they are in thermodynamic equilibrium at that pressure and temperature. But, even for the simplest case of a constant-pressure combustion process (very good for open combustors since the pressure only rises some 2% after a deflagration), the temperature is the unknown result and thus the equilibrium composition cannot be directly computed, yielding an implicit and stiff algebraic mathematical problem.

The energy balance for a generic reactor is:

$$\frac{dE}{dt} = \dot{W} + \dot{Q} + \sum_{j=1}^{\text{openings}} \dot{n}_j h_j = \dot{W} + \dot{Q} + \sum_{j=1}^{\text{openings}} \dot{n}_j \left[\sum_{i=1}^C x_{ij} h_{f,i}^{\oplus} + \sum_{i=1}^C x_{ij} (h_i - h_{f,i}^{\oplus}) \right] \quad (29)$$

where the enthalpy contributions at each opening j is split in a chemical part (proportional to the molar fraction i of each chemical component of standard enthalpies of formation $h_{f,i}^{\oplus}$, and a thermal part (from the standard state to their actual state at the opening) of the participating compounds $i=1..C$. Notice that the components are assumed known at entry and exit openings, but their molar fractions may be functions of the temperature and pressure (e.g. when there is chemical equilibrium at an exit).

A drastic simplification of the energy balance occurs if one assumes complete combustion, because then one can resolve the exhaust composition independently of temperature. This approach is useful for Combustion thermodynamics

combustion of lean mixtures in air, but not for combustion in pure oxygen where temperatures are higher. With this simplification the adiabatic temperature for a stoichiometric H₂/air mixture, for instance, is computed to be 2350±50 K, in good agreement with a measure of 2300±100 K, whereas the adiabatic temperature for a stoichiometric H₂/O₂ mixture is computed to be 5400±200 K, in clear disagreement with a measure of 3000±100 K.

With this complete-oxidation model, separating the entry flows and the exit flows, assuming $\dot{W} = 0$ (no work input/output through the impermeable walls), and assuming there is no phase change from the standard state to the actual input or output states (see below), the energy balance for a steady state combustor is

$$0 = \dot{Q} + \dot{n}_{\text{entry}} \sum_{i=1}^C (x_i h_i^{\oplus} + x_i c_{p_i} (T - T^{\oplus})) - \dot{n}_{\text{exit}} \sum_{i=1}^C (x_i h_i^{\oplus} + x_i c_{p_i} (T - T^{\oplus})) \quad (30)$$

Notice that water must be treated as an ideal gas to apply (30); otherwise, the enthalpy of phase change must be added.

The actual mass balance or, better, molar balance for a combustor may be established in different ways, according to the scale of amount of substance chosen. The main choices to write the so called mixture equation are: per unit amount-of-substance of input stream, per unit amount-of-substance of output stream, and per unit amount-of-fuel in the input stream. The last two usually take the form:

$$aM_{\text{fuel}} + bM_{\text{air}} + cM_{\text{other}} = \sum_{i=1}^C x_i M_i \quad \text{and} \quad M_{\text{fuel}} + AM_{\text{air}} + BM_{\text{other}} = \sum_{i=1}^C v_i M_i \quad (31)$$

where a , b , c , A and B are numeric factors ($A=b/a$ is the air/fuel ratio), M_i the molar masses of each component (associated to the molecular formula stated; e.g. $aC+b\text{Air}=x_{\text{CO}}\text{CO}+x_{\text{CO}_2}\text{CO}_2+x_{\text{O}_2}\text{O}_2+x_{\text{N}_2}\text{N}_2$), x_i are the molar fractions in the exhaust ($\sum x_i=1$), and v_i are the amounts of exhaust species per unit amount of fuel (not the stoichiometric coefficients).

Choosing the first option in (31), i.e. per unit amount-of-substance exiting, the energy balance (30) with the definition of LHV in (27), yields:

$$\begin{aligned} 0 &= q + a \left(h_{\text{fuel}}^{\oplus} + c_{p_{\text{fuel}}} (T - T^{\oplus}) \right) + b \left(h_{\text{air}}^{\oplus} + c_{p_{\text{air}}} (T - T^{\oplus}) \right) + c \left(h_{\text{other}}^{\oplus} + c_{p_{\text{other}}} (T - T^{\oplus}) \right) - \sum_{i=1}^{C_{\text{exhaust}}} x_i \left(h_i^{\oplus} + c_{p_i} (T - T^{\oplus}) \right) \\ &= q + ah_{\text{LHV}} + (ac_{p_{\text{fuel}}} + bc_{p_{\text{air}}} + cc_{p_{\text{other}}}) (T_{\text{in}} - T^{\oplus}) - \sum_{i=1}^{C_{\text{exhaust}}} x_i c_{p_i} (T_{\text{out}} - T^{\oplus}) \end{aligned} \quad (32)$$

which can be read as follows: the thermal energy in the exhaust stream (the last term) is the contribution of the external heat added through the walls per unit of exhaust q (zero for an adiabatic process), plus the chemical heating value of the fuel input (the lower heating value, h_{LHV} , since water is taken as a gas), plus the thermal energy in the intake stream.

The adiabatic combustion temperature is obtained from (32) with $q=0$:

$$T_{ad} = T^{\oplus} + \frac{ah_{LHV} + (ac_{p_{fuel}} + bc_{p_{air}} + cc_{p_{other}})(T_{in} - T^{\oplus})}{\sum_{i=1}^{C_{exhaust}} x_i c_{p_i}} \approx T^{\oplus} + \frac{ah_{LHV}}{c_{p_{air}}} \quad (33)$$

where the last simplification (a most crude approach) neglects the thermal enthalpy input, and approximates the thermal properties of the exhaust gas mixture by those of air, i.e. $c_p=1000 \text{ J}/(\text{kg}\cdot\text{K})=29 \text{ J}/(\text{mol}\cdot\text{K})$ for cold air, or better $c_p=34 \text{ J}/(\text{mol}\cdot\text{K})$ to account for the growth of thermal capacity with temperature. Of course, the best precision is obtained with the integration $\int c_p/T dT$ instead of the approximation $c_p\Delta T$ in (30), but the first form of (33) with $c_p=34 \text{ J}/(\text{mol}\cdot\text{K})$ for any diatomic molecule, $c_p=47 \text{ J}/(\text{mol}\cdot\text{K})$ for water vapour, and $c_p=54 \text{ J}/(\text{mol}\cdot\text{K})$ for carbon dioxide (Table 2), is thought to be the best compromise on precision/effort for non-programmed computations.

One may wonder why all values of the maximum adiabatic combustion temperature in air are so close ($2300\pm 200 \text{ K}$, from combustion data [Table](#)), in spite of the widely different heating values (e.g. $h_{LHV}=10 \text{ MJ}/\text{kg}$ for CO and $h_{LHV}=121 \text{ MJ}/\text{kg}$ for H_2). A simple explanation can be found for hydrocarbons, C_nH_m ; their LHV may be approximated by the LHV of $n\text{C}+(m/2)\text{H}_2$, which is $(n\cdot 394+m\cdot 242/2) \text{ kJ}/\text{mol}$. The adiabatic jump is $T_{ad}-T^{\oplus}=h_{LHV}/\sum n_i c_{p,air}$, and it happens that the amount of substance of the products varies almost proportional to the molar heating value. For the complete stoichiometric combustion in air, $\text{C}_n\text{H}_m+(n+m/4)\cdot(\text{O}_2+3.76\text{N}_2)=n\text{CO}_2+(m/2)\text{H}_2\text{O}+3.76\cdot(n+m/4)\cdot\text{N}_2$, and taking a mean value $c_{p,air}=40 \text{ J}/(\text{mol}\cdot\text{K})$ for the exhaust gas, the total mole number in the products is $n\cdot(1+3.76)+m\cdot(1/2+3.6/4)$, which makes $T_{ad}-T^{\oplus}=(n\cdot 394+m\cdot 121)/(n\cdot 0.190+m\cdot 0.058) \text{ K}$, a biparametric function almost constant, of value $T_{ad}-T^{\oplus}\approx 2000 \text{ K}$.

When dissociation is important due to the high temperatures associated to near-stoichiometric combustion, or due to lack of oxygen in rich flames, computation of adiabatic temperatures is coupled to computation of equilibrium composition. The effect of pressure on adiabatic temperature is through its effect on equilibrium composition: at high pressure dissociation is negligible and the complete-combustion adiabatic temperature gets its highest value, whereas reducing the pressure increases dissociation in accordance with Le Châtelier principle, lowering adiabatic temperature.

EQUILIBRIUM COMPOSITION

The intake to a combustor is not at equilibrium (it would not react if it were), although it may be considered at a metastable equilibrium (it would not react if not ignited), or even at separate fuel and air inlets at their own equilibrium conditions before mixing. The exhaust from a combustor may be at equilibrium (not with the surroundings but within itself, i.e. in chemical equilibrium at a given T and p), if the combustion process has had time enough to develop completely. In practice, there are always some partial reactions so slow that they do not reach equilibrium in the times considered, as for some trace contaminants, but the assumption of perfect chemical equilibrium is a very good approximation to the overall real combustion process, and, on top of that, serves to explain why a further simplification, the complete combustion model, is an acceptable approximation to many combustion processes.

Chemical equilibrium in absence of external force fields implies no gradient of chemical potential, $\nabla\mu_i=0$, for each component $i=1..C$, and no affinity to go on, $A_r=0$, for each reaction $r=1..R$. The latter establishes a relation between molar fractions in the equilibrium composition x_i , and T and p , for a given reaction $0=\sum \nu_i M_i$, that for a reacting ideal gas mixture is (see [Chemical reactions](#)):

$$\prod_{i=1}^C x_i^{\nu_i} = \left(\frac{p}{p^\oplus}\right)^{-\sum \nu_i} K(T, p^\oplus) = \left(\frac{p}{p^\oplus}\right)^{-\sum \nu_i} \exp\left[\frac{-g_r^\oplus}{RT^\oplus} + \frac{h_r^\oplus}{RT^\oplus} \left(1 - \frac{T^\oplus}{T}\right)\right] \quad (34)$$

where the approximation $\ln K=A+B/T$ for the reaction constant K has been applied, and the constants g_r^\oplus (standard Gibbs function of reaction) and h_r^\oplus (standard enthalpy of reaction) are computed from the standard enthalpies and Gibbs functions of formation by:

$$h_r^\oplus = \sum_{i=1}^C \nu_i h_{f_i}^\oplus, \quad g_r^\oplus = \sum_{i=1}^C \nu_i g_{f_i}^\oplus \quad (35)$$

For systems that are not at equilibrium yet, the ratio calculated from the mass-action law is called a reaction quotient Q . The Q -values of a closed system have a tendency to reach a limiting value over time, the equilibrium constant K .

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