Chapter 23
Reacting Mixtures

23.1 Stoichiometric Coefficients

In a chemical reaction, the composition of a mixture changes due to the formation of chemical compounds. The chemical changes are expressed in reaction equations, e.g., for the formation of water from hydrogen and oxygen, where two hydrogen molecules and one oxygen molecule react to form two water molecules,

$$2\mathrm{H}_2 + 1\mathrm{O}_2 \rightleftharpoons 2\mathrm{H}_2\mathrm{O} \tag{23.1}$$

or

$$-2\mathrm{H}_2 - 1\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} = 0\ . \tag{23.2}$$

The first reaction equation uses arrows to indicate the possibility of forward and backward reactions, while the second is written as an actual equation. The coefficients $(-2,\ -1,\ +2)$ are the stoichiometric coefficients γ_α, which count how many particles of species α are involved in the reaction. Positive stoichiometric coefficients refer to products, negative coefficients refer to reactants.

Chemical reactions can occur forward and backward. In chemical equilibrium, the composition of the reacting mixture does not change and there are as many forward as backward reactions. Thus, the definition of "forward" and "backward" is somewhat arbitrary, which implies that the signs of the stoichiometric coefficients can be switched. Moreover, multiplication of all stoichiometric coefficients with the same factor is possible as well, e.g., an alternative chemical equation for the above reaction is (multiplication with $-\frac{1}{2}$)

$$\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 - \mathrm{H}_2\mathrm{O} = 0 \tag{23.3}$$

with the stoichiometric coefficients $\left(1, \frac{1}{2}, -1\right)$.

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23.2 Mass and Mole Balances

Due to chemical reactions, the mole numbers of all components involved in the reaction change. The reaction rate λ is defined as the number of net reactions (counted in moles) per unit time and volume. The reaction rate can be positive or negative, depending whether forward or backward reactions prevail. For each mole of reactions there are γ_α moles of component α produced or consumed. The rate of change of mole number for component α reads

$$\frac{dn_\alpha}{dt} = \gamma_\alpha V \lambda \, . \tag{23.4}$$

Multiplication with the molar mass M_α gives the corresponding rate of change for mass,

$$\frac{dm_\alpha}{dt} = \gamma_\alpha M_\alpha V \lambda \, . \tag{23.5}$$

The total mass, $m = \sum_\alpha m_\alpha$, is conserved,[1] that is

$$\frac{dm}{dt} = V\lambda \sum_\alpha \gamma_\alpha M_\alpha = 0 \, , \tag{23.6}$$

where the summation has to be taken over all substances involved in the reaction, that is products and reactants. Thus, the mass of the products is equal to the mass of the reactants,

$$\sum_\alpha \gamma_\alpha M_\alpha = 0 \, . \tag{23.7}$$

Division of (23.4) by the stoichiometric coefficient, and taking the difference of the result for different components gives a conservation law,

$$\frac{d}{dt}\left(\frac{n_\alpha}{\gamma_\alpha} - \frac{n_\beta}{\gamma_\beta}\right) = 0 \, . \tag{23.8}$$

This can be integrated to give

$$\frac{n_\alpha}{\gamma_\alpha} - \frac{n_\beta}{\gamma_\beta} = \frac{n_\alpha^0}{\gamma_\alpha} - \frac{n_\beta^0}{\gamma_\beta} \, , \tag{23.9}$$

where n_a^0 are the mole numbers at the beginning of the reaction. For the water reaction, for example, we find

$$\frac{n_{H_20}}{2} - \frac{n_{O_2}}{-1} = \frac{n_{H_20}^0}{2} - \frac{n_{O_2}^0}{-1} \quad , \quad \frac{n_{H_2O}}{2} - \frac{n_{H_2}}{-2} = \frac{n_{H_20}^0}{2} - \frac{n_{H_2}^0}{-2} \tag{23.10}$$

or

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[1] As long as we ignore the relativistic mass defect, which is extremely small.

$$\frac{n_{H_2O}}{2} + n_{O_2} = \frac{n^0_{H_2O}}{2} + n^0_{O_2} \quad , \quad n_{H_2O} + n_{H_2} = n^0_{H_20} + n^0_{H_2} \; . \tag{23.11}$$

A third equation, for O_2 and H_2, is not shown; this equation is a linear combination of those above, and does not give additional information.

Alternatively, one can balance the mole numbers of elements, since these must be conserved (nuclear reactions excluded). The only elements in the water reaction are oxygen and hydrogen, and the conservation of elements gives rise to the equations

$$\mathrm{O} : n_{H_2O} + 2n_{O_2} = n^0_{H_2O} + 2n^0_{O_2} \quad , \quad \mathrm{H} : 2n_{H_2O} + 2n_{H_2} = 2n^0_{H_2O} + 2n^0_{H_2} \; . \tag{23.12}$$

Obviously, this is equivalent to the previous equations. Balancing of elements must be used when multiple reactions occur.

23.3 Heat of Reaction

Chemical reactions are accompanied by changes in energy. We consider a mixture in a piston-cylinder system at (T, p), in which reactions take place at constant pressure and temperature. The heat of reaction is defined as the amount of heat that must be exchanged to keep temperature and pressure constant.

Since the system is isobaric, the first law assumes the form

$$H_2 - H_1 = Q_{12} \; . \tag{23.13}$$

The initial enthalpy is

$$H_1 = \sum_\alpha n^1_\alpha \bar{h}_\alpha \; , \tag{23.14}$$

and when a total of $\Lambda = \int_1^2 V\lambda dt$ moles of net reactions take place, the final enthalpy is

$$H_2 = \sum_\alpha \left(n^1_\alpha + \gamma_\alpha \Lambda \right) \bar{h}_\alpha \; . \tag{23.15}$$

Thus, the heat of reaction for one mole of reactions is[2]

$$\Delta\bar{h}_R \left(T, p \right) = \frac{Q_{12}}{\Lambda} = \sum_\alpha \gamma_\alpha \bar{h}_\alpha \; . \tag{23.16}$$

A reaction with $\Delta\bar{h}_R < 0$ is an exothermic reaction, heat must be withdrawn to keep the temperature constant. A reaction with $\Delta\bar{h}_R > 0$ is an endothermic reaction, heat must be added to keep the temperature constant.

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[2] Here we have implicitely assumed an ideal mixture, where the enthalpy $\bar{h}_\alpha$ of the component is not affected by the change of composition, so that $\bar{h}^1_\alpha = \bar{h}^2_\alpha$.

The heat of reaction can be measured. Normally, one finds $\Delta\bar{h}_R$ tabulated at standard conditions, i.e. at $T_0 = 298.15\,\mathrm{K}$, $p_0 = 1\,\mathrm{bar}$. Some values are given in the following table:

$$\begin{array}{lll}
\frac{1}{2}\mathrm{H}_2 \rightleftharpoons \mathrm{H} & : & \Delta\bar{h}_R = 218.0\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{O} & : & \Delta\bar{h}_R = 249.2\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{H}_2\mathrm{O}(l) & : & \Delta\bar{h}_R = -285.8\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{H}_2\mathrm{O}(v) & : & \Delta\bar{h}_R = -241.8\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{C} + \frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{CO} & : & \Delta\bar{h}_R = -110.5\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{C} + \mathrm{O}_2 \rightleftharpoons \mathrm{CO}_2 & : & \Delta\bar{h}_R = -393.5\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\frac{3}{2}\mathrm{H}_2 + \frac{1}{2}\mathrm{N}_2 \rightleftharpoons \mathrm{NH}_3 & : & \Delta\bar{h}_R = -46.2\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\frac{1}{2}\mathrm{H}_2 + \frac{1}{2}\mathrm{J}_2 \rightleftharpoons \mathrm{HJ} & : & \Delta\bar{h}_R = 25.9\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O} \rightleftharpoons \frac{1}{6}\mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6 + \mathrm{O}_2 & : & \Delta\bar{h}_R = 466.3\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{CH}_4 + 2\mathrm{O}_2 \rightleftharpoons \mathrm{CO}_2 + 2\mathrm{H}_2\mathrm{O}(l) & : & \Delta\bar{h}_R = -890.3\frac{\mathrm{kJ}}{\mathrm{mol}} \\
\mathrm{CH}_4 + 2\mathrm{O}_2 \rightleftharpoons \mathrm{CO}_2 + 2\mathrm{H}_2\mathrm{O}(v) & : & \Delta\bar{h}_R = -802.3\frac{\mathrm{kJ}}{\mathrm{mol}}
\end{array}$$

If one of the products is water, the heat of reaction depends on whether the product water is liquid (l) or vapor (v). Note that a change of sign or value of the stoichiometric coefficients changes sign and value of the heat of reaction; e.g., for the reaction $2\mathrm{H}_2\mathrm{O}\,(l) \rightleftharpoons 2\mathrm{H}_2 + 1\mathrm{O}_2$, we find $\Delta\bar{h}_R = 571.6\frac{\mathrm{kJ}}{\mathrm{mol}}$.

23.4 Heating Value

The heating value is defined as the energy released in the combustion of 1 kg of fuel at reference conditions. One distinguishes between the lower heating value (LHV), where the product water is vapor (v) and the higher heating value (HHV), where the product water is liquid (l). The difference is just the heat of evaporation of the the product water at standard reference temperature T_0 which is $2442\frac{\mathrm{kJ}}{\mathrm{kg}}$ or $43.96\frac{\mathrm{kJ}}{\mathrm{mol}}$.

For instance for the combustion of methane (CH_4), the higher and the lower heating values are

$$\mathrm{HHV} = \frac{\left|\Delta\bar{h}_R\,(l)\right|}{M_{\mathrm{CH}_4}} = 55643\frac{\mathrm{kJ}}{\mathrm{kg}} \quad , \quad \mathrm{LHV} = \frac{\left|\Delta\bar{h}_R\,(v)\right|}{M_{\mathrm{CH}_4}} = 50150\frac{\mathrm{kJ}}{\mathrm{kg}} \; .$$

23.5 Enthalpy of Formation

When we discussed the measurement of properties, it became clear that internal energy, enthalpy and entropy cannot be measured directly. What can be measured is, for instance, the specific heat at constant pressure, and the thermal equation of state. The enthalpy follows by integration, as shown in (16.34), which for the molar enthalpy of α assumes the form

$$\bar{h}_\alpha(T,p)-\bar{h}^0_\alpha = \\ =\int_{T_0}^{T}\bar{c}_{p,\alpha}(T',p_0)\,dT'+\int_{p_0}^{p}\left[\bar{v}_\alpha(T,p')-T\left(\frac{\partial v_\alpha}{\partial T}\right)_{p'}\right]dp'+\sum_i \mathit{\Delta}\bar{h}_{\alpha,i}\ . \tag{23.17}$$

When chemical reactions take place, the reference enthalpy $\bar{h}^0_\alpha = \bar{h}_\alpha(T_0,p_0)$ cannot be chosen arbitrarily. Indeed, for a reaction occurring at (T_0,p_0) the heat of reaction—which can be measured—is $\mathit{\Delta}\bar{h}_R(T_0,p_0) = \sum\gamma_\alpha\bar{h}^0_\alpha$. Thus, the reference enthalpies $\bar{h}^0_\alpha$ for different substances must be properly related, so that they give the proper, i.e., measured, heat of reaction—for all possible reactions.

To ensure this, the following convention is used to define the reference enthalpies as *enthalpies of formation* $\bar{h}^0_f$ at (T_0,p_0): Stable elements at (T_0,p_0), such as O_2, N_2, H_2, C are assigned values of zero enthalpy,

$$\bar{h}^0_{f,\alpha}=0\quad\text{(stable elements)}\ . \tag{23.18}$$

The values $\bar{h}^0_{f,\alpha}$ for compounds follows from measurement of $\mathit{\Delta}\bar{h}_R$. For instance for the water reaction

$$\mathit{\Delta}\bar{h}_R=\bar{h}^0_{f,\mathrm{H_2O}}-\bar{h}^0_{f,\mathrm{H_2}}-\frac{1}{2}\bar{h}^0_{f,\mathrm{O_2}}=\bar{h}^0_{f,\mathrm{H_2O}}\ . \tag{23.19}$$

While it would be convenient to use the $\bar{h}^0_{f,\alpha}$ as reference for thermodynamic property tables, this is most often not done. Most property tables that list enthalpy and internal energy as functions of temperature and pressure refer to other reference states. For ideal gas tables it is customary to scale such that the extrapolated enthalpy at $T = 0\,\mathrm{K}$ is zero. Vapor tables often have the internal energy or the enthalpy at the triple point set to zero. Thus, the tabulated values must be re-scaled before they are used for computations involving chemical reactions.

We discuss how the proper data can be found, when the molar enthalpy $\tilde{h}_\alpha(T,p)$ is tabulated. When no chemical reactions occur, the tabulated data can be used as is. However, when chemical reactions are considered, the tabulated values $\tilde{h}_\alpha(T,p)$ must be corrected to the proper reference. Since enthalpy differences are independent of the choice of the reference state, and since the enthalpy of formation is the enthalpy at (T_0,p_0), we have $\bar{h}_\alpha(T,p)-\bar{h}^0_{f,\alpha}=\tilde{h}_\alpha(T,p)-\tilde{h}_\alpha(T_0,p_0)$, or

$$\bar{h}_\alpha(T,p)=\bar{h}^0_{f,\alpha}+\left[\tilde{h}_\alpha(T,p)-\tilde{h}_\alpha(T_0,p_0)\right]\ . \tag{23.20}$$

Here, $\tilde{h}_\alpha(T,p)$ denotes tabulated enthalpy values, and $\bar{h}_\alpha(T,p)$ denotes the enthalpies with proper reference value that must be used for the discussion of chemical reactions.

Water is a common reaction product, in particular when combustion of fuels is considered. Pure water at (T_0, p_0) is liquid, with $\bar{h}^0_{f,\mathrm{H_2O}}(l) = -285.83\frac{\mathrm{kJ}}{\mathrm{mol}}$, but when the product is a gas mixture some or all of the water can be in the vapor state, with $\bar{h}^0_{f,\mathrm{H_2O}}(v) = -241.82\frac{\mathrm{kJ}}{\mathrm{mol}}$; see the section on psychrometrics for more discussion.

23.6 The Third Law of Thermodynamics

Also the entropy of a substance can be determined from integration based on measurements of specific heat and the thermal equation of state. Equation (16.35) written for the molar entropy of component α reads

$$\bar{s}_\alpha(T,p) - \bar{s}^0_{f,\alpha} = \int_{T_0}^{T} \frac{\bar{c}_{p,\alpha}(T', p_0)}{T'} dT' - \int_{p_0}^{p} \left(\frac{\partial \bar{v}_\alpha}{\partial T}\right)_{p'} dp' + \sum_i \frac{\Delta \bar{h}_{\alpha,i}}{T_i}\,, \tag{23.21}$$

with the entropies of formation $\bar{s}^0_{f,\alpha} = \bar{s}_\alpha(T_0, p_0)$.

The *Third Law of Thermodynamics*, formulated by Walther Nernst (1864-1941) based on experimental evidence, states that at absolute zero ($T = 0\,\mathrm{K}$), the entropy of any crystalline substance is a constant, and independent of pressure and other properties (e.g. magnetization). Based on the microscopic definition of entropy, $S = k \ln \Omega$, Max Planck (1858-1947) found that the value of the constant depends on the quantum mechanical ground state, and it is zero for crystals that only have one ground state ($\Omega = 1$); then $s(T = 0\,\mathrm{K}) = 0$. Systems with more ground states have a residual entropy.

The third law allows to determine the entropy of formation $\bar{s}^0_{f,\alpha} = \bar{s}_\alpha(T_0, p_0)$ from (23.21) by evaluating it at $T = 0\,\mathrm{K}$ and $p = p_0$, which yields [3]

$$\bar{s}^0_{f,\alpha} = \bar{s}_\alpha(T_0, p_0) = \int_0^{T_0} \frac{\bar{c}_{p,\alpha}(T', p_0)}{T'} dT' + \sum_i \frac{\Delta \bar{h}_{\alpha,i}}{T_i}\,. \tag{23.22}$$

For substances with residual entropy, the latter must be added on the right hand side. Thus, the third law assigns absolute values to the entropy constants $\bar{s}^0_\alpha = \bar{s}_\alpha(T_0, p_0)$, i.e., the entropies of formation, which can be found in tables.

Most data tables for ideal gases show the entropy values $\bar{s}_\alpha(T, p_0)$ with respect to the proper reference, so that the tabulated value $\bar{s}_\alpha(T_0, p_0)$ is the entropy of formation of α at standard reference conditions. In other words, in contrast to enthalpy data, tabulated entropy data normally needs not to be corrected. A notebale exception are saturation tables, e.g., for water one

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[3] Note that the sign of the enthalpies of phase change, $\Delta \bar{h}_{\alpha,i}$, depends on the direction of the phase change as the line of integration crosses a saturation curve in the p-T-plane. When the integration goes from (T_0, p_0) to $(0\mathrm{K}, p_0)$, the $\Delta \bar{h}_{\alpha,i}$ are negative. For (23.22) the sign was switched, so that the $\Delta \bar{h}_{\alpha,i}$ appear with a plus sign.

often finds the reference set such that the entropy of liquid at the triple point is set to zero.

23.7 The Third Law and Absolute Zero

An interesting implication of the third law is that a temperature of absolute zero cannot be reached in a finite number of process steps. This can best be shown with the help of the T-s-diagram in Fig. 23.1, which shows lines of constant property ψ (e.g., pressure, magnetization, ...).

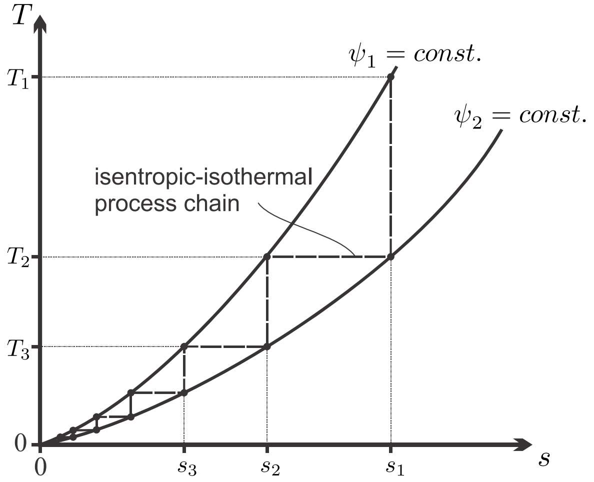

Fig. 23.1 Series of isothermal-isentropic processes between lines of constant ψ to reach low temperatures; ψ can be any property (except T, s)

Due to the third law, the lines of constant ψ all emerge from one point at $T = 0\,\mathrm{K}$. To reach low temperatures, one can take a relatively large amount of substance at (T_1, ψ_1) and subject it to an adiabatic process ending at (T_2, ψ_2). Next, one takes a part of the substance at (T_2, ψ_2) and brings it to (T_2, ψ_1) isothermally, where the rest of substance at (T_2, ψ_2) serves as a temperature reservoir. Now one repeats the series of adiabatic and isothermal processes, with smaller and smaller amounts of substance. The resulting zigzag process is shown in the figure, where for simplicity the adiabatic processes are drawn as adiabatic reversible—i.e., isentropic—processes. Since the curves of constant ψ meet in the origin, the distance between the curves becomes smaller and smaller, and each step leads to a temperature reduction smaller than the previous. Accordingly, the heat $\delta q = T ds$ removed per unit mass in each isothermal step becomes smaller and smaller as well. Evidently, absolute zero cannot be reached with a finite number of steps.

Another conclusion from the third law refers to the specific heat: When phase changes are excluded, specific heat and entropy are related by

$$\bar{s}(T,p) = \int_0^T \frac{\bar{c}_p(T',p)}{T'} dT' \ . \tag{23.23}$$

Entropy must remain finite in the limit $T \to 0\,\mathrm{K}$, which implies that the specific heat must vanish in the limit,

$$\lim_{T \to 0\,\mathrm{K}} \bar{c}_p(T',p) = 0 \ . \tag{23.24}$$

23.8 Law of Mass Action

In equilibrium at constant pressure and temperature, the Gibbs free energy assumes a minimum, $G(T,p,n_\alpha) \longrightarrow \min$. In a chemical reaction, the mole numbers n_α are related by stoichiometry. From the mole balance (23.8) follows

$$n_\alpha = n_\alpha^0 + \gamma_\alpha \Lambda \ , \tag{23.25}$$

where $\Lambda = \int_1^2 V\lambda dt$ is the net number of reactions between the actual state (n_α) and a reference state (n_α^0). The net number of reactions, Λ, is the only variable in the system, thus the equilibrium condition is

$$\frac{dG}{d\Lambda} = \sum_{\alpha=1}^{\nu} \left(\frac{\partial G}{\partial n_\alpha}\right)_{p,T,n_\beta} \frac{\partial n_\alpha}{\partial \Lambda} = \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha \gamma_\alpha = 0 \ . \tag{23.26}$$

The resulting equilibrium condition for chemical reacting mixtures is known as the law of mass action,

$$\sum_{\alpha=1}^{\nu} \gamma_\alpha \bar{\mu}_\alpha = 0 \ . \tag{23.27}$$

The computation of reactive equilibria requires knowledge of the chemical potential. In the following we shall study equilibria in ideal mixtures.

Phase changes can be interpreted as chemical reactions, e.g., with stoichiometric coefficients $\gamma_V = 1$ and $\gamma_L = -1$ for evaporation. Since for single substances the chemical potentials are just the Gibbs free energies, the law of mass action gives the equilibrium condition, $\sum_{\alpha=1}^{\nu} \gamma_\alpha \bar{\mu}_\alpha = \bar{g}_V - \bar{g}_L = 0$.

23.9 Law of Mass Action for Ideal Mixtures and Ideal Gases

For ideal mixtures the chemical potential is given by $\bar{\mu}_\alpha = \bar{g}_\alpha(T,p) + \bar{R}T \ln X_\alpha$, and the law of mass action gives

$$\sum_{\alpha=1}^{\nu} \gamma_\alpha \ln X_\alpha = -\frac{\sum_{\alpha=1}^{\nu} \gamma_\alpha \bar{g}_\alpha (T,p)}{\bar{R}T} . \tag{23.28}$$

We define the Gibbs free energy of reaction as

$$\Delta \bar{g}_R (T,p) = \sum_{\alpha=1}^{\nu} \gamma_\alpha \bar{g}_\alpha (T,p) \ , \tag{23.29}$$

and rewrite the equilibrium conditions as

$$\prod_{\alpha=1}^{\nu} X_\alpha^{\gamma_\alpha} = \exp \left[-\frac{\Delta \bar{g}_R (T,p)}{\bar{R}T} \right] = K_X (T,p) \ . \tag{23.30}$$

The chemical equilibrium is determined through the equilibrium constant[4] $K_X (T,p)$ which, in ideal mixtures, can be determined from property data tables for single substances.

For ideal gases, the pressure dependence of the Gibbs free energy is explicitly known, we have $\bar{g}_\alpha (T,p) = \bar{g}_\alpha (T,p_0) + \bar{R}T \ln \frac{p}{p_0}$, where $\bar{g}_\alpha (T,p_0) = \bar{h}_\alpha (T) - T\bar{s}_\alpha^0 (T)$ is the temperature dependent part of the Gibbs free energy. Thus, the previous equation can be recast as

$$\prod_{\alpha=1}^{\nu} p_\alpha^{\gamma_\alpha} = K_p (T) \ , \tag{23.31}$$

where $K_p (T)$ is known as the chemical constant, and is given by

$$K_p (T) = \prod_{\alpha=1}^{\nu} p_0^{\gamma_\alpha} \exp \left[-\frac{\Delta \bar{g}_R (T,p_0)}{\bar{R}T} \right] . \tag{23.32}$$

Here, $\Delta \bar{g}_R (T,p_0) = \sum_{\alpha=1}^{\nu} \gamma_\alpha \bar{g}_\alpha (T,p_0)$ is the Gibbs free energy of reaction at standard pressure $p_0 = 1\,\text{bar}$.

Remarkably, the chemical constant $K_p (T)$ depends only on temperature, but not on pressure. Nevertheless, as we shall see, the chemical equilibrium is affected by total pressure $p = \sum_\alpha p_\alpha$.

As presented in (23.31) the chemical constant has the unit $[\,\text{bar}]^{\sum_\alpha \gamma_\alpha}$. Some authors prefer a dimensionless form, and write[5]

$$\prod_{\alpha=1}^{\nu} \left(\frac{p_\alpha}{p_0} \right)^{\gamma_\alpha} = \tilde{K}_p (T) \ . \tag{23.33}$$

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[4] It might be a bit misleading to refer to $K_X (T,p)$ and $K_p (T)$ as "constants", since they are functions of temperature and pressure, but this is the name they have.

[5] Of course, they write without the tilde that was introduced to distinguish between the two definitions.

with

$$\tilde{K}_p(T) = \prod_{\alpha=1}^{\nu} \exp\left[-\frac{\Delta\bar{g}_R(T,p_0)}{\bar{R}T}\right] . \tag{23.34}$$

23.10 Example: NH_3 Production (Haber-Bosch Process)

Ammonia (NH_3) is one of the most important materials in chemical industry. It is used for the production of fertilizers and explosives, as cooling fluid in refrigeration systems, and as source material for many other chemical processes. The world ammonia production is about $130 \times 10^6 \frac{\mathrm{t}}{\mathrm{y}}$, and an ammonia plant that produces $1500 \frac{\mathrm{t}}{\mathrm{d}}$ consumes about 650 MW of energy; the energy required to produce one ton is ca. 35 GJ. Approximately 1% of the world's energy usage is devoted to the production of ammonia!

Before Haber and Bosch found out how to produce ammonia industrially, the supply came from guano fields off the cost of South America (guano is ... bird droppings). Here, we discuss the basic principles of the Haber-Bosch process which was developed by Fritz Haber (1868-1934) and brought to industrial production by Carl Bosch (1874-1940).

Ammonia is produced by combining hydrogen, normally obtained from natural gas by steam methane reforming, with nitrogen from air, where the oxygen is removed by reaction with carbon monoxide and hydrogen from the hydrogen production step. The chemical equation for ammonia synthesis reads

$$-\mathrm{N}_2 - 3\mathrm{H}_2 + 2\mathrm{NH}_3 = 0 ,$$

and the law of mass action (23.31) for this reaction assumes the form

$$\frac{p_{\mathrm{NH}_3}^2}{p_{\mathrm{N}_2} p_{\mathrm{H}_2}^3} = K_p(T) .$$

In order to determine the equilibrium compositions of ammonia, nitrogen and hydrogen at given (T,p), we require the balances of hydrogen and nitrogen mole numbers, and the total pressure,

$$n_{\mathrm{NH}_3} + 2n_{\mathrm{N}_2} = 2n_{\mathrm{N}_2}^0 \quad , \quad 3n_{\mathrm{NH}_3} + 2n_{\mathrm{H}_2} = 2n_{\mathrm{H}_2}^0 \quad , \quad p = p_{\mathrm{NH}_3} + p_{\mathrm{N}_2} + p_{\mathrm{H}_2} .$$

Pressures and mole numbers are related via the ideal gas law

$$n_\alpha = \frac{p_\alpha V}{\bar{R}T} ,$$

where V is the reactor volume. Thus, we have four equations for the four unknowns $(p_{\mathrm{NH}_3}, p_{\mathrm{N}_2}, p_{\mathrm{H}_2}, V)$,

$$\frac{p_{\mathrm{NH}_3}^2}{p_{\mathrm{N}_2}p_{\mathrm{H}_2}^3}=K_p(T)\quad,\quad p=p_{\mathrm{NH}_3}+p_{\mathrm{N}_2}+p_{\mathrm{H}_2}\;.$$

$$p_{\mathrm{NH}_3}+2p_{\mathrm{N}_2}=2n_{\mathrm{N}_2}^0\frac{\bar{R}T}{V}\quad,\quad 3p_{\mathrm{NH}_3}+2p_{\mathrm{H}_2}=2n_{\mathrm{H}_2}^0\frac{\bar{R}T}{V}\;.$$

We assume a stoichiometric mixture of the reactants, $n_{\mathrm{H}_2}^0=3n_{\mathrm{N}_2}^0$, to find

$$p_{\mathrm{H}_2}=3p_{\mathrm{N}_2}\quad,\quad p_{\mathrm{N}_2}=\frac{p-p_{\mathrm{NH}_3}}{4}\quad,\quad V=\frac{4n_{N_2}^0}{1+\frac{p_{\mathrm{NH}_3}}{p}}\frac{\bar{R}T}{p}\;,$$

and a quadratic equation for the equilibrium ammonia mole fraction $X_{NH_3}=\frac{p_{NH_3}}{p}$, with the solution

$$X_{\mathrm{NH}_3}=1+\frac{8}{3p\sqrt{3K_p(T)}}-\sqrt{\left(1+\frac{8}{3p\sqrt{3K_p(T)}}\right)^2-1}\;.$$

Tabulated values for the chemical constant are

$$K_p(300\,\mathrm{K})=4.67\times10^5\frac{1}{\mathrm{bar}^2}\;,$$
$$K_p(600\,\mathrm{K})=1.862\times10^{-3}\frac{1}{\mathrm{bar}^2}\;,$$
$$K_p(773\,\mathrm{K})=1.585\times10^{-5}\frac{1}{\mathrm{bar}^2}\;.$$

Thus, a larger ammonia fraction is encountered for smaller temperatures, where $K_p(T)$ is larger, and for larger pressures. For instance, at $T=300\,\mathrm{K}$ and $p=1\,\mathrm{bar}$, one finds $X_{NH_3}=0.935$ and this increases to $X_{NH_3}=0.9970$ when the pressure is increased to 500 bar.

However, when one mixes hydrogen and nitrogen at $(300\,\mathrm{K},1\,\mathrm{bar})$, the mixture does not approach thermodynamic equilibrium, but remains in a metastable state; nothing happens, since the reaction rate is too slow. As Haber found out, iron catalysts are required to advance the reaction, but these work only at relatively high temperatures, where the ammonia yield is relatively small. In order to have a significant yield, the process must be performed under high pressures. For a reactor temperature of $T=773\,\mathrm{K}$, the mole fraction is $X_{NH_3}=0.309$ for $p=500\,\mathrm{bar}$, but only $X_{NH_3}=0.0013$ for $p=1\,\mathrm{bar}$.

In continuous reactors, the product is cooled (at pressures below p_{sat}), the ammonia condenses and is removed, while the unused portions of hydrogen and nitrogen are fed back into the production process.

23.11 Le Chatelier Principle

The ammonia reaction shifts its equilibrium towards the desired product when the temperature is lower, and the pressure is higher. To study how changes of temperature and pressure affect the chemical equilibrium in other reactions (for ideal mixtures), we turn to (23.30) and compute the change of the equilibrium constant $K_X\left(T,p\right)$ with pressure and temperature. According to the definition, larger K_X implies more product.

We compute first the change of K_X with temperature, as

$$\left(\frac{\partial \ln K_X}{\partial T}\right)_p = -\frac{1}{\bar{R}T}\left[\left(\frac{\partial \Delta\bar{g}_R\left(T,p\right)}{\partial T}\right)_p - \frac{\Delta\bar{g}_R\left(T,p\right)}{T}\right] = \frac{\Delta\bar{h}_R\left(T,p\right)}{\bar{R}T^2}\ . \tag{23.35}$$

Here we have used $\left(\frac{\partial\bar{g}}{\partial T}\right)_p = -\bar{s}$, which implies

$$\left(\frac{\partial \Delta\bar{g}_R\left(T,p\right)}{\partial T}\right)_p = -\sum_\alpha \gamma_\alpha \bar{s}_\alpha = -\Delta\bar{s}_R\ . \tag{23.36}$$

It follows that an endothermic reaction ($\Delta\bar{h}_R > 0$) will advance further at larger temperatures, while an exothermic reaction ($\Delta\bar{h}_R < 0$) will advance further at lower temperatures. The ammonia reaction is exothermic, and thus temperature increase reduces the yield. Dissociation processes, e.g., $H_2 \rightleftharpoons 2H$, are endothermic and thus pronounced dissociation takes place at high temperatures.

For the change of K_X with pressure we find

$$\left(\frac{\partial \ln K_X}{\partial p}\right)_T = -\frac{1}{\bar{R}T}\left(\frac{\partial \Delta\bar{g}_R\left(T,p\right)}{\partial p}\right)_T = -\frac{\Delta\bar{v}_R\left(T,p\right)}{\bar{R}T}\ . \tag{23.37}$$

Here we have used $\left(\frac{\partial\bar{g}}{\partial p}\right)_T = \bar{v}$, which implies

$$\left(\frac{\partial \Delta\bar{g}_R\left(T,p\right)}{\partial p}\right)_T = \sum_\alpha \gamma_\alpha \bar{v}_\alpha\left(T,p\right) = \Delta\bar{v}_R\left(T,p\right)\ ; \tag{23.38}$$

we might call $\Delta\bar{v}_R$ the volume of reaction. Note that $\bar{v}_\alpha\left(T,p\right)$ is the volume of component α alone at temperature and pressure of the mixture. We have $\Delta\bar{v}_R < 0$ when the volume of the product is less than the volume of the reactants, and $\Delta\bar{v}_R > 0$ when the volume of the product is larger than the volume of the reactants. The reaction will advance further at higher pressures for negative volumes of reaction, $\Delta\bar{v}_R < 0$.

For ideal gases, we have $\bar{v}\left(T,p\right) = \bar{R}T/p$, hence, when all components are ideal gases, the volume of reaction becomes

$$\Delta \bar{v}_R\left(T,p\right)=\sum_\alpha \gamma_\alpha \bar{v}_\alpha\left(T,p\right)=\frac{\bar{R}T}{p}\sum_\alpha \gamma_\alpha\ . \tag{23.39}$$

In the ammonia reaction one mole of N_2 and three moles of H_2 combine to two moles of NH_3, hence $\sum_\alpha \gamma_\alpha = -2$. Thus, the product has half the volume of the reactants, the volume of reaction is negative, and pressure increase advances the reaction. In dissociation processes, e.g., $H_2 \to 2H$, the product has a larger volume, and pressure increase reduces the amount of dissociated gas.

The above statements are examples, for ideal mixtures, of Le Chatelier's Principle (Henry Le Châtelier, 1850-1936) which states that *A change in one of the variables (temperature, pressure, concentration, ...) that describe a system in equilibrium, produces a shift in the position of the equilibrium that counteracts the change.*

For instance, when a reactive mixture with exothermic reaction is heated to a higher temperature, backward reactions occur which consume energy and reduce the temperature. When the pressure is increased on a reactive mixture of ideal gases with negative reaction volume $\Delta \bar{v}_R$, reactions occur that reduce the overall particle number, and increase the mole volume $\bar{v}$, to reduce the pressure $p=\frac{RT}{\bar{v}}$.

23.12 Multiple Reactions

In many technical applications multiple reactions occur simultaneously. We denote the reaction rate densities for the various reactions as λ_a and the stoichiometric coefficient for component α in reaction a as γ_α^a, where the superscript $a=1,\ldots,N$ indicates the reaction. The mole balance for component α then reads

$$\frac{dn_\alpha}{dt}=\sum_a \gamma_\alpha^a \lambda_a V\ . \tag{23.40}$$

Integration upon time yields

$$n_\alpha = n_\alpha^0 + \sum_a \gamma_\alpha^a \Lambda_a\ , \tag{23.41}$$

where Λ_a is the net number of reactions of type a. The Λ_a are the free parameters for the establishment of equilibrium, hence the equilibrium conditions are

$$\frac{dG}{d\Lambda_a}=\sum_\alpha \frac{\partial G}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial \Lambda_a}=\sum_\alpha \bar{\mu}_\alpha \gamma_\alpha^a = 0 \quad \text{for} \;\; a=1,\ldots,N\ . \tag{23.42}$$

In other words, the law of mass action must hold for all reactions individually, that is

$$\sum_{\alpha} \bar{\mu}_\alpha \gamma_\alpha^a = 0 \quad \text{for} \ \ a = 1, \ldots, N\,. \tag{23.43}$$

For ideal mixtures and ideal gases we obtain generalizations of (23.30, 23.31),

$$\prod_{\alpha=1}^{\nu} X_\alpha^{\gamma_\alpha^a} = K_X^a\,(T,p) \quad \text{for} \ \ a = 1, \ldots, N. \tag{23.44}$$

and

$$\prod_{\alpha=1}^{\nu} p_\alpha^{\gamma_\alpha^a} = K_p^a\,(T) \quad \text{for} \ \ a = 1, \ldots, N. \tag{23.45}$$

Problems

23.1. Enthalpy of Formation and Heat of Reaction

Measurement of the heat of reaction at standard reference state T_0, p_0 for several reactions gave the following values:

$C + \frac{1}{2}O_2 = CO$: $\Delta\bar{h}_R^0 = -110\frac{\text{kJ}}{\text{mol}}$,
$CO_2 = CO + \frac{1}{2}O_2$: $\Delta\bar{h}_R^0 = 280\frac{\text{kJ}}{\text{mol}}$,
$H_2 + \frac{1}{2}O_2 = H_2O$: $\Delta\bar{h}_R^0 = -240\frac{\text{kJ}}{\text{mol}}$,
$CH_4 + 2O_2 = CO_2 + 2H_2O$: $\Delta\bar{h}_R^0 = -800\frac{\text{kJ}}{\text{mol}}$.

1. Use this data to determine the heat of formation $\bar{h}_f^0$ for H_2O, CO_2, CH_4. Do not read values from tables, but show how you use the data given above!
2. Measurements show that for temperatures below 800 K the specific heat of methane (CH_4) can be approximated as $\bar{c}_p = 20.1\frac{\text{kJ}}{\text{kmol K}} + 0.053T\frac{\text{kJ}}{\text{kmol K}^2}$. Use this and the data from above to determine the enthalpy of methane at 600 K.
3. Use the results from above and the gas tables for oxygen, carbon dioxide and water to compute the heat of reaction for $CH_4 + 2O_2 = CO_2 + 2H_2O$ at 600 K.

23.2. Dimethyl Ether (DME)

The heat of reaction at standard conditions for the combustion of gaseous dimethyl ether, C_2H_6O, is experimentally found as $-1460\frac{\text{kJ}}{\text{mol}}$, when the product water is liquid.

1. Use this measurement and tabled data to determine the enthalpy of formation of DME.
2. Determine the heat of reaction when the product water is vapor.

23.3. Shifting the Chemical Equilibrium

Consider a mixture of CO_2, CO and O_2 in chemical equilibrium. Now the pressure is doubled. Will the number of moles of CO_2, CO and O_2 change? How? How does the equilibrium change when the temperature is increased?

23.4. Changes in Chemical Equilibrium

An equimolar mixture of CO and H_2O(g) reacts to form an equilibrium mixture of CO_2, CO, H_2O and H_2 at 1727 °C, 1 atm.

1. Will decreasing the pressure while keeping the temperature constant increase or decrease the amount of H_2 present? Explain.
2. Will lowering the temperature increase or decrease the amount of H_2 present? Explain.

23.5. Shift in Chemical Equilibrium through Inert Addition

An equimolar mixture of O_2 and H_2 reacts to form an equilibrium mixture of O_2, H_2, and H_2O. After equilibrium is reached, N_2 is added to the mixture isobarically. As nitrogen is added, does the amount of water increase or decrease? Use Le Chatelier's principle for a first answer. Then perform a detailed analysis to find a relation between the amounts of N_2 added and H_2O present (assume stoichiometric mix of H_2 and O_2).

23.6. Shift in Chemical Equilibrium

Methane, CH_4, reacts with stoichiometric air to form an equilibrium mixture of CH_4, CO_2, H_2O, O_2, N_2. Will the equilibrium between CH_4, CO_2, H_2O, O_2 be different when the reaction takes place at the same temperature and pressure, but no nitrogen is present? State your arguments, e.g., consider the quotient p_{CH_4}/p_{CO_2}.

23.7. Dissociation of Oxygen

Measurement of oxygen at 3800 K shows equal mole fractions of $O_2$and O.

1. Determine the pressure.
2. Now the pressure is doubled. Determine the mole fractions of O_2 and O.

23.8. Law of Mass Action: Methanol Synthesis

Methanol (CH_3OH) is produced by catalytic hydrogenation of carbon monoxide according to the reaction

$$CO + 2H_2 - CH_3OH = 0 \, .$$

Assume that all partners in the reaction are ideal gases.

1. Carbon monoxide and hydrogen are mixed in stoichiometric ratio. Find an expression that relates the chemical constant $K_p\,(T)$, the methanol mol ratio X_{CH_3OH} and the total pressure p of the mixture.
2. A measurement at 600 K shows that $K_p\,(600\,\mathrm{K}) = 12000\,\mathrm{bar}^2$. For which total pressure p do we have a methanol ratio of 30%?
3. The reaction is exothermal. What does that mean? Would a further increase of temperature increase the methanol ratio?

23.9. Law of Mass Action: Formation of NO

Air (79% N_2 and 21% O_2) is heated to 2000 K at a constant pressure of 2 bar. Assume that the equilibrium mixture at this temperature consists of N_2, O_2, and NO.

For the reaction equation $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ one finds at this temperature that $\ln K_p(T) = -3.931$.

1. Compute the mole fractions of the three components in equilibrium.
2. Will the equilibrium composition change when the pressure is doubled?
3. For this reaction, $\ln K_p$ grows with temperature. Does that mean the reaction is exothermic or endothermic?

23.10. Law of Mass Action: N_2O_4

One kmol of N_2O_4 dissociates at 25 °C, 1 atm to form an equilibrium ideal gas mixture of N_2O_4 and NO_2, in which the amount of N_2O_4 is 0.8154 kmol.

1. Determine the mole number of NO_2 in equilibrium.
2. Determine the chemical constant $K_p\,(T)$ at 25 °C for the reaction.
3. Determine the amount of N_2O_4 that would be present if the pressure is 0.5 bar.

Hint: Determine first the absolute mole numbers of NO_2 and N_2O_4.

23.11. Chemical Reaction

Consider the combustion of hydrogen with oxygen according to $H_2O - H_2 - \frac{1}{2}O_2 = 0$, when the pressure in the combustion chamber is fixed at 2 bar. Hydrogen and oxygen enter the chamber in the stoichiometric ratio at $T_{in} = 298.15\,\text{K}$, and the mass flow of hydrogen is $1\,\frac{\text{kg}}{\text{min}}$. The temperature in the chamber can be fixed by controlling the heat flux.

1. Compute the mass flow of oxygen.
2. The partial pressure of water vapor in the exhaust should be larger than 95% What is the maximum temperature for the combustion chamber, and what heat flux must be removed? Repeat for water conent of 98%.
3. Discuss the flame temperature under adiabatic conditions. Derive an equation that contains only T_{flame} as the unknown (or a set of equations, which will serve for the same purpose) – that equation will contain $K_p(T)$, $h_\alpha(T)$ for all components).

T/K	298.15	300	400	500	600	700	800	900	1000
$\text{Log}[\frac{K_p(T)}{\sqrt{\text{bar}}}]$	40.047	39.7868	29.2307	22.8855	18.6323	15.5832	13.2285	11.4978	10.0010

T/K	1100	1200	1300	1400	1500	1750	2000	2500	3000
$\text{Log}[\frac{K_p(T)}{\sqrt{\text{bar}}}]$	8.8830	7.8980	7.0637	6.3475	5.7254	4.4796	3.546	2.232	1.344

23.12. Steam Methane Reforming

Steam methane reforming is used to produce hydrogen from methane, in particular for further use in ammonia production. The first reaction step in steam methane reforming is the reaction

$$\mathrm{CH_4 + H_2O \leftrightarrow 3H_2 + CO}\ ,$$

which is then followed by the water gas shift reaction discussed in the next two problems.

At 1173 K, the chemical constant for this reaction is $K_p\,(1173\,\mathrm{K}) = 1.43 \times 10^3\,\mathrm{bar}^2$. Methane and steam are mixed in the ratio 1 to α by mole, and react with help of catalysts at a pressure of 30 bar.

Find the equations to determine the partial pressures $p_{\mathrm{CH_4}}$, $p_{\mathrm{H_2O}}$, $p_{\mathrm{H_2}}$, p_{CO}. Use a computer to determine the mole fractions of all components in chemical equilibrium at the given pressure and temperature for $\alpha = 1$ and $\alpha = 5$. Also determine as a measure for the relative conversion of methane into hydrogen the ratio $p_{\mathrm{CH_4}}/p_{\mathrm{H_2}}$. Interpret the result–can you explain it?

Assume that all components behave as ideal gases.

23.13. Property data: Water Gas Shift Reaction I

The water gas shift reaction is the second reaction for the production of hydrogen from methane. The reaction equation reads

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2}\ .$$

1. Assuming that all components are ideal gases, determine the heat of reaction for the temperature $T = 600\,\mathrm{K}$. Is the reaction exothermic or endothermic?
2. Determine the Gibbs free energy of reaction at $T = 600\,\mathrm{K}$ and $p = 1\,\mathrm{atm}$.
3. Compute the chemical constant $K_X(T,p)$. Note: this asks for K_X, not for K_p.
4. For this reaction, does the Gibbs free energy of reaction depend on pressure? Explain! Determine $K_p\,(T)$.

23.14. Law of Mass Action: Water Gas Shift Reaction II

Consider the chemical equilibrium of carbon monoxide, carbon dioxide, water and hydrogen through the water gas shift reaction, as above, at $T = 800\,\mathrm{K}$ and $p = 1\,\mathrm{atm}$. The chemical constant for this reaction is $K_X(800\,\mathrm{K}, 1\,\mathrm{atm}) = 16.424$.

1. Determine the equilibrium mole fractions for all components, when the initial state was a stoichiometric mixture of carbon monoxide and water vapor.
2. Can the equilibrium be shifted by a change of pressure? Explain!

23.15. Law of Mass Action: High Temperature Combustion

Reaction of a stoichiometric mixture of benzene (C_6H_6) and dry air at 200 kPa, with a small heat loss, results in a flame temperature of 2400 K. Assume that nitrogen, oxygen and water do *not* dissociate, and consider the equilibrium between CO_2, COand O_2. Determine the partial pressures of all components in the mixture.

23.16. Law of Mass Action: Incomplete Combustion

Octane (C_8H_{18}) is burned with 95% theoretical air. The resulting equilibrium mixture consists of CO_2, CO, H_2O, H_2 and N_2. Determine the mole fractions of all constituents when the mixture is at 1000 K and 2 bar.

23.17. Law of Mass Action: Methane

At 3000 K and 8 bar, methane (CH_4) reacts with the stoichiometric amount of pure oxygen according to $CH_4+2O_2 \leftrightarrow CO_2+2H_2O$. The chemical constants for the following reactions are given (all at 3000 K):

$$\begin{array}{lll} C + 2H_2 \leftrightarrow CH_4 & \text{with} & K_p(T) = 9.685\frac{1}{\text{bar}^2}\ , \\ 2H_2 + O_2 \leftrightarrow 2H_2O & \text{with} & K_p(T) = 484.9\frac{1}{\text{bar}}\ , \\ C + O_2 \leftrightarrow CO_2 & \text{with} & K_p(T) = 15.87\frac{1}{\text{bar}}\ , \\ 2CO_2 \leftrightarrow 2CO + O_2 & \text{with} & K_p(T) = 0.1089\,\text{bar}\ . \end{array}$$

Determine the mole fraction of CH_4 in equilibrium.

23.18. Law of Mass Action with Multiple Reactions

A mixture consists originally of 3 kmol of CO_2 and 1 kmol of O_2. Assume that in equilibrium at 3000 K and 3 bar only CO_2, CO, O_2 and O are present, and determine the equilibrium composition.

23.19. Law of Mass Action: Nitrogen and Oxygen

A gas mixture consisting of 1 kmol of NO, 10 kmol of O_2 and 40 kmol of N_2 reacts to form an equilibrium mixture of N_2, NO_2, NO, and O_2 at 500 K, 0.1 atm. Determine the composition of the equilibrium mixture.

1. Solve for the case that the molecular nitrogen stays inert.
2. Solve for the case that the molecular nitrogen reacts.