Chemical equilibrium, the law of mass action, and the reaction heat

Supplementary notes for the astrochemistry course, spring 2013

Jorma Harju

March 21, 2013

1 Equilibrium constant and the law of mass action

Most reactions we are dealing with in astrochemistry are of the type

\[ A + B \xrightleftharpoons[k_-]{k_+} C + D. \]

The equilibrium constant, \( K(T) \), is defined by

\[ K(T) \equiv \frac{k_+}{k_-} = \frac{N_{C,eq}N_{D,eq}}{N_{A,eq}N_{B,eq}}, \]

where \( N_{A,eq}, N_{B,eq}, \ldots \) are the numbers of the substances A, B, ... in given volume and temperature when chemical equilibrium is established, that is, when the number densities do not change.

The equilibrium constant can be calculated from the partition functions (sums over states), \( Z(T) \), of the species. For the reaction given above we obtain the formula:

\[ K(T) = \frac{Z_CZ_D}{Z_AZ_B}. \]

The partition function \( Z \) depends on energy spectrum of the molecule. For a particle obeying the Boltzmann statistics \( Z(T) = \Sigma g_i \exp(E_i/kT) \), where \( g_i \) is the statistical weight (degeneracy), and \( E_i \) is the energy of the state \( i \). The total partition function is a product of the electronic, translational, vibrational, and rotational partition functions, \( Z = Z_{el}Z_{tr}Z_{vib}Z_{rot} \). Normally only the ground electronic state is thermally accessible, so \( Z_{el} = g_{el} \), where \( g_{el} \) is the degeneracy of the ground state (usually = 1).

The energies in the partition functions are usually given relative to the zero-point vibrational energy, ZPVE, which we denote by \( E_0 \). The partition function in terms of \( E_0 \) is

\[ Z' = \Sigma g_i e^{-(E_i-E_0)/kT} = e^{E_0/kT}Z, \]

implying

\[ Z = Z'e^{-E_0/kT}. \]

Omitting the primes, \( K(T) \) can be written as

\[ K(T) = \frac{Z_CZ_D}{Z_AZ_B} \exp\left(-\frac{\Delta E_0}{kT}\right), \]

where \( \Delta E_0 \) is the difference in energy between the forward and reverse reactions.
where \( \Delta E_0 \) is the difference between the ZPVEs (products \(-\) reactants):
\[
\Delta E_0 = E_0^C + E_0^D - E_0^A - E_0^B .
\]

Sometimes \( \Delta E_0 \) is called the enthalpy of the reaction (e.g., Ramanal & Tennyson). Why this assignment can be made is discussed below.

The translational partition function, \( Z_{\text{tr}} \), contains the term \( m^{3/2} \), where \( m \) is the molecular mass. In our example reaction other terms of \( Z_{\text{tr}} \) are reduced in the expression of \( K(T) \), and therefore the equilibrium constant can be written as
\[
K(T) \equiv \frac{N_{\text{C,eq}}N_{\text{D,eq}}}{N_{\text{A,eq}}N_{\text{B,eq}}} = \left( \frac{m_cm_D}{m_Am_B} \right)^{3/2} \frac{Z_{\text{C, int}}Z_{\text{D, int}}}{Z_{\text{A, int}}Z_{\text{B, int}}} \exp \left( -\frac{\Delta E_0}{kT} \right) ,
\]
where \( Z_{\text{int}} = Z_{\text{rot}}Z_{\text{vib}} \) is the partition function related to the internal energy states of the molecule. This form is known as the law of mass action.

As an example we consider the most important deuteration reaction in interstellar molecular clouds:
\[
\text{H}_3^+ + \text{HD} \xleftrightarrow[k_+]{k_-} \text{H}_2\text{D}^+ + \text{H}_2
\]

The equilibrium constant is
\[
K(T) = \frac{N(\text{H}_2\text{D}^+)_{\text{eq}}N(\text{H}_2)_{\text{eq}}}{N(\text{H}_3^+)_{\text{eq}}N(\text{HD})_{\text{eq}}} = \frac{4 \cdot 2}{3 \cdot 3} \left( \frac{Z(\text{H}_2\text{D}^+, \text{int})Z(\text{H}_2, \text{int})}{Z(\text{H}_3^+, \text{int})Z(\text{HD}, \text{int})} \right) \exp \left( -\frac{\Delta E_0}{kT} \right) ,
\]
The difference between the ZPVEs is \( \Delta E_0/k = E_0(\text{H}_2\text{D}^+)/k + E_0(\text{H}_2)/k - E_0(\text{H}_3^+)/k - E_0(\text{HD})/k = -139.5 \text{ K} \). A negative \( \Delta H \sim \Delta E_0 \) means that the reaction from left to right is exothermic.

In Fig. 1 we show the partition functions \( Z(\text{H}_2\text{D}^+, \text{int}), Z(\text{H}_2, \text{int}), Z(\text{H}_3^+, \text{int}), \) and \( Z(\text{HD}, \text{int}) \) as functions of \( T \). The equilibrium constant calculated from these partition functions is shown in Fig. 1.

The van ‘t Hoff equation relates the temperature dependence of the equilibrium constant to the enthalpy change, \( \Delta H \), of the reaction (reaction heat in constant pressure). For a single elementary reaction this equation can be written as
\[
T^2 \frac{\partial}{\partial T} \ln K(T) = \frac{\Delta H}{k} ,
\]
or equivalently
\[
\frac{\partial}{\partial T} \ln K(T) = -\frac{\Delta H}{k} .
\]
The latter form shows that the reaction enthalpy can be obtained from the slope of the \( \ln K \) vs. \( 1/T \) diagram. It is evident from Fig. 1 that the reaction enthalpy depends on the temperature. At low temperatures \( (1/T > 0.1 \text{ K}^{-1}) \) the slope indicates that \( \Delta H/k \sim -232 \text{ K} \) \( (\Delta \text{ZPVE minus the “rotational ZPE” of } \text{H}_3^+) \), whereas at elevated temperatures \( (1/T < 0.02 \text{ K}^{-1}) \) where the rotational levels of \( \text{H}_3^+ \) are populated, \( \Delta H/k \sim -140 \text{ K} \) \( (= \Delta \text{ZPVE}) \).

In what follows we derive the equations used in this example.

---

1. The ground rotational state of \( \text{H}_3^+ \) is forbidden by the Pauli exclusion principle, and the lowest allowed state \( J, K = 1, 1 \) lies 92.3 K above the ground state. Often this “rotational zero-point energy” is added to the zero-point energy of \( \text{H}_3^+ \), and \( \Delta E_0/k \) becomes -231.8 K. When using this value, we should also give the energies of \( Z(\text{H}_3^+, \text{int}) \) with respect to the state \( J, K = 1, 1 \).
Figure 1: Internal partition functions, $Z_{\text{int}} = Z_{\text{vib}} Z_{\text{rot}}$, of $H_2D^+$, $H_2$, $H_3^+$, and HD as functions of $T$. Note that for $H_3^+$ the energies are calculated from the forbidden rotational ground state, and therefore $Z(H_3^+, \text{int}) \to 0$ when $T \to 0$. For other molecules, $Z$ approaches the statistical weight of the ground state. The contributions of different nuclear spin variants are indicated when applicable. The partition functions are adopted from Hugo et al.

Figure 2: The natural logarithm of the equilibrium constant, $\ln K$, of reaction $H_3^+ + HD \leftrightarrow H_2D^+ + H_2$ as functions of $T$ (left) and $1/T$ (right). Also shown are two approximations $\ln K(T) \sim -\Delta H/kT$ from the van ‘t Hoff equation. At elevated temperatures, the assumption $\Delta H/k = \Delta ZPE_1/k = -139.5$ K (the difference of zero-point vibrational energies) seems to work well, whereas at low temperatures $\Delta H/k = \Delta ZPE_2/k = -231.8$ K ($\Delta ZPVE$ combined with the “rotational zero-point energy” of $H_3^+$) gives a better agreement.
2 Thermodynamic potentials

The thermodynamic properties of a gas, e.g., the equation of state, can be derived from one of the following thermodynamic potentials: the internal energy $E(S, V, N)$ (the total energy contained by a thermodynamic system), the enthalpy $H(S, P, N)$ (the total energy of a thermodynamic system including the internal energy and the energy needed to establish the space and pressure of the system), the free energy $F(T, V, N)$ (also called the Helmholtz function, the energy that can be converted into work at a constant temperature and volume), or the Gibbs energy $G = G(T, P, N)$ (also called the Gibbs function, the energy that can be converted into work at a uniform temperature and pressure).

The choice of the most appropriate potential for our purpose depends on which of the quantities $S$ (entropy), $V$ (volume), $N$ (number of particles), $T$ (temperature), and $P$ (pressure) we wish to use as variables. If one of potentials is known, the others can be derived using the following relations: $H = E + PV$, $F = E - TS$, and $G = H - TS = F + PV$. In chemical applications the Gibbs energy, $G(T, P, N)$, is particularly useful because the pressure and the temperature are usually under control, when the number of particles and the composition changes.

If the number of the gas particles, $N$, is allowed to change the first law of thermodynamics (conservation of the energy) is expressed by the equation $dE = T dS - P dV + \mu dN$, where $\mu$ is the chemical potential of the gas. Correspondingly, the total differentials of the enthalpy, the free energy, and the Gibbs energy can be written as $dH = T dS + V dP + \mu dN$ and $dF = -SdT + VdP + \mu dN$ and $dG = -SdT + VdP + \mu dN$. In a mixture of gases the chemical potential $\mu$ is defined separately for each component $i$, and a general change of the Gibbs energy can be written as

$$dG = -SdT + VdP + \sum_i \mu_i dN_i.$$ (1)

This formula is sometimes called the master equation of chemical thermodynamics (Atkins, Ch. 8). From this we can make the identifications

$$\left(\frac{\partial G}{\partial T}\right)_{P,N_i} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T,N_i} = V, \quad \left(\frac{\partial G}{\partial N_i}\right)_{P,T} = \mu_i.$$ (2)

The variables kept constant in the derivates are indicated with subscripts. The chemical potential can be obtained also from the other thermodynamic potentials in the following way:

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V}.$$ (3)

3 Chemical equilibrium

Consider the chemical reaction

$$\nu_A A + \nu_B B \xrightleftharpoons[k_-]{k_+} \nu_C C + \nu_D D,$$

occurring in a mixture of reacting substances. The coefficients $\nu_A$ etc. are the stoichiometric coefficients. For example, in the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 (+\Delta E)$, the coefficients are 1, 3, and 2, and in the reaction $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ all coefficients have the value 1. The numbers of particles $A, ..., D$, denoted by $N_A, ..., N_D$, in a volume element $V$ change until
an equilibrium state is established in which the numbers no more change. In this state the reaction proceeds in both direction at equal rates. In what follows we derive the condition for chemical equilibrium.

The reaction equation can be also written as

$$-\nu_A A - \nu_B B + \nu_C C + \nu_D D = 0 \, .$$

(4)

The stoichiometric coefficients of the products of a reaction proceeding from left to right are chosen here to be positive, and the coefficients of the reactants are negative.

Assume that the reaction occurs at constant pressure, \( P \), and temperature, \( T \). In such processes the Gibbs energy, \( G \), tends to a minimum. This is an implication of the second law of thermodynamics which can be formulated, e.g., in the following way: In natural processes the entropy of a closed system increases, and reaches a maximum in the state of equilibrium. When the system can exchange heat with its surroundings, the “closed system” where the entropy must increase is the universe.

For a reaction occurring in constant temperature the change in the Gibbs energy can be written as

$$\Delta G = \Delta H - T \Delta S \quad (T = \text{const.}) \, ,$$

(5)

where \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy changes of the system respectively. For spontaneous reactions \( \Delta G < 0 \).

At low temperatures \( T \Delta S \) is often small, and so \( \Delta G \sim \Delta H \), whereas at higher temperatures \( T \Delta S \) may dominate. For an exothermic reaction the enthalpy change is negative (\( \Delta H < 0 \)). Also endothermic reactions (\( \Delta H > 0 \)) can occur spontaneously provided that the overall entropy in the universe (system plus surroundings) increase. The entropy change of the surroundings is \(-\Delta H/T\) (heat transferred to the surroundings at constant pressure is \(-\Delta H\)). This change must be compensated by the entropy change \( \Delta S \) of the system.

The natural variables of the Gibbs energy are the temperature, the pressure, and the number of particles: \( G = G(T, P, N) \). Therefore the minimum Gibbs energy in constant pressure and temperature corresponds to the zero point of its derivative with respect to the number of one of the substances participating in the reaction. We choose the substance \( A \):

$$\frac{dG}{dN_A} = \frac{\partial G}{\partial N_A} + \frac{\partial G}{\partial N_B} \frac{dN_B}{dN_A} + \frac{\partial G}{\partial N_C} \frac{dN_C}{dN_A} + \frac{\partial G}{\partial N_D} \frac{dN_D}{dN_A} = 0 \, .$$

(6)

The relative changes of the numbers \( N_A, \ldots N_D \) are determined by the reaction equation (4):

$$\frac{dN_B}{dN_A} = \frac{\nu_B}{\nu_A} \, , \, \frac{dN_C}{dN_A} = \frac{-\nu_C}{\nu_A} \, , \, \frac{dN_D}{dN_A} = \frac{-\nu_D}{\nu_A} \, .$$

Multiplying Equation (6) by \(-\nu_A\) and using the definition of the chemical potential:

$$\mu_A = \frac{\partial G}{\partial N_A} \, , \, \mu_B = \frac{\partial G}{\partial N_B} \, \ldots \, ,$$

we obtain the condition of chemical equilibrium:

$$-\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C + \nu_D \mu_D = 0 \, .$$

In other words, the reaction is in equilibrium when the chemical potentials of the reactants and products are equal.
We express this in a more compact form by denoting the substances by $A_1, A_2, \ldots$ instead of $A, B, \ldots$. Then the reaction equation becomes

$$\sum \nu_i A_i = 0 .$$

(7)

Note that now the sign $+$ or $-$ is incorporated in the stoichiometric coefficient $\nu_i$. Using this notation the condition for chemical equilibrium can be written as

$$\sum \nu_i \mu_i = 0 .$$

(8)

The choice that the stoichiometric coefficients of reactants are negative depends on the fact that we will define the equilibrium constant, $K(T)$, as the abundance ratio of the products over the reactants in equilibrium, e.g. $K(T) \equiv \frac{N_{C,eq} N_{D,eq}}{N_{A,eq} N_{B,eq}}$ (see below).

4 Mixtures of ideal gases

Tenuous gas consisting of various substances can be approximated by a mixture of ideal gases. In an ideal gas, the interaction between molecules are negligible from the thermodynamic point of view. In this mixture thermodynamic quantities like the internal energy, $E$, and the entropy, $S$, are sums of those of the component gases. Using the ideal gas equation of state,

$$P = \frac{N k T}{V}$$

(9)

the partial pressure $P_i$ of the component $i$ can be written as

$$P_i = \frac{N_i k T}{V} = \frac{N_i}{N} \frac{N k T}{V} = \frac{N_i}{N} P ,$$

where $N_i$ is the number of molecules $i$, $P$ is the total pressure of the gas, $T$ is the kinetic temperature of the gas, and $V$ is the volume filled by the gas. The total pressure is the sum of the partial pressures: $P = \Sigma P_i$.

Furthermore, the free energy and the Gibbs energy of the mixture can be written as sums:

$$F(N, T, V) = \Sigma F_i(N_i, T, V)$$

(10)

$$G(N, T, P) = \Sigma G_i(N_i, T, P_i)$$

(11)

In the following we derive the Gibbs energy and the chemical potential for a mixture of ideal gases.

5 Free energy of an ideal gas

In statistical physics the following expression is derived for the free energy of an ideal gas:

$$F(T, V, N) = -kT \ln \left\{ \frac{1}{N!} Z(T, V)^N \right\} \approx -N k T \ln \left\{ \frac{e}{N} Z(T, V) \right\} ,$$

(12)
where $Z(T, V)$ is the partition function (or sum over states) of an individual molecule, and $e = 2.71828\ldots$ is the base of natural logarithms. Stirling’s approximation in Eq. 12 is valid for large numbers $N$. The free energy for a single molecule in volume $V$ is

$$F(T, V) = -kT \ln \{Z(T, V)\}.$$  

The distribution of molecules of an ideal gas among the various states is called the Boltzmann distribution. According to this distribution the probability $p_j$ that a molecule is in the energy state $E_j$ can be obtained from

$$p_j = \frac{1}{Z(T)} e^{-E_j/k_B T},$$

where $k_B$ is the Boltzmann constant $(1.38 \times 10^{-23} \text{ J K}^{-1})$, and $T$ is the gas temperature. From the normalization condition $\sum p_j = 1$ we obtain for the partition function the expression

$$Z = \sum e^{-E_j/kB T}.$$  

In a mixture of gases, the free energy of component $i$ is

$$F_i(N, T, V) = -N_i kT \ln \left\{ \frac{e^{N_i Z_i(T, V)}}{N_i} \right\},$$

where $N_i$ is the number of particles $i$ in volume $V$ and $Z_i(T, V)$ is the partition function for a particle of type $i$. The temperature of the mixture is $T$. The free energy of the whole mixture is then

$$F(N, T, V) = \sum F_i(N, T, V) = -\sum N_i kT \ln \left\{ \frac{e^{N_i Z_i(T, V)}}{N_i} \right\}. \quad (13)$$

### 6 Partition function

The partition function $Z(T, V)$ can be divided into translational or kinetic and internal parts. The translational partition function, $Z_{\text{tr}}(T, V)$, takes into account the energy quantization of a particle in a vessel of confined volume. The internal partition function, $Z_{\text{int}}(T)$, depends on the particle’s internal degrees of freedom (electronic states, vibration, rotation, etc.). So the total partition function can be written as

$$Z(T, V) = Z_{\text{tr}}(T, V) Z_{\text{int}}(T). \quad (14)$$

The translational partition function of an ideal gas can be derived quasi-classically by analyzing the distribution of molecules in the phase space extended by the moments $p$ and coordinates $q$ (see, e.g. Mandl Ch. 7.2; Landau & Lifshitz § 38), resulting in the expression

$$Z_{\text{tr}}(T, V) = V \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2}.$$  

The internal partition function can be divided into the following factors (which are independent in the first approximation):

$$Z_{\text{int}}(T) = e^{-\varepsilon_e/kT} Z_{\text{rot}}(T) Z_{\text{vib}}(T),$$
where $\epsilon_e$ is the electronic energy of the molecule, $Z_{\text{rot}}$ is the rotational partition function:

$$Z_{\text{rot}}(T) \approx \sum_{j=0}^{\infty} (2J + 1) e^{-BJ(J+1)/kT},$$

and $Z_{\text{vib}}$ is the vibrational partition function:

$$Z_{\text{vib}}(T) \approx \sum_{v=0}^{\infty} e^{-h\nu_0(v+\frac{1}{2})/kT}.$$

(Above we have use the approximations of a rigid linear rotor and a harmonic oscillator. More accurate formula for $Z_{\text{rot}}$ and $Z_{\text{vib}}$ can be found in the literature.)

The logarithm of a product can be written as the sum of logarithms, and therefore also $F$ can be presented as the sum of the 'kinetic free energy', $F_{\text{tr}}$, 'rotational free energy', $F_{\text{rot}} = -NkT \ln(Z_{\text{rot}})$, the 'vibrational free energy', $F_{\text{vib}} = -NkT \ln(Z_{\text{vib}})$, and the 'electronic free energy', $N\epsilon_e$.

According to the Boltzmann distribution, at low temperatures almost all molecules are at their ground states: $p_j = e^{-E_j/kT} \to 0$, when $E_j > 0$.

The behaviour of the partition function at a low temperature depends on the ground state energy. We can choose the electronic ground state as the zero point, $\epsilon_{e,0} = 0$, implying $e^{-\epsilon_{e,0}/kT} = 1$. At low temperatures, the rotational partition function approaches the statistical weight of the ground rotational state, $Z_{\text{rot}}(T) \to g_0$ (1 for a linear rotor), when $T \to 0$, because the rotational energy levels (normally) start from zero. In contrast, the vibrational partition function $Z_{\text{vib}}(T) \to e^{-\frac{3}{2}h\nu_0/kT}$. The lowest possible vibrational energy of a molecule, $\frac{1}{2}h\nu_0$, is called the zero-point energy (ZPVE). This energy is important for chemical fractionation at low temperatures.

7 The Gibbs energy of a mixture of ideal gases

According to the relationship between the Gibbs and free energies, we can write the Gibbs energy of the component $i$ as $G_i = F_i + P_i V$. Because the natural variables of $G$ are $N, T,$ and $P$, we replace $V$ using the ideal gas equation of state:

$$V = \frac{N_i kT}{P_i}.$$

We have to make this substitution also in the translational partition function:

$$Z_{i,\text{tr}}(T,P_i) = \frac{N_i kT}{P_i} \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2}.$$

After these substitutions we obtain

$$G_i(N_i,T,P_i) = -N_i kT \ln \left\{ \frac{e^{kT}}{P_i} \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_{i,\text{int}}(T) \right\} + N_i kT.$$

This expression can be simplified by separating the term $\ln e (= 1)$ from the logarithm, because $-N_i kT \ln e + N_i kT = 0$:

$$G_i(N_i,T,P_i) = -N_i kT \ln \left\{ \frac{kT}{P_i} \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_{i,\text{int}}(T) \right\}$$

$$= N_i kT \ln P_i - N_i kT \ln \left\{ kT \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_{i,\text{int}}(T) \right\}.$$
We can spare some pain by collecting the terms that depend on \( T \) only on the right hand side under a function \( f_i(T) \), defined as

\[
f_i(T) \equiv -kT \ln \left\{ kT \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_i(T) \right\}.
\]  

(16)

The Gibbs energy of the mixture is then

\[
G(N, T, P) = \sum_i G_i(N_i, T, P_i) = \sum_i N_i kT \ln P_i + \sum_i N_i f_i(T).
\]  

(17)

If we wish to use the total pressure \( P \) instead of the partial pressure \( P_i \), we can make the substitution \( P_i = N_i/N P \):

\[
G(N, T, P) = \sum_i N_i kT \ln P + \sum_i N_i kT \ln \frac{N_i}{N} + \sum_i N_i f_i(T).
\]  

(18)

8 Chemical potential of an ideal gas

It is straightforward to derive the chemical potential of a component \( i \) in a mixture of ideal gases starting from one of the thermodynamical potentials (see Eqs. (2) and (3)). Using the free energy we obtain

\[
\mu_i = \left( \frac{\partial F_i}{\partial N_i} \right)_{T,V} = -kT \ln \left\{ \frac{e}{N_i} Z_i(T, V) \right\} - N_i kT \left( -\frac{1}{N_i} \right) = -kT \ln \left\{ \frac{Z_i(T, V)}{N_i} \right\}.
\]  

(19)

Here we again utilized algebraic rules:

\[
\ln \left\{ \frac{e}{N_i} Z_i(T, V) \right\} = \ln e - \ln N_i + \ln Z_i(T, V).
\]

The case of the Gibbs energy is very simple:

\[
\mu_i = \left( \frac{\partial G_i}{\partial N_i} \right)_{T,P_i} = kT \ln P_i + f_i(T).
\]  

(20)

By substituting \( P_i = N_i kT/V \) and the definition of the function \( f_i(T) \) one can see that this expression is identical with the one obtained from \( F_i \). On grounds of the relationship \( \mu_i = G_i/N_i \) we can interpret \( \mu \) as the Gibbs energy per molecule (e.g., Mandl Ch. 8.1.; Landau & Lifshitz § 24).

In Atkins (Ch. 6) the chemical potential of a species is defined as the molar Gibbs function, \( G_m \), i.e. the Gibbs energy per mole. Atkins defines a “standard Gibbs function”, \( G^\circ \), as the Gibbs energy of an ideal gas at a pressure of 1 atm, and writes the pressure dependence of the \( G \) as

\[
G(P) = G^\circ + NkT \ln(P/atm).
\]

For the molar Gibbs function, i.e. the chemical potential as defined by Atkins, one gets

\[
G_m(P) = \mu(P) = \mu^\circ + RT \ln(P/atm),
\]
where $R$ is the gas constant ($R = N_0 k$, $N_0$ is the Avogadro number). Using the expression for $G$ we obtained previously, and the same reference pressure as Atkins, $P_{\text{ref}} = 1$ atm, the Gibbs energy of one mole of ideal gas can be written as
\[
G_m(P, T) = N_0 kT \ln (P/\text{atm}) + N_0 kT \ln (P_{\text{ref}}) + N_0 f(T) .
\]
We can thus make the following identifications:
\[
G^\ominus(T) \text{ (Atkins)} = NkT \ln (P_{\text{ref}}) + Nf(T) .
\]
Similarly one could have defined a “standard” chemical potential per molecule as
\[
\mu^\ominus_i = kT \ln (P_{\text{ref}}) + f(T) .
\]
We note that the reference pressure $P_{\text{ref}} = 1$ atm $\sim 10^5$ Pa is extremely high compared with interstellar conditions. In molecular clouds, the pressure is typically $P \sim 10^{-12}$ Pa, and a perhaps a few orders of magnitude higher in the nuclei of dense cores.

9 The equilibrium constant in terms of numbers $N_i$

Here we use the expression for the chemical potential obtained from the free energy. Substituting Eq. 19,
\[
\mu_i = -kT \ln \left\{ \frac{Z_i(T,V)}{N_i} \right\} ,
\]
to the condition for chemical equilibrium we get
\[
\Sigma \nu_i \mu_i = -kT \Sigma \nu_i \ln \left\{ \frac{Z_i(T,V)}{N_i,\text{eq}} \right\} = 0 .
\]
The number of molecules $i$ in chemical equilibrium are denoted by $N_{i,\text{eq}}$. Dividing by $-kT$ and using some algebra the equation can be written as
\[
\Sigma \nu_i \ln \left\{ \frac{Z_i(T,V)}{N_{i,0}} \right\} = \Sigma \ln \{Z_i(T,V)\}^{\nu_i} - \Sigma \ln \{N_{i,0}\}^{\nu_i} = 0 .
\]
We move the second term to the right and take both sides as arguments of an exponential function:
\[
\Leftrightarrow e^{\Sigma \ln(Z_i(T,V))^{\nu_i}} = e^{\Sigma \ln[N_{i,0}]^{\nu_i}} ,
\]
which is equivalent with
\[
Z_1(T,V)^{\nu_1} Z_2(T,V)^{\nu_2} Z_3(T,V)^{\nu_3} \ldots = N_{1,\text{eq}}^{\nu_1} N_{2,\text{eq}}^{\nu_2} N_{3,\text{eq}}^{\nu_3} \ldots
\]
or
\[
\Pi (N_{i,\text{eq}}^{\nu_i}) = \Pi (Z_i(T,V)^{\nu_i}) .
\]
The left hand side is called the equilibrium constant, $K$. Here it is expressed in terms of the numbers of molecules in constant volume $V$ and temperature $T$. We therefore write
\[
K(T,V) \equiv \Pi (N_{i,\text{eq}}^{\nu_i}) = \Pi (Z_i(T,V)^{\nu_i}) .
\]

As an example we consider the reaction
\[
A + B \overset{k_+}{\underset{k_-}{\rightleftharpoons}} C + D .
\]
For this reaction the total number of particles is constant, \( \Sigma \nu_i = 0 \), and \( |\nu_i| = 1 \) for all \( i \). Eq. 23 means that the relative numbers in equilibrium can be calculated from the following formula:

\[
\frac{N_{\text{C,eq}}N_{\text{D,eq}}}{N_{\text{A,eq}}N_{\text{B,eq}}} = \frac{k_+}{k_-} \equiv K(T) = \frac{Z_C Z_D}{Z_A Z_B}.
\]

\( K \) does not depend on the volume because \( V_s \) is reduced: \( V \Sigma i \nu_i = 1 \). Here the numbers \( N_i \) can be replaced by number densities \( n_i \).

10  The equilibrium constant in terms of partial pressures

The equilibrium constant in terms of partial pressures, \( K_P(T) \), for an ideal gas can be derived either from the expression for \( K(T,V) \) above (Eq. 23), or by substituting the chemical potential from Eq. 20 to the condition for chemical equilibrium (Eq. 8). The latter method gives

\[
\Sigma_i \nu_i \mu_i = \Sigma_i \nu_i [kT \ln P_i + f_i(T)] = 0.
\]

Dividing by \( -kT \) we obtain

\[
\Sigma_i \nu_i \ln P_i = kT \left( \frac{\ln a_i}{kT} \right) = \frac{\Sigma_i \nu_i f_i(T)}{kT}.
\]

The function \( f_i(T)/(\ln a_i) \) on the right is a logarithm as can be seen in the definition of \( f(T) \) (Eq. 16), and both sides can be written as products. First we, however, leave the right hand side unaltered, and note that the equation above is equivalent with

\[
e^{\Sigma_i \nu_i \ln P_i} = e^{\Sigma_i \ln P_i \nu_i} = \Pi (P_i^{\nu_i}) = e^{-\Sigma_i \nu_i f_i(T)/(kT)},
\]

where \( \Pi (P_i^{\nu_i}) = P_1^{\nu_1} P_2^{\nu_2} P_3^{\nu_3} ... \). Here we have used the relations \( \ln a^p = p \ln a \) and \( e^{\ln a} = a \).

The product \( \Pi (P_i^{\nu_i}) \) is defined as the equilibrium constant for partial pressures, \( K_P(T) \), and it can be thus written as

\[
K_P(T) \equiv \Pi (P_i^{\nu_i}) = e^{-\Sigma_i \nu_i f_i(T)/(kT)}.
\]

The same result can be obtained from Eq. 23 by using the equation of state of an ideal gas, \( PV = NkT \), and the relationship between the numbers \( N_i \), partial pressures, \( P_i \), and concentrations \([i]\):

\[
[i] \equiv \frac{N_i}{N} = \frac{P_i}{P}.
\]

Substituting \( N_{i,0} = NP_{i,0}/P \) to Eq. 23,

\[
\Pi (N_{i,0}^{\nu_i}) = \Pi (Z_i(T,V)^{\nu_i})
\]

we obtain \( K \) in terms of partial pressures:

\[
\Pi (P_{i,0}^{\nu_i}) \equiv K_P(T) = \Pi \left( \frac{P_i^{\nu_i}}{N^{\nu_i}} \right) K(T,V) = \Pi \left( \frac{PV}{N} \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_{i,\text{int}}(T) \right)^{\nu_i} = \Pi \left( kT \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_{i,\text{int}}(T) \right)^{\nu_i} = \Pi \left( \exp \left\{ -\frac{f_i(T)}{kT} \right\} \right)^{\nu_i} = \exp \left\{ -\Sigma_i \nu_i f_i(T)/(kT) \right\},
\]

11
Likewise, we can derive the equilibrium constant in terms of concentrations substituting $N_i = N[i]$

$$\Pi([i]^0_0) \equiv K_C(T, P) = N^{-\Sigma \nu_i} K(T, V). \quad (25)$$

Eq. 24 is equivalent with the one presented in textbooks of chemistry (e.g. Atkins Ch. 9), relating $K_P$ to the “standard molar Gibbs function", $\Delta G_m^\circ$ (= $G_m^\circ$(products) - $G_m^\circ$(reactants)) of the reaction:

$$RT\ln K_P \quad (Atkins) = -\Delta G_m^\circ \quad (26)$$

Here the partial pressures in $K_P$ are replaced by ratios $P_i/P_{ref}$, where the reference pressure is 1 atm. Making the substitution $P_i \to (P_i/P_{ref})P_{ref}$ in Eq. 24 we obtain:

$$K_P(T) = \Pi(P_i^{\nu_i}) = \Pi((P_i/P_{ref})^{\nu_i}) \Pi(P_{ref}^{\nu_i}) = e^{-\Sigma \nu_i f_i(T)/(kT)}. \quad (27)$$

Taking the natural logarithm of the equation on the right we obtain

$$\ln\Pi((P_i/P_{ref})^{\nu_i}) = -\ln\Pi(P_{ref}^{\nu_i}) - \Sigma \nu_i f_i(T)/(kT)$$

$$= -\Sigma \nu_i [(\ln P_{ref} + f_i(T))/(kT)]$$

$$= -\Sigma \nu_i \mu_i^\circ / (kT).$$

In the last equation we have used the “standard chemical potential per molecule” defined in Eq. 22. The left hand side the equilibrium constant $K_P$ as defined by Atkins. Multiplying by $N_0kT \quad (= RT)$ we obtain the desired formula, because $N_0\mu_i^\circ = G_m^\circ$ and $\Sigma \nu_i G_m^\circ = \Delta G_m^\circ$, i.e. the change of molar Gibbs energy in the reaction. On grounds of this equation one can estimate $\Delta G_m^\circ(T)$ of a reaction by determining the equilibrium constant (i.e. equilibrium partial pressures) as a function of temperature.

### 11 The law of mass action

The law of mass action can be obtained from the formula for the equilibrium constants, $K(T, V)$ and $K_P(T)$ (Eqs. 23 and 24), simply by writing the expressions of the translational partition function explicitly on the right hand side. So we get

$$K(T, V) \equiv \Pi(N_i^{\nu_i}) = \Pi(Z_i(T, V)^{\nu_i})$$

$$= (Z_{i,tt}(T, V)Z_{i,nt}(T))^{\nu_i}$$

$$= \Pi(\left[V \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} Z_{i,nt}(T)\right]^{\nu_i})$$

$$= \Pi(\left[\frac{2\pi V kT}{h^2}\right]^{3/2} m_i^{3/2 \nu_i} Z_{i,nt}(T)^{\nu_i})$$

In the situation where the total number of particles does not change, $\Sigma \nu_i = 0$, the constants on the right, except the masses $m_i$ are reduced (note that also $V$ and $T$ are constants here), and the equation above can be simplified:

$$K(T) = \Pi(N_i^{\nu_i}) = \Pi(m_i^{3/2 \nu_i} Z_{i,nt}(T)^{\nu_i}). \quad (28)$$

We now manipulate the right hand side of Eq. 24:

$$\exp\left\{-\Sigma \nu_i f_i(T)\right\} = \exp\left\{-\Sigma \nu_i \ln f_i(T)\right\}$$

$$= \exp\left\{\Sigma \nu_i \ln \left[kT \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} Z_{i,nt}(T)\right]\right\}$$

$$= \Pi\left(kT \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} Z_{i,nt}(T)^{\nu_i}\right).$$

In case $\Sigma \nu_i = 0$ all the constants except the masses $m_i$ cancel each other in the product, and we obtain

$$K_P(T) \equiv \Pi(P_i^{\nu_i}) = \Pi(m_i^{3/2 \nu_i} Z_{i,nt}(T)^{\nu_i}). \quad (28)$$
12 Reaction heat

The heat absorbed by a reaction in constant pressure corresponds to the change of the enthalpy, $H$, of the system,

$$\delta Q_P = \delta H = \delta (E + PV) ,$$

whereas the heat absorbed in constant volume equals to the change of internal energy, $E$:

$$\delta Q_V = \delta E .$$

The enthalpy can be derived from the Gibbs energy using the previously mentioned relationships between $H$, $G$, and $S$:

$$H = G + TS = G - T \left( \frac{\partial G}{\partial T} \right)_{N,P} = -T^2 \left[ -\frac{G}{T^2} + \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_{N,P} \right] = -T^2 \left( \frac{\partial}{\partial T} \frac{G}{T} \right)_{N,P} .$$

Similarly, we see from the differential of the free energy, $F$, that

$$S = - \left( \frac{\partial F}{\partial T} \right)_{N,V} ,$$

and the internal energy can be obtained from

$$E = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_{N,V} = -T^2 \left[ -\frac{F}{T^2} + \frac{1}{T} \left( \frac{\partial F}{\partial T} \right)_{N,V} \right] = -T^2 \left( \frac{\partial}{\partial T} \frac{F}{T} \right)_{N,V} .$$

Consider the change of the Gibbs energy in $\delta n$ elementary reactions. For the mixture of gases the Gibbs energy can be written as $G = \Sigma \mu_i N_i$, and then

$$\delta G = \Sigma \mu_i \delta N_i .$$

According to the reaction equation, the number of molecules $i$ change in $\delta n$ elementary reactions by $\delta N_i = \nu_i \delta n$. Note that here we use the convention that the coefficients $\nu_i$ of the products (on the right) are positive, and the coefficients of the reactants are negative. Substituting $\delta N_i$ to the expression of $\delta G$ we get

$$\delta G = \delta n \Sigma \nu_i \mu_i .$$

We can proceed by writing the chemical potential in either of the forms derived above. Choosing the expression $\mu_i = kT \ln P_i + f_i(T)$ which is more natural in connection with the Gibbs energy we obtain

$$\delta G = \delta n \Sigma \nu_i [kT \ln P_i + f_i(T)] = \delta nkT [\Sigma \nu_i \ln P_i + \Sigma \nu_i \frac{f_i(T)}{kT}] = \delta nkT [\Sigma \nu_i \ln P_i - \ln K_P(T)] ,$$

In the last form we have used the formula of $K_P(T)$ derived above. The substitution of $\mu_i$ in terms of numbers yields

$$\delta G = \delta nkT [\Sigma \nu_i \ln N_i - \ln K(T, V)] = \delta nkT [\ln \Pi \left( N_i^{\nu_i} \right) - \ln \Pi \left( N_i^{\nu_i}_{i_0} \right)]$$
The general direction of the reaction can be seen in the sign of $\delta G$. In natural processes the Gibbs energy tends to a minimum. The reaction proceeds from the left to the right if $\delta G < 0$, and from the right to the left if $\delta G > 0$:

$$\rightarrow: \; \delta G < 0 \iff \Sigma \nu_i \ln P_i < \ln K_P(T) \iff \Pi (P_i^{\nu_i}) < \Pi (P_{i,eq}^{\nu_i})$$

$$\leftarrow: \; \delta G > 0 \iff \Sigma \nu_i \ln P_i > \ln K_P(T) \iff \Pi (P_i^{\nu_i}) > \Pi (P_{i,eq}^{\nu_i})$$

The reaction heat in constant pressure can be calculated using the relationship between $H$ and $G$:

$$\delta Q_p = \delta H = -T^2 \left( \frac{\partial}{\partial T} \frac{\delta G}{T} \right)_{T,P} = -\delta n k T^2 \frac{\partial}{\partial T} \left[ \Sigma \nu_i \ln P_i - \ln K_P(T) \right] = \delta n k T^2 \frac{\partial}{\partial T} \ln K_P(T)$$

If we choose $\delta n = N_0$ (the Avogadro number) the number of reactions corresponds to one mole, and we get the equation to a more familiar form (van ’t Hoff’s equation):

$$\frac{\partial}{\partial T} \ln K_P(T) = \frac{\Delta H}{RT^2}, \quad (29)$$

where $R \equiv N_0 k$ is the so called gas constant. From this equation we see that the heat absorbed by the reaction is positive, $\delta Q_p > 0$, when $\frac{\partial}{\partial T} \ln K_P(T) > 0$, i.e. when the equilibrium constant increases as a function of temperature. The reaction is then endothermic. Similarly, when $\frac{\partial}{\partial T} \ln K_P(T) < 0$, also $\delta Q_p < 0$, and the reaction is exothermic. Eq. 29 is equivalent with

$$\frac{\partial}{\partial T} \ln K_P(T) = -\frac{\Delta H}{R}.$$ (30)

The temperature parameter, $\beta \equiv \frac{1}{kT}$, is useful in calculations involving the partition function ($Z(\beta) = \Sigma g_i e^{-\beta E_i}$, $\frac{\partial}{\partial T} = -\frac{1}{kT^2} \frac{\partial}{\partial \beta}$). Using $\beta$ we get for the enthalpy of a single elementary reaction in constant pressure:

$$\delta H = -\frac{\partial}{\partial \beta} \ln K_P(\beta).$$

The reaction heat in constant volume, $\delta Q_V = \delta E$, can be derived starting from the change of free energy:

$$\delta F = \Sigma \frac{\partial E_i}{\partial N_i} \delta N_i = \Sigma \mu_i \nu_i \delta n = -\delta n k T \Sigma \nu_i \ln \left\{ \frac{Z(T,V)}{N_i} \right\} = -\delta n k T [\ln K(T,V) - \Sigma \nu_i \ln N_i],$$

which implies

$$\delta E = -T^2 \left( \frac{\partial}{\partial T} \frac{\delta F}{T} \right)_{N,V} = \delta n k T^2 \frac{\partial}{\partial T} \ln K(T,V).$$

Using the temperature parameter $\beta$ we get for a single reaction in constant volume:

$$\delta E = -\frac{\partial}{\partial \beta} \ln K(\beta,V).$$
References