ESTABLISHMENT OF THE CHEMICAL EQUILIBRIUM

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A chemical equilibrium in a closed system can be considered as a set of states lying inside the band of equilibrium fluctuations of the system composition. This concept enables to define a further characteristic reaction time — the time necessary for reaching the band of equilibrium fluctuations (the time necessary for establishing the equilibrium). It is shown that this time is a linear function of the logarithm of the number of reactant particles in the system. Several ways can be used to define the width of the band of equilibrium fluctuations, but all of them yield approximately identical times necessary for establishing the equilibrium.

The composition in a closed isothermal system of mutually chemically reacting components is changing until the chemical equilibrium is established. According to the classical deterministic theory of chemical reactions, the time dependence of the composition in the system is determined by the order of proceeding reactions and it is characterized by an asymptotic approach to the steady-state composition, which determines the thermodynamic chemical equilibrium[1]. In the classical theory of the chemical kinetics, the time necessary for establishing the equilibrium composition is infinitely large, so that, strictly speaking, the exact state of the chemical equilibrium cannot be reached experimentally at all. In the classical chemical kinetics it is also assumed that chemically reacting components represent a continuum, that the reaction can be described by a set of simple differential equations derived from the law of mass action, and that solutions to these equations yield unambiguously concentrations of all components in the system at an arbitrary moment of time. However, the composition in a system is an integer-valued quantity (the number of particles, *i.e.*, atoms, molecules, radicals) and any change in composition represents a random, *i.e.*, stochastic process[2,3]. As a matter of fact, the chemical equilibrium is a state characterized not only by a sharp mean value of composition, but also by equilibrium fluctuations about this mean value. Consequently, we can denote as an equilibrium system such a system whose composition lies in a band surrounding symmetrically the mean equilibrium value. The width of this band can be defined in several ways and some of them will be discussed below. The time in which a system reaches the boundary of this band, can be taken as the time necessary for establishing the chemical equilibrium.

Stochastic Description of a Reaction

For the sake of simplicity, the establishment of the chemical equilibrium will be illustrated on the simplest chemical reaction of the type

$$A \rightleftarrows B\,, \tag{1}$$

which is characterized by rate parameters k_1 and k_2: the probability that a randomly selected particle A will change to B during the time interval $(t,\ t + \Delta t)$, $\Delta t \to 0$, is equal to $k_1\ \Delta t$ and the probability that a randomly selected particle B will react during the same time interval is equal to $k_2\ \Delta t$. If, at the beginning $(t = 0)$, no particle B is present in the system containing N particles of the type A, then the probability that the system will contain $N_A(t) = j$ particles A at time t is equal to[3,4]

$$\text{Prob}\,\{N_A(t) = j\} \equiv P_j(t) = \binom{N}{j}\,[p_A(t)]^j\,[p_B(t)]^{N-j}\,, \tag{2}$$

where

$$p_A(t) = \{k_2 + k_1 \exp\,[-(k_1 + k_2)\,t]\}/(k_1 + k_2)\,, \tag{3}$$

$$p_B(t) = k_1\{1 - \exp\,[-(k_1 + k_2)\,t]\}/(k_1 + k_2)\,. \tag{4}$$

The mean number of particles A in the system is

$$\langle N_A(t)\rangle \equiv \sum_{j=0}^{N} jP_j(t) = Np_A(t) \tag{5}$$

and the variance of the number of particles A at time t is

$$D^2\{N_A(t)\} \equiv \sum_{j=0}^{N} j^2P_j(t) - (\sum_{j=0}^{N} jP_j(t))^2 = Np_A(t)\,p_B(t)\,. \tag{6}$$

In the limit of $t \to \infty$ (which corresponds to the macroscopic chemical equilibrium) it holds

$$\lim_{t\to\infty} P_j(t) \equiv P_{j,e} = \binom{N}{j} K^{N-j}/(1 + K)^N\,, \tag{7}$$

$$\lim_{t\to\infty} \langle N_A(t)\rangle \equiv \langle N_A\rangle_e = N/(1 + K)\,, \tag{8}$$

$$\lim_{t\to\infty} D^2\{N_A(t)\} \equiv D_e^2\{N_A\} = KN/(1 + K)^2\,, \tag{9}$$

and $K = k_1/k_2$ is the equilibrium reaction constant. The distribution $P_{j,e}$ defines the equilibrium in an ensemble of systems containing the same total number of particles. The mean number of particles A, $\langle N_A(t)\rangle$, is identical with the deterministic solution of the differential equation for the concentration of component A and, with increasing t, it approaches asymptotically its equilibrium value, $\langle N_A\rangle_e$.

The Band of Equilibrium Composition Fluctuations

According to Eq. (*9*), the standard deviation (the square root of the variance) of the number of particles A at equilibrium is equal to

$$D_e\{N_A\} = (KN)^{1/2}/(1 + K)\,. \tag{9a}$$

Let us then define the band of equilibrium fluctuations as the region of $N_A(t)$ values satisfying the inequality

$$\langle N_A\rangle_e - D_e\{N_A\} < N_A(t) < \langle N_A\rangle_e + D_e\{N_A\}\,. \tag{10}$$

A system the composition of which lies within the band determined by inequality (*10*) can be considered to be at equilibrium. The time necessary for establishing the chemical equilibrium[5], t_e, is consequently defined as the time in which the mean number of particles A in the system will reach the value $\langle N_A(t_e)\rangle = \langle N_A\rangle_e + D_e\{N_A\}$ (Fig. 1). It follows from Eqs (*3*), (*5*), (*8*) and (*9a*) that

$$t_e = (1/2(k_1 + k_2))\ln(KN)\,. \tag{11}$$

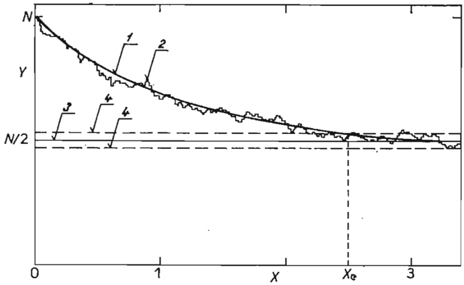

FIG. 1

The Reaction Course and the Equilibrium Fluctuation Band ($K = 1$)

1 Mean value of the number of particles A, *2* the composition in an individual system (schematically), *3* the mean equilibrium value of the number of particles A, *4* the boundary of the equilibrium fluctuation band. $X = kt$, $Y = N_A(t)$, $X_e = kt_e$.

Since the relaxation time of the reaction[5,6] – defined by the relation $[\langle N_A(t_r)\rangle - \langle N_A\rangle_e]/(N - \langle N_A\rangle_e) = 1/e$ – is $t_r = 1/(k_1 + k_2)$, Eq. (*11*) can be rewritten as

$$t_e/t_r = (1/2)\ln(KN)\,. \tag{11a}$$

The time necessary for establishing the chemical equilibrium defined in this manner is an increasing linear function of the logarithm of the total number of particles in the system. With K close to unity and N assuming its usual experimental value ($N \sim 10^{20}$), it holds $t_e/t_r \approx 23$: the composition in the system reaches the band of equilibrium fluctuations during a time which is approximately 23 times longer than the relaxation time of the reaction.

Now let us show how t_e depends on the choice of the width of the band. We extend the width of the band of equilibrium fluctuations by one order, so that an equilibrium system will be determined by the inequality

$$\langle N_A\rangle_e - 10\,.\,D_e\{N_A\} < N_A(t) < \langle N_A\rangle_e + 10\,.\,D_e\{N_A\}\,. \tag{12}$$

A calculation shows that in this case we obtain

$$t_e/t_r = (1/2)\ln(KN) - 2{\cdot}3\,, \tag{13}$$

so that – at the same conditions ($K \approx 1$, $N \approx 10^{20}$) – it holds $t_e/t_r \approx 20{\cdot}7$. An extension of the band width by one order makes the value of t_e/t_r decrease by 10% only. With a choice of the band width according to relation (*10*), the ratio between times during which the system in the steady state resides outside the band and inside it, respectively, is approximately 1/2, whereas with a choice of the band width according to (*12*), this ratio is of the order of 10^{-23} (the latter value means that the system will be found in a state satisfying inequality (*12*) with a probability which can be denoted as certainty). Even though the choice of the band width is to a certain extent arbitrary, from the foregoing it obviously follows that Eqs (*11*) and (*11a*) yield a sufficiently accurate estimate of the time necessary for reaching a composition which can be considered as the equilibrium one. Let us only note that the time necessary for reaching a mean composition in the system which differs from the mean equilibrium value by 0·01% (*i.e.*, the time for which it holds $(\langle N_A(t)\rangle - \langle N_A\rangle_e)/(N - \langle N_A\rangle_e) = 10^{-4}$) is equal approximately to $9t_r$. For $k_1 = k_2 = k$, the number of elementary reaction events (*i.e.*, of transitions of particles A to B and B to A) in the system and in unit time is equal to kN (*cf.*[7,8]). According to Eq. (*11*), the number of elementary reaction events realized during the time necessary for establishing the chemical equilibrium is equal to $kNt_e = (N/4)\ln N$ for $K = 1$. For N of the order of 10^{20}, this quantity is of the order of 10^{21}.

The Indicator of the Location of the Composition with Respect to Its Mean Equilibrium Value

Let us introduce a new random variable

$$X_A(t) = N_A(t) - \langle N_A \rangle_e \,, \tag{14}$$

and let us define the step function of this random variable as

$$H(X_A(t)) = \begin{cases} 1 & \text{for} \quad X_A(t) > 0 \\ 0 & \text{for} \quad X_A(t) < 0 \,. \end{cases} \tag{15}$$

The function $H(X_A(t))$ indicates the location of the composition of the system with respect to the chemical equilibrium: its value is unity for a system in which the number of particles A is higher than the mean equilibrium value $\langle N_A \rangle_e$ or zero for a system with the number of particles A lower than $\langle N_A \rangle_e$ (the indicator of the stochastic phenomenon has been introduced, *e.g.*, in[9]). To make the calculations easier, we shall limit ourselves to the case of $N_A(0) = N$, N large, $k_1 = k_2 = k(K = 1)$.

In an ensemble of systems, the mean value of this indicator, $\langle H(X_A(t)) \rangle = \sum_{j=0}^{N} H(j - N/2)\, P_j(t)$, decreases during the reaction from 1 to 1/2 (which is the mean equilibrium value of the indicator, $\langle H(X_A) \rangle_e$) in accordance with the relation[10]

$$\langle H(X_A(t)) \rangle = (1/2)\,(1 + \operatorname{erf}(z)) \,, \tag{16}$$

where $\operatorname{erf}(z) = (2/\pi^{1/2}) \int_0^z \exp(-u^2)\, du$ and $z = (N/2) \exp(-2kt)/[N(1 - \exp(-4kt))/2]^{1/2}$ (this dependence is illustrated in Fig. 2). The relaxation time, t'_e, of the

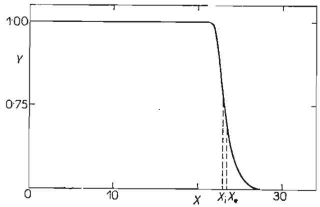

FIG. 2

The Mean Value of the Indicator $H(X_A(t))$
$N = 10^{20}$, $X = t/t_r$, $X_e = t'_e/t_r$, $X_i = t_i/t_r$, $Y = \langle H(X_A(t)) \rangle$.

normalized function $[\langle H(X_A(t))\rangle - \langle H(X_A)\rangle_e]/\langle H(X_A)\rangle_e = \mathrm{erf}(z)$ is defined[10] by the relation $\mathrm{erf}(z_e) = 1/\mathrm{e}$, where $z_e = (N/2)\exp(-2kt'_e)/[N(1 - \exp(-4kt'_e))/2]^{1/2}$. Hence it follows

$$t'_e \approx (1/4k)(\ln N + 1{\cdot}4)\,, \tag{17}$$

or

$$t'_e/t_r \approx (1/2)\ln N + 0{\cdot}7\,. \tag{17a}$$

The quantity t'_e/t_r differs numerically only little from the value of t_e/t_r according to Eq. (*11a*) and it can be considered as a further possible definition of the time necessary for establishing the chemical equilibrium.

Let us further show how t'_e depends on the choice of the upper bound of the interval of values of $\langle H(X_A(t))\rangle$, which defines the equilibrium composition band. The time required for the decrease of the function $\mathrm{erf}(z)$ to $1/10\mathrm{e}$ is

$$t'_e/t_r \approx (1/2)\ln N + 3{\cdot}0\,. \tag{18}$$

For N of the order of 10^{20}, the value of t'_e/t_r is, according to relation (*17a*), equal approximately to 24, according to relation (*18*) it is approximately 26. The time coordinate of the inflexion point of the function $\langle H(X_A(t)\rangle$ is $t_i \approx \ln N/4k$ and $t_i/t_r \approx \approx (1/2)\ln N$, which agrees with the right-hand side of Eq. (*11a*). Even in this case the choice of the equilibrium fluctuation band affects only little the value of the time necessary for reaching the concentration region taken for corresponding to the equilibrium, since the dependence of $\langle H(X_A(t))\rangle$ on t approaches that of the step function $1 - H(t - t_i)/2$.

Fluctuations of the Reaction Entropy in the Vicinity of the Equilibrium

The quantity S_j, which is defined through the relation

$$S_j = \boldsymbol{k}_B \ln P_{j,e} + c\,, \tag{19}$$

where $\boldsymbol{k}_B$ is Boltzmann's constant and c is an arbitrary additive constant, represents a stochastic analogy to the entropy of the system in the state j. The mean value of S_j is a stochastic analogy to the reaction entropy- a function defined in the irreversible thermodynamics[11] (the definition and properties of the stochastic reaction entropy are discussed in more detail in[4,12]). The reaction entropy, $\langle S_j\rangle \equiv \boldsymbol{k}_B \sum_{j=0}^{N} P_j(t) \ln P_{j,e} + c$, depends on the composition of the system through the relation[4]

$$\langle S_j\rangle - \langle S_j\rangle_e \approx -\boldsymbol{k}_B[(\langle N_A(t)\rangle + 1/2)\ln(\langle N_A(t)\rangle/\langle N_A\rangle_e) + (N - \langle N_A(t)\rangle + 1/2)\ln((N - \langle N_A(t)\rangle)/(N - \langle N_A\rangle_e))]\,, \tag{20}$$

where $\langle S_j \rangle_e = k_B \sum_{j=0}^{N} P_{j,e} \ln P_{j,e} + c$. In the vicinity of the deterministic equilibrium, the right-hand side of Eq. (*20*) can be approximated by the expression

$$-k_B(1 + K)^2 \langle X_A(t) \rangle^2 / 2KN = -k_B(KN/2) \exp\left(-2(k_1 + k_2)\, t\right). \qquad (21)$$

Since, in the vicinity of the equilibrium (*i.e.*, for $t \to \infty$), the variance of the reaction entropy is equal to[4] $k_B^2/2$ and the standard deviation assumes the value of $k_B/2^{1/2}$, the time necessary for establishing the chemical equilibrium, t''_e, can be defined as the time in which the difference $\langle S_j \rangle - \langle S_j \rangle_e$ reaches the value of $-k_B/2^{1/2}$. That system will now be considered as an equilibrium one, for which it holds $S_j - \langle S_j \rangle_e > > - k_B/2^{1/2}$. Hence and from relation (*21*) we obtain

$$t''_e/t_r \approx (1/2) \ln KN - 0{\cdot}2\,, \qquad (22)$$

which, for large N, yields practically the same result as Eq. (*11a*). The width of the equilibrium fluctuation band is in this case determined by the universal constant of the statistical mechanics, *i.e.*, by Boltzmann's constant k_B.

The Determination of the Equilibrium Constant

Let us assume that the state of chemical equilibrium is determined by the fluctuation band according to inequality (*10*), resp. (*12*). A determination of the number of particles A in the system, performed after time t_e from the beginning of the reaction, will yield a result which (even at an arbitrarily high accuracy of the measurement) will generally differ from the mean equilibrium value $\langle N_A \rangle_e$, on the average by $D_e\{N_A\}$ resp. $10 \,.\, D_e\{N_A\}$. Consequently, the ratio between the numbers of particles B and A will not generally be identical with the quantity K, but it will display some difference. In the least favourable case it holds (for $t > t_e$)

$$N_B(t)/N_A(t) = K \pm 10(1 + K)(K/N)^{1/2}\,. \qquad (23)$$

For large N, the second term on the right-hand side of this equation is so small, that it can be entirely neglected. For N of the order of 10^{20} and K close to unity, its value oscillates about 10^{-9}. Therefrom it can be deduced that any determination of the composition in the system performed at a time $t > t_e$ will yield reliable values of the equilibrium constant. The mathematical limit of $t \to \infty$, which defines the macroscopic equilibrium, can be therefore interpreted physically by values of $t > t_e$.

Dynamics of the Reaction in the Equilibrium Fluctuation Band

The macroscopic reaction rate, r, is defined as the negative value of the actual time change of the mean number of particles A in the system: $r = -\mathrm{d}\langle N_A(t) \rangle/\mathrm{d}t$. In accordance with the law of mass action, the first order reaction rate must obey the relaxation equation

$$r = k_1\langle N_A(t)\rangle - k_2(N - \langle N_A(t)\rangle) = (k_1 + k_2)\langle X_A(t)\rangle\,. \tag{24}$$

At the boundary of the equilibrium fluctuation band, according to (*10*) it holds $\langle X_A(t)\rangle = (KN)^{1/2}/(1 + K)$ and the reaction rate is equal to

$$r = (k_1k_2N)^{1/2}\,. \tag{25}$$

In the reaction kinetics, the term $k_1\langle N_A(t)\rangle$ represents the rate of the elementary reaction A → B, r_+, the term $k_2(N - \langle N_A(t)\rangle)$ is the rate of the elementary reaction B → A, r_-. The sum $r_+ + r_-$ is equal to the number of elementary reaction events in the system per unit time and, in the vicinity of the mean equilibrium composition, it is equal approximately[7,8] to $2k_1k_2N/(k_1 + k_2)$. Hence and from Eq. (*25*) it follows that inside the equilibrium fluctuation band, *i.e.* after a time $t > t_e$ from the beginning of the reaction, the ratio r_+/r_- is less than $1 + (1 + K)/(KN)^{1/2}$. In the limit of $t \to \infty$, the mean value $\langle N_A(t)\rangle$ is equal to $\langle N_A\rangle_e$, $r = 0$, and the dynamics of the reaction manifests itself only through equilibrium fluctuations of the composition[13]. The mean amplitude of these fluctuations is of the order of $D_e\{N_A\}$ and the mean time between two succeeding transitions of the system through the state $N_A(t) = \langle N_A\rangle_e$ is[7] $t_0 \approx (\pi/2k_1k_2N)^{1/2}$ (for the sake of simplicity we assume that $\langle N_A\rangle_e$ is an integer). For illustration let us remark that for $k_1 = k_2$ and $N = 10^{20}$, t_0/t_r is of the order of 10^{-10}.

The mean time interval during which the system can be found in the state $N_A(t) = \langle N_A\rangle_e$ is equal to $[k_1\langle N_A\rangle_e + k_2(N - \langle N_A\rangle_e)]^{-1} = (k_1 + k_2)/2k_1k_2N$. The ratio of this quantity to the time t_0 gives the probability of finding the system in the state $\langle N_A\rangle_e$ in time $t > t_e$: $\text{Prob}\,\{N_A(t) = \langle N_A\rangle_e;\, t \to \infty\} \sim (1 + K)/(2\pi KN)^{1/2}$. The value of this expression is extremely small: for K close to unity and N of the order of 10^{20}, it is of the order of 10^{-10}. The probability that the system – at the same conditions – will be found in the equilibrium fluctuation band, *i.e.*, $\text{Prob}\,\{\langle N_A\rangle_e - \alpha D_e\{N_A\} < N_A(t) < \langle N_A\rangle_e + \alpha D_e\{N_A\};\, t \to \infty\}$, is approximately 0·7 for $\alpha = 1$ and practically unity for $\alpha > 2$. The number of states, *i.e.*, of values of $N_A(t)$, in this band is equal to $\alpha N^{1/2} = \alpha 10^{10}$.

We can conclude our results by stating that the chemical equilibrium of reaction (*1*) can be considered *1*) in the deterministic theory as a singular state $\langle N_A\rangle_e$, which is being approached asymptotically in time by the system composition, *2*) in an ensemble of systems containing the same total number of particles as a limiting steady-state distribution of compositions of the individual systems according to distribution $P_{j,e}$ and *3*) in an individual system as a set of values of $N_A(t)$ lying inside the equilibrium fluctuation band. The last concept enables to define a further characteristic time of the reaction – the time necessary for reaching the equilibrium fluctuation band. At usual laboratory conditions, *i.e.*, for N of the order of 10^{20}, this time is approximately 23 times longer than the relaxation time of the reaction and two to three times longer than the time necessary for reaching a composition which differs from its mean equilibrium value by 0·01% (which can be considered as an upper bound to the accuracy of common analytical methods for determining the composition).

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