

## Thermodynamic restrictions on the temperature and pressure dependence of the rate constant in chemical reaction kinetics

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### Abstract

Based on classical thermodynamic arguments, an equation relating the partial derivatives of the kinetic rate constant with respect to temperature and pressure is derived for a reversible elementary chemical reaction at equilibrium.

It is argued that the rate constant is in principle a state function with temperature, pressure and composition as independent variables in non-equilibrium states. It reduces to a state function of temperature and pressure only at equilibrium, or when the rate constant is (explicitly assumed to be) independent of composition. The reaction rate is a state function of temperature and pressure only in the case of equilibrium.

On this basis an alternative interpretation of observed correlations between experimental rate data reported in the literature is proposed.

### INTRODUCTION

At thermodynamic equilibrium, a closed, reactive chemical system is in a classical thermodynamic state. The thermodynamic functions describing the time-independent properties of the system are thermodynamic state [1] (point [2]) functions. By analogy, this should also apply to other functions characterizing the equilibrium state, such as the related, classical kinetic functions including the rate constant of an elementary reaction.

The time-dependent, non-equilibrium state, however, is not a classical thermodynamic state. But by assuming thermal and mechanical equilibrium in the system [3], an analogous (more or less) approximate description of the non-equilibrium state becomes possible in terms of classical thermodynamic functions.

The main point here is that these functions are (state) functions of temperature, pressure (or volume) and composition as independent variables in a given, closed system, as opposed to only two at equilibrium. By analogy, this should also in principle apply to other functions characteristic of the state, such as the rate constant, for instance.

On the basis an alternative interpretation of the correlation derived from experimental reaction rate data reported in the literature [4] becomes possible.

Before discussing this in more detail, an equation relating the partial derivatives of the kinetic rate constant with respect to temperature and pressure will be derived for a reversible, elementary chemical reaction at equilibrium, using classical, thermodynamic arguments.

#### THERMODYNAMIC CONSIDERATIONS

Consider a reversible reaction  $\sum_i a_i A_i = 0$ . The reaction coefficients  $a_i$  are taken to be negative for those species  $A_i$  that appear on the left-hand side of the reaction equation as normally written, and positive for those to the right. The differential of the thermodynamic equilibrium constant is completely specified in terms of  $T$  and  $P$

$$d \ln K = \frac{\partial \ln K}{\partial T} dT + \frac{\partial \ln K}{\partial P} dP \quad (1)$$

We define  $K$  in terms of mole fractions  $x_i$  and rational activity coefficients  $f_i$  [5] in the general case

$$K \equiv \prod_i^N (f_i x_i)^{a_i}$$

The  $f_i$  coefficients are functions of composition, i.e. the mole fractions. The latter vary in general with temperature and pressure in a closed system at equilibrium. Introducing the number of moles of the  $i$ th species  $n_i$  as variables, we may write alternatively

$$K(x_1, x_2, \dots) = K(n_1, n_2, \dots)$$

given that

$$x_i \equiv n_i / \sum_i n_i$$

Hence

$$d \ln K = \sum_i \frac{\partial \ln K}{\partial n_i} dn_i \quad (2)$$

We limit the discussion to a reaction in a given, closed system that evolves from one equilibrium state to another as the temperature and pressure change. Thus, other equilibrium states, which are accessible to open systems by mass transfer across phase boundaries between the system and its surroundings at constant  $T$ ,  $P$  and  $K$ , are ignored.

In this case, the change in  $n_i$  is completely specified by

$$dn_i = \frac{\partial n_i}{\partial T} dT + \frac{\partial n_i}{\partial P} dP \quad (3)$$

Provided there is (approximately) no net conversion of actual reaction species in intermediate reactions the mass balance becomes

$$\frac{dn_i}{a_i} = \frac{dn_j}{a_j} \quad (\text{independent of } i, j) \quad (4)$$

There are, in principle, two free variables in the present system. Possible choices are  $TP$ ,  $Tn_i$  or  $Pn_i$ , for instance. The change in the third of these variables due to changes in the other two is given by eqn. (3), while changes in the remaining  $n_j$ 's are given by eqn. (4), etc. The variables themselves may be obtained by integrating from the starting point, given the initial conditions.

Thus, by substituting eqn. (4) into eqn. (2) and then using eqn. (3)

$$d \ln K = \frac{dT}{a_k} \frac{\partial n_k}{\partial T} \sum_i \frac{\partial \ln K}{\partial n_i} a_i + \frac{dP}{a_k} \frac{\partial n_k}{\partial P} \sum_i \frac{\partial \ln K}{\partial n_i} a_i$$

which may be compared with eqn. (1) to give

$$\frac{1}{a_k} \frac{\partial n_k}{\partial T} \sum_i \frac{\partial \ln K}{\partial n_i} a_i = \frac{\partial \ln K}{\partial T} \left( = \frac{\Delta H^\circ}{RT^2} \right) \quad (5)$$

and

$$\frac{1}{a_k} \frac{\partial n_k}{\partial P} \sum_i \frac{\partial \ln K}{\partial n_i} a_i = \frac{\partial \ln K}{\partial P} \left( = -\frac{\Delta V^\circ}{RT} \right) \quad (6)$$

using the convention  $\mu_i^\circ = \mu_i^\circ(TP)$ , in  $\mu_i = \mu_i^\circ + RT \ln f_i x_i$ , such that  $\partial \mu_i^\circ / \partial P = V_i^\circ$ , as required in the ideal gas and ideal solution cases [6].

$\Delta V^\circ = 0$  for an ideal gas reaction when  $\sum_i a_i = 0$ .

If the reactants and products are related by symmetry as are, for instance, enantiomers, then both  $\Delta H^\circ$  and  $\Delta V^\circ$  are zero, so that  $\partial \ln K / \partial T = \partial \ln K / \partial P = dn_k \equiv 0$ , for all  $k$ . The probability that  $\Delta H^\circ$  and/or  $\Delta V^\circ$  vanish completely is zero in the absence of any such restriction.

#### KINETIC-THERMODYNAMIC CONSIDERATIONS

Assuming the reversible reaction to be elementary [7], we may put

$$K = k_+ / k_- \quad (7)$$

where  $k_+$  and  $k_-$  are the rate constants of the forward and reverse reaction, respectively. (This somewhat unusual form of the rate constant ratio is related to the usual one based on molarity below.) The rate constants are, in principle, functions of  $T$ ,  $P$  and composition, whereas the ratio is independent of composition at fixed  $T$  and  $P$ .

Substituting eqn. (7) into eqn. (1) gives, after rearranging terms

$$\begin{aligned} d \ln k_+ - \frac{\partial \ln k_+}{\partial T} dT - \frac{\partial \ln k_+}{\partial P} dP &= d \ln k_- - \frac{\partial \ln k_-}{\partial T} dT - \frac{\partial \ln k_-}{\partial P} dP \\ &\equiv d \ln f \quad (\text{say}) \end{aligned} \quad (8)$$

where  $f = f(TPn_1n_2 \dots n^*)$ , including independent and dependent variables for completeness;  $n^*$  is the mole number of transition state complexes, which is another quantity common to both reactants and products, introduced for completeness;  $f$  may, in principle, vary with composition at fixed  $T$  and  $P$ . However, such states are ruled out at the outset by eqn. (3). Thus,  $n^*(TPn_1n_2 \dots)$  and  $f$  and hence,  $k_+$  and  $k_-$  are here completely specified by  $T$  and  $P$  given the initial conditions. Furthermore, if eqn. (8) is to be reduced to the normal differential form of  $k_+$  and  $k_-$  in terms of  $T$  and  $P$ ,  $f$  must simply be taken to be constant. In this way we obtain

$$d \ln k_{\pm} = \frac{\partial \ln k_{\pm}}{\partial T} dT + \frac{\partial \ln k_{\pm}}{\partial P} dP \quad (9)$$

where  $\pm$  denotes either + or -.

Similarly, we obtain from eqns. (2) and (7)

$$d \ln k_+ - \sum_i \frac{\partial \ln k_+}{\partial n_i} dn_i = d \ln k_- - \sum_i \frac{\partial \ln k_-}{\partial n_i} dn_i \equiv d \ln g \quad (\text{say}) \quad (10)$$

where  $g = g(TPn_1n_2 \dots n^*)$ . In agreement with statements made above,  $g$  may be written as a function of the  $n_i$ 's only. Thus

$$d \ln g = \sum_i \frac{\partial \ln g}{\partial n_i} dn_i$$

which gives, with eqn. (10)

$$\begin{aligned} d \ln k_{\pm} &= \sum_i \frac{\partial \ln(k_{\pm}g)}{\partial n_i} dn_i = \frac{dn_k}{a_k} \sum_i \frac{\partial \ln(k_{\pm}g)}{\partial n_i} a_i \\ &= \frac{1}{a_k} \left( \frac{\partial n_k}{\partial T} dT + \frac{\partial n_k}{\partial P} dP \right) \sum_i \frac{\partial \ln(k_{\pm}g)}{\partial n_i} \end{aligned} \quad (11)$$

using eqns. (4) and (3), respectively. Comparing eqns. (9) and (11) leads to

$$\frac{1}{a_k} \frac{\partial n_k}{\partial T} \sum_i \frac{\partial \ln(k_{\pm}g)}{\partial n_i} a_i = \frac{\partial \ln k_{\pm}}{\partial T}$$

and

$$\frac{1}{a_k} \frac{\partial n_k}{\partial P} \sum_i \frac{\partial \ln(k_{\pm}g)}{\partial n_i} a_i = \frac{\partial \ln k_{\pm}}{\partial P}$$

from which we obtain by dividing by eqns. (5) and (6), respectively

$$\frac{\partial \ln k_{\pm}}{\partial P} \frac{\partial \ln K}{\partial T} = \frac{\partial \ln k_{\pm}}{\partial T} \frac{\partial \ln K}{\partial P} \quad (12)$$

Thus, thermodynamics postulates a definite relationship between the partial derivatives of the rate constant with respect to temperature and pressure. (A further analysis indicates that the auxiliary function  $g$  cannot be determined along these lines alone. Alternatively it may be chosen. Thus, put equal to a constant,  $g$  simply drops out of the equations.)

Equation (12) may also be applied to heterogeneous processes in simple one-component systems (mass transfer across phase boundaries).  $P$  and  $T$  are no longer independent variables: eqn. (1), equated to zero, provides the Clapeyron equation; using eqns. (5) and (6),  $dP = (\Delta H/T\Delta V) dT$ . The  $n_i$  represent molecules at interfacial (reactive) sites, or the like.

One finds from eqns. (9) and (12)

$$d \ln k_{\pm} = \frac{\partial \ln k_{\pm} / \partial T}{\partial \ln K / \partial T} \left( \frac{\partial \ln K}{\partial T} dT + \frac{\partial \ln K}{\partial P} dP \right)$$

The expression in parentheses on the right-hand side ( $=d \ln K$ ) is an exact differential of  $T$  and  $P$  according to classical thermodynamics, i.e.  $\partial^2 \ln K / \partial P \partial T = \partial^2 \ln K / \partial T \partial P$ . There is a priori no such restriction on the ratio (denoted  $R$  below) on the right-hand side, so that  $d \ln k_{\pm}$  may in principle be an inexact differential of  $T$  and  $P$  under equilibrium conditions.

However, if  $d \ln k_{\pm}$  is inexact,  $k_{\pm}$  would not be uniquely defined in a given equilibrium state, since it would in principle depend on the actual path chosen in the  $P, T$  plane, when preparing the actual equilibrium state. This would also apply to the reaction rate, which is clearly untenable.

It may therefore be assumed explicitly that  $k_{\pm}$  is a state function of  $T$  and  $P$  at equilibrium. This is in accordance with the transition state theory of reaction rates (TST), according to which reactants and TS complexes are assumed to be in equilibrium, clearly a reasonable assumption at thermodynamic equilibrium [7].

The exactness criteria for  $d \ln K$  and  $d \ln k_{\pm}$  require that there be a relation between the partial derivatives of  $R$  with respect to  $T$  and  $P$ , respectively, under equilibrium conditions. This may be written as

$$\frac{\partial R}{\partial P} \frac{\partial \ln K}{\partial T} = \frac{\partial R}{\partial T} \frac{\partial \ln K}{\partial P}$$

However, reactions are generally studied in non-equilibrium states, characterized by  $T, P$  and composition ( $x$ ) as independent variables. In such cases the temperature of the system has no longer a clear meaning [7] (and this also holds in principle for the pressure). In thermodynamics [3, 8] the temperature of a reacting system in a non-equilibrium state is generally identified with that of the heat reservoir in thermal contact with the system, and mechanical equilibrium is assumed [3]. The thermodynamic functions can thus be defined as in the equilibrium case, but now they are merely

approximate descriptions of the reactive, non-equilibrium system. Thus the molar Gibbs function of a (reacting) mixture  $G_x$  is a function of  $T$ ,  $P$  and  $x$  as independent variables, and a differential change in  $G_x$   $dG_x$  requires  $dT$ ,  $dP$  and  $dx$  to be given explicitly. Similar remarks apply in principle to the Gibbs function of the transition state.

Likewise,  $k_{\pm}$  becomes in principle a function of  $T$ ,  $P$  and  $x$  as free variables. It is believed to be a state function of these variables for the same reason as given in the equilibrium case above (where  $x$  is a dependent variable). The differential

$$d \ln k_{\pm} = \left( \frac{\partial \ln k_{\pm}}{\partial T} \right)_{Px} dT + \left( \frac{\partial \ln k_{\pm}}{\partial P} \right)_{Tx} dP + \left( \frac{\partial \ln k_{\pm}}{\partial x} \right)_{PT} dx$$

is accordingly exact. Thus  $d \ln k_{\pm}$  cannot be considered as an exact differential of  $T$  and  $P$  in the general case [4]. This is merely true at equilibrium (eqn. (9)), or when  $x$  is a constant, or  $(\partial \ln k_{\pm} / \partial x)_{PT} = 0$  (preceding equation). The last condition is in principle an assumption (approximation). The differential of the reaction rate expression, containing concentration terms, is an exact differential of  $T$  and  $P$  only when equilibrium states are considered, i.e. when  $x$  is a dependent variable.

Empirically,  $d \ln k_{\pm}$  comes fairly close to being an exact differential of  $T$  and  $P$  in various cases [4]. This indicates merely that  $k_{\pm}$  is relatively insensitive to changes in composition, not that  $d \ln k_{\pm}$  is actually an exact differential of  $T$  and  $P$ .

Similar results as obtained above, may be derived in terms of  $T$ ,  $V$  and  $x$  as independent variables, instead of  $T$ ,  $P$  and  $x$ .

#### THE RATE CONSTANT ON THE MOLARITY SCALE

(A) The rate constant may be put on either a mole fraction or a molarity basis. Thus, ignoring activity coefficients as a first approximation, we have at fixed  $T$  and  $P$

$$v_{\pm} = k_{\pm} \pi_{\pm} x_i^{|a_i|} = k_{c\pm} \pi_{\pm} c_i^{|a_i|} \quad (13)$$

where

$$v_{\pm} \left( \equiv \pm \frac{1}{V} \frac{dn_i/a_i}{dt} \right)$$

is the reaction rate [7] and  $c_i$  the molar concentration;  $\pi_{+}$  comprises all molecular species on the left-hand side of the reaction equation as normally written, and  $\pi_{-}$  those on the right-hand side. From this we get the well-known relation at equilibrium

$$k_{c+}/k_{c-} = \pi_i c_i^{a_i} \quad (14)$$

Using  $x_i = c_i / \sum_i c_i$ , one obtains from eqn. (13)

$$k_{c_{\pm}} = k_{\pm} \left/ \left( \sum_i c_i \right)^{\pm \sum |a_i|} \right. \quad (15)$$

Furthermore

$$\frac{\partial \ln k_{c_{\pm}}}{\partial T} = \frac{\partial \ln k_{\pm}}{\partial T} - \frac{\partial \ln \sum_i c_i}{\partial T} \sum_{\pm} |a_i|$$

and

$$\frac{\partial \ln k_{c_{\pm}}}{\partial P} = \frac{\partial \ln k_{\pm}}{\partial P} - \frac{\partial \ln \sum_i c_i}{\partial P} \sum_{\pm} |a_i|$$

The second terms on the right may be relatively small in general, because the various  $c_i$  changes are of opposite sign.

The right-hand side of eqn. (14) is not a thermodynamic equilibrium constant, unless the reaction is an ideal gas reaction ( $K_c \equiv \pi_i (\gamma_i c_i)^{a_i}$ ,  $\gamma_i = 1$ ), or a reaction in a diluted solution ( $K_c, \gamma_i \rightarrow 1, \sum_i c_i \rightarrow c_0$ , the pure solvent concentration), or the numbers of molecules on either side of the reaction equation are equal in a thermodynamic ideal solution ( $K, f_i = 1$ ).

(B) Redefining  $k_{c_{\pm}}$  in the general case

$$\pm v_{\pm} = k_{\pm} \pi_{\pm} (f_i x_i)^{|a_i|} / \beta = k_{c_{\pm}} \pi_{\pm} (\gamma_i c_i)^{|a_i|} / \beta \quad (16)$$

we obtain at equilibrium

$$k_{c_{+}} / k_{c_{-}} = \pi_i (\gamma_i c_i)^{a_i} \equiv K_c$$

replacing eqn. (14). The rate constant ratios in (B) are thus equal to thermodynamic equilibrium constants in general, which is not true in (A), as noted.  $\beta$  is a factor that may be a function of concentration [7]. It is assumed equal in the two rate expressions for simplicity.

Simplifying, we obtain in general, using  $x_i = c_i / \sum_i c_i$

$$k_{c_{\pm}} = k_{\pm} \pi_{\pm} \left( \frac{f_i}{\gamma_i} \right)^{|a_i|} \left/ \left( \sum_i c_i \right)^{\pm \sum |a_i|} \right.$$

The formal relation between the two types of activity coefficient is

$$\mu_i = \mu_i^{\circ} + RT \ln f_i x_i = \mu_i^{\square} + RT \ln \gamma_i c_i$$

where  $\mu_i^{\circ}$  and  $\mu_i^{\square}$  are the chemical potentials of the  $i$ th species in the two standard states based on the mole fraction and molarity scale, respectively. These states, or  $f_i$  and  $\gamma_i$ , have to be chosen.

Thus, in general

$$f_i / \gamma_i = \left( \sum_i c_i \right) \exp[(\mu_i^{\square} - \mu_i^{\circ}) / RT]$$

*Ideal gas:*  $f_i$  and  $\gamma_i$  are constants. Choosing  $f_i = \gamma_i (= 1)$ , eqn. (15) is recovered;  $k_{c_{\pm}}$  and  $\pm v_{\pm}$  are identical in (A) and (B), respectively.

*Ideally diluted solution:*  $f_i$  and  $\gamma_i$  become constant as  $x_i \rightarrow 0$  for the solutes and hence unity for the solvent. Choosing these constants to be equal ( $= 1$ ), and noting that  $\sum_i c_i \rightarrow c_0$ , we obtain

$$k_{c_{\pm}} = k_{\pm} / c_0^{\sum_i |a_i|}$$

and  $k_{c_{\pm}}$  and  $\pm v_{\pm}$  are equal in (A) and (B), respectively.

*Ideal solution:*  $f_i = \text{constant} (= 1)$  in general. Choosing  $\mu_i^{\square} = \mu_i^{\circ}$ , the chemical potential of the pure component at the same  $T$  and  $P$  in this case, we find

$$\gamma_i = 1 / \sum_i c_i$$

and

$$k_{c_{\pm}} = k_{\pm}$$

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