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THERMODYNAMIC RESTRICTIONS ON NON-ISOTHERMAL CHEMICAL REACTION RATES

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ABSTRACT

Using arguments derived from classical chemical thermodynamics, it is found that the isobaric, non-isothermal chemical reaction rate is in general a function of heating rate as well as of temperature and composition. However, non-isothermal reaction rate expressions have usually been identified with the corresponding isothermal rate expressions in the literature on non-isothermal chemical reaction kinetics.

Generalizing from a specific example, a method is proposed according to which changes in isothermal reaction kinetic expressions may be made to agree with thermodynamics.

INTRODUCTION

The isobaric chemical reaction rate has generally been taken as a function of temperature (and composition) only in non-isothermal reaction kinetics [1,2]. An exception is a recent report according to which the non-isothermal, chemical reaction rate contains an extra term that vanishes under isothermal conditions [3].

The present inquiry into non-isothermal restrictions on chemical reaction rates in general is based on classical, chemical thermodynamics. The results have consequences for classical, chemical kinetics, taking both theories to be compatible (macroscopic) subtheories of chemical substances.

The analysis rests on the fundamental assumption that a definite temperature and pressure may be assigned to systems out of equilibrium, an assumption on which isothermal analysis is also based. This requires that the system remains fairly close to thermal and mechanical equilibrium, but not to reaction (chemical) equilibrium [4,5], at any instant. This might be accomplished in a well-stirred sample under varying external conditions, provided the rate of external change is not too high. In a solid or less well-stirred sample, the temperature and pressure (?) may vary throughout the system. Nevertheless, local thermal and mechanical equilibrium may exist approximately [4,5]. In such cases, T and P may be taken as the average values over the system, and may be used to derive approximate,

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average changes in thermodynamic and related functions. In the last section of the present work, an example is given in which the analysis requires the system to be divided into two parts, each of slightly different temperature.

THERMODYNAMIC RESTRICTIONS ON NON-ISOTHERMAL REACTION RATES

Part A

A chemical reaction $\Sigma_i a_i A_i = 0$ in a closed system comprising one or several homogeneous phases is considered. A_i is a participating species and a_i the corresponding stoichiometric coefficient, taken to be negative (or positive) for species on the left- (or right-) hand side of the reaction equation as usually written. The reaction may consist of several kinetic steps, but the number of any intermediate species formed is assumed to be zero or constant. This means that $\epsilon \equiv (n_i - n_{i0})/a_i$ is the same for all i. n_i and n_{i0} are the number of moles of species i present at any time and before the reaction starts, respectively.

The change in Gibbs energy ΔG is in general a function of T, P and ϵ. In accordance with assumptions made in the Introduction, we may write $\Delta G = \Delta G(T(t), P(t), \epsilon(t))$ to indicate the dependence on time t. For a change in the variables we have

$$\Delta\dot{G} = (\partial\Delta G/\partial\epsilon)\dot{\epsilon} + (\partial\Delta G/\partial T)\dot{T} + (\partial\Delta G/\partial p)\dot{P} \tag{1}$$

where $\Delta\dot{G} \equiv \delta\Delta G/\delta t$, etc. δt is in principle a free variable, only limited by the requirement of approximate thermal and mechanical equilibrium, as stressed in the preceding section. ϵ is in principle a function of T, P, $\dot{T}$ and $\dot{P}$. Also, $\dot{\epsilon}(TP \text{ const.}) \neq 0$ except at equilibrium, when $\dot{T} = \dot{P} = 0$. Equation (1) reduces to $0 = \Delta\dot{G}_{\text{eq}}(TP \text{ const.}) = (\partial\Delta G/\partial\epsilon)\dot{\epsilon}_{\text{eq}}(TP \text{ const.})$ at equilibrium when T and P are constant. Hence $\dot{\epsilon}_{\text{eq}}(TP \text{ const.}) = 0$, provided $\partial\Delta G/\partial\epsilon \neq 0$.

If equilibrium states only are traversed as T and P are changed, we have likewise

$$0 = \Delta\dot{G}_{\text{eq}} = (\partial\Delta G/\partial\epsilon)\dot{\epsilon}_{\text{eq}} + (\partial\Delta G/\partial T)\dot{T} + (\partial\Delta G/\partial p)\dot{P} \tag{2}$$

Hence $\dot{\epsilon}_{\text{eq}} \neq 0$ in the general case when $\partial\Delta G/\partial\epsilon$, $\partial\Delta G/\partial T$ and $\partial\Delta G/\partial P \neq 0$. Thus $\dot{\epsilon}_{\text{eq}} \neq \dot{\epsilon}_{\text{eq}}(TP \text{ const.})$ in general at a given T and P.

This difference in reaction rate, $\dot{\epsilon}_{\text{eq}} - \dot{\epsilon}_{\text{eq}}(TP \text{ const.})$, is associated with the circumstance that the energy exchanged between the system and the surroundings is different in the two cases. The reactive species are thereby differently activated or deactivated in the two cases.

The system may not in general have time to restore equilibrium when T and P vary. Then $\Delta\dot{G} \neq 0$, according to eqn. (1). The net conversion of reacting species is less than that implied by eqn. (2): thus $|\dot{\epsilon}| < |\dot{\epsilon}_{\text{eq}}|$. Chemical reactions usually involve molecular motion, which is generally much slower than vibrational and rotational (librational) processes. The latter form the basis of local thermal and mechanical equilibrium [4,5], which is thus established faster than reaction equilibrium. Hence, in general,

$$|\dot{\epsilon}_{\mathrm{eq}}| \geqslant |\dot{\epsilon}| \geqslant \dot{\epsilon}_{\mathrm{eq}}(TP \text{ const.}) \ (=0) \tag{3}$$

The special case $\dot{\epsilon} \approx \dot{\epsilon}_{\mathrm{eq}}$ requires that the reaction is relatively rapid and that $\dot{T}$ and $\dot{P}$ are not too high. $\dot{\epsilon} \approx 0$ corresponds to a slow reaction. This may be due to small concentrations and/or a complicated reaction mechanism and/or high energy barriers, or else, may imply a low reaction probability. ($\dot{\epsilon} = 0$ corresponds to an infinitely slow reaction, or to reactants and products being mirror images of each other.)

The conclusion is that the reaction rate referred to a given T and P is generally not the same when T and P vary as when T and P are constant. This presupposes that $\partial \Delta G/\partial \epsilon \neq 0$, as already noted. However, according to the results of the last section, a similar conclusion applies when $\partial \Delta G/\partial \epsilon = 0$.

The above discussion refers to changes originating in an equilibrium state. There is apparently no reason why a similar conclusion should not apply to processes out of equilibrium in general. In that case, $\dot{\epsilon} \neq \dot{\epsilon}(TP \text{ const.})$ in general for a closed system.

This result is thus not in accordance with common practice in non-isothermal reaction kinetics, according to which $\dot{\epsilon}$ is a function of T and P only, i.e. the same as in isothermal kinetics.

Part B

It is assumed that

$$\Delta G = \Delta G^{\ominus} + RT \ln Q = RT \ln Q/K \tag{4}$$

where $K = K(T(t), P(t))$ is the thermodynamic equilibrium constant, and $Q = Q(T(t), P(t), \epsilon(t))$ the corresponding proper activity quotient in general. From eqn. (4), by differentiation, we obtain

$$\Delta \dot{G} = R \ln(Q/K)\dot{T} + RT \,\mathrm{l\dot{n}}\, Q - RT \,\mathrm{l\dot{n}}\, K \tag{5}$$

where $\mathrm{l\dot{n}}\, Q \equiv \delta \ln Q/\delta t$, etc. Hence $\Delta \dot{G}(TP \text{ const.}) = RT \,\mathrm{l\dot{n}}\, Q(TP \text{ const.})$, and by difference

$$\begin{aligned} \mathrm{l\dot{n}}\, Q = {} & \mathrm{l\dot{n}}\, Q(TP \text{ const.}) + \mathrm{l\dot{n}}\, K - (\Delta G/RT^2)\dot{T} \\ & + \left[\Delta \dot{G} - \Delta \dot{G}(TP \text{ const.})\right]/RT \end{aligned} \tag{6}$$

It is assumed, for simplicity, that the reaction system is thermodynamically ideal [6]. The activity coefficients on a mole fraction basis are then constant ($\gamma_i = 1$) and

$$\mathrm{l\dot{n}}\, Q = \dot{\epsilon} \sum_i (\partial \ln Q/\partial n_i) a_i \tag{7}$$

(see Appendix A). With eqns. (6) and (7), this gives

$$\dot{\epsilon} = \dot{\epsilon}(TP\text{ const.}) + \Big(\mathrm{l\dot{n}}\,K - (\Delta G/RT^2)\dot{T} + \big\{\big[\Delta\dot{G} - \Delta\dot{G}(TP\text{ const.})\big]/RT\big\}\Big) \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \tag{8}$$

$\dot{\epsilon}(TP$ const.) corresponds to the isothermal rate expression for a reversible reaction. The corresponding differential $\delta\epsilon \equiv \dot{\epsilon}\ \delta t$ is inexact in T and P. Since the term in parentheses on the right-hand side of eqn. (8) can apparently not be shown to vanish in the general case, one may conclude that $\dot{\epsilon} \neq \dot{\epsilon}(TP$ const.) in general. A simplification of the expression in parentheses may be required in practice (see below).

When equilibrium states only are involved, eqn. (8) reduces to

$$\dot{\epsilon}_{\mathrm{eq}} = \dot{\epsilon}_{\mathrm{eq}}(TP\text{ const.}) + \mathrm{l\dot{n}}\,K \Big/ \sum_i (\partial \ln K/\partial n_i) a_i = \mathrm{l\dot{n}}\,K \Big/ \sum_i (\partial \ln K/\partial n_i) a_i \tag{9}$$

since $\Delta G_{\mathrm{eq}} = \Delta\dot{G}_{\mathrm{eq}} = \Delta\dot{G}_{\mathrm{eq}}(TP$ const.) $= \dot{\epsilon}_{\mathrm{eq}}(TP$ const.) $= 0$ in that case. Thus $\dot{\epsilon}_{\mathrm{eq}} \neq \dot{\epsilon}_{\mathrm{eq}}(TP$ const.) in general.

The denominator on the right-hand side of eqn. (9), or (8), may vary considerably during reaction, depending on the initial conditions (see e.g. eqn. (A7) in Appendix A). It is expected that the ratio as given by eqn. (9) will normally reflect this variation, whereas this may not be so in the case of eqn. (8) because of the additional dependence on ΔG, etc.

Opposing reactions

The reaction rate will be written, in the usual way, as a sum of two terms [7,8], $\dot{\epsilon} = \dot{\epsilon}_+ + \dot{\epsilon}_-$, where $\dot{\epsilon}_+(\geqslant 0)$ is the rate in the forward direction, referring to the reaction equation written in the usual way, and $\dot{\epsilon}_-(\leqslant 0)$ is the rate in the backward direction. Furthermore, $\mathrm{l\dot{n}}\,K = (\Delta H^{\ominus}/RT^2)\dot{T} - (\Delta V^{\ominus}/RT)\dot{P}$ (see Appendix A). $\Delta H^{\ominus} \equiv H^{\ominus}_- - H^{\ominus}_+ = H_- - H_+$ (ideal solution [6]). $H_\pm = \Sigma_i |a_{\pm i}| \overline{H}_{\pm i}$, where $\overline{H}_{+i}$ $(\overline{H}_{-i}) \equiv$ partial molar enthalpy of the ith participating species on the left- (or right-) hand side of the reaction equation as normally written. Similarly, $\Delta V^{\ominus} \equiv V^{\ominus}_- - V^{\ominus}_+ = V_- - V_+$, etc. $\Delta G_\pm \equiv G_- - G_+$ and $\partial\Delta G/\partial\epsilon \equiv (\partial G_-/\partial\epsilon) - (\partial G_+/\partial\epsilon)$, etc. Substituting these expressions into eqn. (8) and rearranging terms, we obtain

$$\begin{aligned}
&\dot{\epsilon}_+ - \dot{\epsilon}_+(TP\text{ const.}) - \Big[-\big(H^{\ominus}_+/RT^2\big)\dot{T} + \big(V^{\ominus}_+/RT\big)\dot{P} + \big(G_+/RT^2\big)\dot{T} \\
&\quad - \big(\dot{G}_+/RT\big) + \big(\dot{G}_+(TP\text{ const.})/RT\big)\Big] \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \\
&\quad = -\Big\{\dot{\epsilon}_- - \dot{\epsilon}_-(TP\text{ const.}) - \Big[+\big(H^{\ominus}_-/RT^2\big)\dot{T} - \big(V^{\ominus}_-/RT\big)\dot{P} \\
&\qquad - \big(G_-/RT^2\big)\dot{T} + \big(\dot{G}_-/RT\big) - \big(\dot{G}_-(TP\text{ const.})/RT\big)\Big] \\
&\qquad \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \Big\} \equiv -F_\pm \text{ (say)}
\end{aligned} \tag{10}$$

It is assumed that

$$F_{\pm} \equiv \left[f_{\pm}(TP\epsilon,\ \dot{T}\dot{P}\dot{\epsilon}) + \left(G^{\mathrm{eq}}_{\pm}/RT^2\right)\dot{T} - \left(\dot{G}^{\mathrm{eq}}_{\pm}/RT\right) + \left(\dot{G}^{\mathrm{eq}}_{\pm}(TP\ \mathrm{const.})/RT\right)\right] \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \tag{11}$$

where $f_{+} = f_{-}$ are unspecified functions depending on the particular reaction (mechanism) in question. First, using this definition of $F_{\pm}$, we can recover the equilibrium $\dot{\epsilon}_{\pm}$-expression obtained directly from eqn. (9) (namely eqn. (13) below) because $\Delta G_{\pm} \equiv G_{\pm} - G^{\mathrm{eq}}_{\pm} \equiv 0$ at equilibrium, in which case $G_{\pm}$ are not needed in the first place. Secondly, by choosing the proper expression for $f_{\pm}$ (see below) when the reaction is an elementary kinetic step, for which $K = k_{+}/k_{-}$, we can obtain the correct expression for $\dot{\ln}\, k_{\pm}$. k_{+} (k_{-}) is the rate constant in the forward (backward) direction. Other general restrictions on $F_{\pm}$ are not known.

This leads to

$$\dot{\epsilon}_{\pm} = \dot{\epsilon}_{\pm}(TP\ \mathrm{const.}) \pm \left[f_{\pm} - \left(H^{\ominus}_{\pm}/RT^2\right)\dot{T} + \left(V^{\ominus}_{\pm}/RT\right)\dot{P} + \left(\Delta G_{\pm}/RT^2\right)\dot{T} - \left(\Delta\dot{G}_{\pm}/RT\right) + \left(\Delta\dot{G}_{\pm}(TP\ \mathrm{const.})/RT\right)\right] \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \tag{12}$$

in general. $\dot{\epsilon}_{+}(TP$ const.) (or $\dot{\epsilon}_{-}(TP$ const.)) corresponds to the isothermal rate expression in the forward (or backward) direction.

For a thermodynamically ideal system, $\Delta H_{\pm} = \Delta V_{\pm} = 0$ and $\Delta G_{\pm} = -T\Delta S_{\pm} = RT\Sigma_i |a_{\pm i}| \ln(x_{\pm i}/x^{\mathrm{eq}}_{\pm i})$. At equilibrium, $\Delta G_{\pm} = \Delta S_{\pm} = \Delta\dot{G}_{\pm} = \Delta\dot{G}_{\pm}(TP\ \mathrm{const.}) \equiv 0$, so that eqn. (12) reduces to

$$\dot{\epsilon}_{\pm} = \dot{\epsilon}_{\pm}(TP\ \mathrm{const.}) \pm \left[f^{\mathrm{eq}}_{\pm} - \left(H^{\ominus}_{\pm}/RT^2\right)\dot{T} + \left(V^{\ominus}_{\pm}/RT\right)\dot{P}\right] \Big/ \sum_i (\partial \ln K/\partial n_i) a_i \tag{13}$$

when only equilibrium states are traversed. Equation (13) may be obtained directly from eqn. (9) in a similar way.

There is apparently no exact way of simplifying eqn. (12) in the general case. One approximate procedure is to ignore the last two terms in parentheses in eqn. (12). They are of opposite sign and may generally be relatively small. The corresponding approximate form of eqn. (12) is

$$\dot{\epsilon}_{\pm} = \dot{\epsilon}_{\pm}(TP\ \mathrm{const.}) \pm \left[f_{\pm} - \left(H^{\ominus}_{\pm}/RT^2\right)\dot{T} + \left(V^{\ominus}_{\pm}/RT\right)\dot{P} - \left(\Delta S_{\pm}/RT\right)\dot{T}\right] \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \tag{14}$$

where $\Delta S_{\pm}$ may also be relatively insignificant in many cases. The corresponding expression for $\dot{\epsilon}$, obtained from eqns. (14) or (8), is

$$\dot{\epsilon} = \dot{\epsilon}(TP\ \mathrm{const.}) + \left[\dot{\ln}\, K - \left(\Delta G/RT^2\right)\dot{T}\right] \Big/ \sum_i (\partial \ln Q/\partial n_i) a_i \tag{15}$$

but closer consideration indicates that the latter approximation may generally be relatively less satisfactory than eqn. (14).

If the reaction is an elementary step, $K = k_+/k_-$, as noted above. Introducing this relationship into eqn. (8) and proceeding as above, we eventually obtain

$$\begin{aligned}\dot{\epsilon}_\pm = \dot{\epsilon}_\pm(TP\ \text{const.}) \pm \Big[\dot{\ln}\ k_\pm + \left(\Delta G_\pm/RT^2\right)\dot{T} - \left(\Delta \dot{G}_\pm/RT\right) \\ + \left(\Delta \dot{G}_\pm(TP\ \text{const.})/RT\right)\Big] \Big/ \sum_\iota (\partial \ln Q/\partial n_\iota) a_\iota \qquad (16)\end{aligned}$$

where

$$\begin{aligned}\dot{\ln}\ k_\pm &= (\partial \ln k_\pm/\partial T)\dot{T} + (\partial \ln k_\pm/\partial P)\dot{P} \\ &\approx \left(\Delta H_\pm^{\ominus\star}/RT^2\right)\dot{T} - \left(\Delta V_\pm^{\ominus\star}/RT\right)\dot{P} \\ &\equiv f_\pm - \left(H_\pm^{\ominus}/RT^2\right)\dot{T} + \left(V_\pm^{\ominus}/RT\right)\dot{P} \qquad (17)\end{aligned}$$

using eqn. (12). This identifies $f_\pm$. $\Delta H_\pm^{\ominus\star}$ and $\Delta V_\pm^{\ominus\star}$ are the activation enthalpy and volume, respectively. We could then proceed to derive equations similar to eqns. (13) and (14).

PHASE REACTIONS AT CONSTANT COMPOSITION

When $\partial \Delta G/\partial \epsilon = 0$, the last term in eqn. (8) becomes a 0/0 expression, because the terms in parenthesis cancel and $\partial \Delta G/\partial \epsilon = RT\Sigma_\iota(\partial \ln Q/\partial n_i)a_\iota$ for thermodynamically ideal systems (see Appendix A). ϵ is therefore indeterminate in this formulation. A simple example is the one-component system where water evaporates slowly from a liquid surface of constant area in a steady state close to thermodynamic equilibrium of zero net evaporation. Interfacial effects are almost constant as long as T and P are constant. Thus, although ΔG (referred to the bulk) is influenced by interfacial effects in general, it is practically independent of ϵ in this case.

(Generally, however, the interfacial area changes with ϵ, and so, therefore, will interfacial effects on ΔG at constant T and P, even when phase compositions are constant. Hence $\Delta G = \Delta G(T(t), P(t), \epsilon(t))$ in general. Although we may put $\ln Q/K = \Delta G/RT$, as before, $Q(\epsilon)$ and K are not known.)

Assume, for simplicity, that the water vapour in the above example is an ideal gas. The differential of the corresponding state equation on logarithmic form is

$$\delta n/n_g = -(\delta T/T) + (\delta p/p_g) + (\delta V/V) \qquad (18)$$

where n_g, p_g and V are the mole number, pressure and volume of the vapour, respectively.

If phase equilibrium exists, this reduces first, using the Clausius–Clapeyron equation, to

$$\delta n/n_g = [(\Delta H/RT) - 1](\delta T/T) + (\delta V/V)$$

where ΔH is the heat of vaporization, and then further to

$$\delta n = n_g(\delta V/V) \tag{19}$$

at constant temperature. The equilibrium state is independent of V and n_g, since $K \equiv p_g$.

DIRECT MODIFICATION OF ISOTHERMAL REACTION KINETIC RATE EXPRESSION

By contrast, the isothermal reaction rate is taken to be zero at equilibrium, implying that $\delta V = 0$ in eqn. (19). This may, for example, be written kinetically as a very simple two-term rate equation. Thus

$$\dot{n} = k_{\pm}(T)A - k_{-}(T)p_g(T) = 0 \tag{20}$$

where A is the interfacial area, and $k_{+}(T)$ (or $k_{-}(T)$) is the rate constant for the vaporization (or condensation) process at T.

To bring the reaction kinetics description into agreement with the thermodynamic requirement above, the variables in the rate expression, such as T and/or p_g in eqn. (20), may be (temporarily) slightly modified, corresponding to the creation of a small (temporary) disturbance of the equilibrium state.

For example, a sudden volume change δV produces, at constant T, a change in pressure $\delta p(\delta n = 0)$, as given by eqn. (18), putting $\delta n = \delta T = 0$. This is followed by a net transfer of substance between the phases, to restore equilibrium at T according to eqn. (19). This process may be expressed as

$$\dot{n}\delta t = \delta t\left\{k_{+}A - k_{-}\left[p_g + \delta p(\delta n = 0)\right]\right\} = (\delta V/V)n_g \tag{21}$$

where δt is the time required to re-establish equilibrium at constant temperature (reaction time). (The time actually taken to produce $\delta p(\delta n = 0)$ in the first place is irrelevant, as long as no net transfer occurs during this time element. In a continued process, this time becomes (almost completely) subsumed in the reaction time.) Equation (21) reduces to

$$\delta t = -(1/k_{-})[\delta V/\delta p(\delta n = 0)] = (1/k_{-})(n_g/p_g) = (1/k_{-})(V/RT) \tag{22}$$

using eqns. (20) and (18), with $\delta T = \delta n = 0$, as noted above, along with the ideal gas state equation. The net transfer of matter between the two phases is associated with a corresponding net heat transfer between the system and the surroundings to keep the temperature constant.

The effect of a small temperature change $\delta T(\delta n = 0)$, i.e. a small thermal energy change at T, in addition to the volume change, may be represented as $\dot{n}\delta t = \delta t\{k_{+}(T + \delta T) - k_{-}(T + \delta T)[p_g(T + \delta T) + \delta p(\delta n = 0)]\}$, where $p_g(T + \delta T)$ is different from the equilibrium vapour pressure at $T + \delta T$.

The same result as given by eqn. (19), for instance, may then be obtained in a different reaction time, provided the original temperature T is finally restored.

Alternatively, we could restrict the temperature change to the liquid phase only, for instance, and then proceed as above.

There are thus various ways of modifying e.g. eqn. (20) to bring about the result of eqn. (19). The reaction time, however, is different in the various cases.

A similar procedure may also be used out of equilibrium. For instance, for the spontaneous process at constant temperature, we obtain

$$\delta t\left(k_{+}A - k_{-}p_{g}\right) = \delta n_{o} = n_{g}\left[\left(\delta p_{o}/P_{g}\right) + \left(\delta V_{o}/V\right)\right] \tag{23}$$

analogous to eqn. (19). δn_o is the change in the vapour phase mole number which is due to the spontaneous reaction during time element δt, and δp_o and δV_o are the corresponding thermodynamic changes in pressure and volume, respectively (only one of which is free when δn_o is given). $p_g = p_g^{eq} \exp(\Delta G/RT)$, with $\Delta G = \mu_g - \mu_l$, where $\mu_{g(l)}$ is the chemical potential of the vapour (liquid).

An arbitrary change in pressure and volume at constant temperature likewise yields

$$\delta t\left\{k_{+}A - k_{-}\left[p_{g} + \delta p(\delta n = 0)\right]\right\} = \delta n = n_{g}\left[\left(\delta p/p_{g}\right) + \left(\delta V/V\right)\right] \tag{24}$$

which is similar to eqn. (21). The further derivation is in principle as before, although the results are somewhat more involved.

This indicates that the method outlined is in principle quite general. The corrections are applied to each kinetic term separately. A single-term rate equation describing an irreversible reaction may be modified accordingly in a similar fashion. The isothermal (isobaric) rate constant $k(T)$ may be replaced by $k(T + \delta T)$ in non-isothermal kinetics, where δT is (somewhat arbitrarily) identified as the actual temperature change in the system during δt. δT may be taken to be proportional to $\dot{T}$ in reactions involving more than one phase at constant composition. For a homogeneous reaction this is only approximately true, if thermodynamic requirements are to be fulfilled. The proportionality constant may be treated as a trial parameter. More exact $\delta T(\dot{T})$ relations may be obtained by comparing with previous equations.

CONCLUSIONS

According to the results of the present work, the non-isothermal, isobaric reaction rate is in general a function of heating rate, besides T and ϵ. It is thus distinctly different from the isothermal, isobaric reaction rate. Although the difference may be quite small in many cases, the distinction may become increasingly more important—for instance, as the accuracy of experimental data improves still further. So far the difference has mostly been overlooked in the literature on non-isothermal reaction kinetics.

APPENDIX A

The thermodynamic equilibrium constant K is a function of two independent variables only, here taken to be T and P. This requires in general the use of activity coefficients γ_i. An exception is provided by a thermodynamically ideal system [6] when mole fraction x_i is used as a composition variable. Then $\gamma_i = 1$.

It is convenient to write K as a function of n_i and γ_i at the outset. Thus

$$K = K(\gamma_i,\ n_i,\ i = 1, 2, \ldots) \qquad (= K(TP)) \tag{A1}$$

Hence

$$\overset{\cdot}{\ln}\, K = \sum_i (\partial \ln K/\partial n_i)\dot{n}_i + \sum_i (\partial \ln K/\partial \gamma_i)\dot{\gamma}_i \tag{A2}$$

γ_i is a function of T, P and composition. Thus

$$\dot{\gamma}_i = \sum_1 (\partial \dot{\gamma}_1/\partial n_1)\dot{n}_1 + (\partial \gamma_i/\partial T)\dot{T} + (\partial \gamma_i/\partial P)\dot{P} \tag{A3}$$

and, since $\dot{\epsilon} \equiv \dot{n}_i/a_i$ is assumed to be independent of i, we obtain

$$\begin{aligned}\overset{\cdot}{\ln}\, K = {} & \dot{\epsilon}_{\text{eq}} \sum_i \left[(\partial \ln K/\partial n_i)a_i + (\partial \ln K/\partial \gamma_i) \sum_1 (\partial \gamma_i/\partial n_1)a_1 \right] \\ & + \dot{T} \sum_i (\partial \ln K/\partial \gamma_i)(\partial \gamma_i/\partial T) + \dot{P} \sum_i (\partial \ln K/\partial \gamma_i)(\partial \gamma_i/\partial P)\end{aligned} \tag{A4}$$

Also

$$\overset{\cdot}{\ln}\, K = (\partial \ln K/\partial T)\dot{T} + (\partial \ln K/\partial P)\dot{P} = (\Delta H^{\ominus}/RT^2)\dot{T} + (\partial \ln K/\partial P)\dot{P} \tag{A5}$$

where the last term depends on the choice of standard state in the general case [6].

As an example, consider

$$K \equiv \prod_i (\gamma_i x_i)_{\text{eq}}^{a_i} \tag{A6}$$

(mole fraction basis). Then [9] $(\partial \ln K/\partial P) = -(\partial V^{\ominus}/RT)$ and

$$(\partial \ln K/\partial n_i)a_i = (a_i^2/n_i)(1 - x_i) \geqslant 0 \tag{A7}$$

where $x_i \equiv n_i/\Sigma_i n_i$.

The sum is over the species in the phase containing the ith component (when the system comprises several phases). Also

$$(\partial \ln K/\partial \gamma_i) = (a_i/\gamma_i) \tag{A8}$$

For an ideal system [6], $\gamma_i = 1$ and, from eqn. (A4),

$$\mathrm{l}\dot{\mathrm{n}}\, K = \dot{\epsilon}_{\mathrm{eq}} \sum_i (\partial \ln K/\partial n_i) a_i \tag{A9}$$

If, in addition, the system consists of a single phase of volume $V =$ constant (as is often nearly true for a single, homogeneous phase), then $\dot{c}_i = \dot{n}_i/V = a_i\dot{\epsilon}/V$, and

$$\mathrm{l}\dot{\mathrm{n}}\, K = (\dot{c}_i/a_i) \sum_i (\partial \ln K/\partial c_i) a_i \tag{A10}$$

The expression is more complicated when V is a variable.

$K(TP)$ is replaced by the proper quotient of the activities $Q(TP\epsilon)$ in states out of equilibrium. The equilibrium activities (e.g. $\gamma_i x_i$) are then replaced by the corresponding non-equilibrium ones. The corresponding expressions for $\mathrm{l}\dot{\mathrm{n}}\, Q$, etc. are obtained by replacing K by Q in eqns. (A1)–(A10) and $\dot{\epsilon}_{\mathrm{eq}}$ by $\dot{\epsilon}$ in eqns. (A4) and (A9).

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