Temperatures of the Maximum Reaction Rate and Their Relation to the Equilibrium Temperatures

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This paper derives the relationship between the temperatures of maximum reaction rate and the equilibrium temperatures for exothermic reactions. For a reversible reaction described by Arrhenius type rate coefficients the relation is found to be $(1/T_{r,\max}) - (1/T_{eq}) = (R/(E_2 - E_1))\ln(E_2/E_1)$, where R is the gas constant and E_1 and E_2 are the activation energies of the forward and backward reaction. The result implies that the operating line of the maximum reaction rate will be parallel to the equilibrium line in a $1/T$ versus conversion diagram when the activation energies (or enthalpy change of reaction) are constant. For systems with constant pressure, the constant distance between the two curves is then equivalent to a constant driving force of the reaction, $\Delta G/T$. Thus, we have shown that a recently developed principle for an energy efficient process design, called equipartition of forces, can be applied also near the maximum reaction rate for elementary, exothermic reactions with Arrhenius' type kinetics at constant pressure.

Introduction

The search for maximum reaction rates is one of the classic quests in chemical engineering. The determination of the optimum temperature profile for a reactor is an important part of this search. Today this temperature profile is often found either by computer optimization techniques or by experimental procedures. Recent experimental and numerical results, however, indicate that an analytical solution might exist, and these constituted a major motivation for this work. Ten years ago, for instance, both Dybkjaer and Gam[1] and Månsson and Andresen[2] presented an operating line (reaction trajectory) with maximum reaction rate in the temperature-conversion space for the synthesis of ammonia and pointed out that it was nearly parallel to the equilibrium curve; see Figure 1. More recently, Schön and Andresen[3] presented a numerical study of three example reactions on the form $nA = mB$. They observed that the difference between the inverse temperature of a mixture at equilibrium and the inverse temperature of maximum reaction rate (for the same mixture) was nearly constant. *Equilibrium temperature* was here defined to be the temperature at which the reactive mixture would be in equilibrium. The average difference $\Delta(1/T)$ between the equilibrium line and the line of the maximum reaction rate varied with 2−9% in the three example reactions they studied. They thus concluded that "clearly, if and when it can be shown that optimality implies a constant $\Delta(1/T)$, this optimality criterion could then be used to determine the optimal path for those systems of chemical reactions that do not yield easily to optimization methods like the one [they] used. This will be of special importance since for general chemical systems it is considerably easier to determine the curve of equilibrium values than the actual optimal paths."

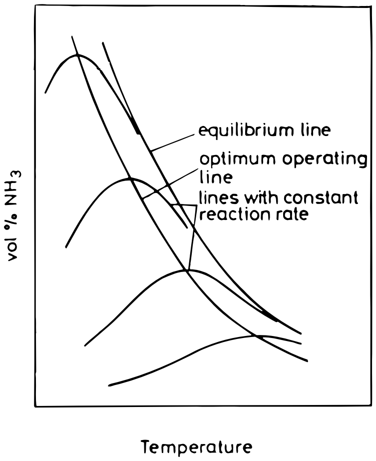

Figure 1. Equilibrium curve and the curve of maximum reaction rate (called optimum) for the ammonia synthesis.[1] Reproduced with the permission from ref 1. Copyright 1985 American Institute of Chemical Engineers.

At the same time Sauar et al.[4] published a new physical principle for process optimization, called equipartition of forces. This principle states that *minimum entropy production* in a process unit with a given size and yield can be achieved when the thermodynamic forces (see, e.g., ref 5) are uniformly distributed over the transfer area (for heat and charge conduction, mass diffusion) or system volume (rate-controlled chemical reactions). Formulated in another way, such uniformly distributed driving forces in a process were also shown to give *maximum yield* for a given entropy production and process size. For a chemical reactor[6] with a rate-controlled chemical reaction this means that a constant affinity of reaction divided by the absolute temperature (eq 1) in all parts of the reactor and at all times specifies the optimum *combinations* (or trade-offs) between conversion and entropy production. The validity of

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the result (1), however, was restricted to systems close to equilibrium.

$$A/T = \text{constant} \tag{1}$$

For systems with constant pressure the affinity of the reaction equals the change in Gibbs energy for the reaction. Assuming constant pressure, Sauar et al.[6] integrated the Gibbs–Helmholtz equation from the equilibrium temperature to the operating temperature T_{op} and found that

$$\left(\frac{A}{T}\right)_P = \frac{\Delta G}{T} = \Delta H\left(\frac{1}{T_{\mathrm{op}}} - \frac{1}{T_{\mathrm{eq}}}\right) \tag{2}$$

where ΔG is the change in the Gibbs energy of reaction, ΔH is the enthalpy change of reaction, T_{eq} is the equilibrium temperature of a mixture, and T_{op} is the operating temperature. Thus, they concluded that a chemical reactor with an optimal trade-off between entropy production (which is proportional to the energy loss) and conversion should be designed with a temperature profile as described by eq 2 with constant $\Delta G/T$. We call such temperature profiles *isoforce* operating lines. In cases where the ΔH of the reaction is independent of temperature and concentrations, eq 2 will thus specify isoforce operating lines with a constant difference in $1/T$ between the equilibrium temperature and the operating temperature. For *exothermic* reactions such trade-offs between entropy production and reaction rate only exist between the equilibrium line and the line of maximum reaction rate (see Figure 1). At temperatures below the curve of the maximum reaction rate there is nothing to gain since entropy production increases *and* reaction rate decreases with decreasing temperature in this region. At temperatures above the equilibrium temperature the reaction goes in the reverse direction.

The derivation of equipartition of forces was based on linear phenomenological equations:

$$r = -l\frac{A}{T} \tag{3}$$

which for chemical reactions are valid only near equilibrium. r is the reaction rate, and l is a kinetic (phenomenological) coefficient. The results in this paper, however, will demonstrate that eq 1 can be used to optimize conversion also near the maximum reaction rate for elementary exothermic reactions occurring at constant pressure.

The main derivation will be similar to Denbigh,[9] but his work was apparently unknown to Maanson and Andresen[2] and Schön and Andresen.[3] The current work extends the results reported by Denbigh by specifying how the different experimentally determined activation energies shall be applied and by relating the results to a constant $\Delta_r G/T$ for the reaction. The results are also of more practical interest now as more activation energies have been experimentally determined.

The mathematical results will be derived from Arrhenius type rate equations and specify the difference between the equilibrium temperatures and the temperatures of maximum reaction rates. Thus, the problem posed more or less explicitly by Schön and Andresen, Dybkjar and Gam, and others will be solved.

Temperature of the Maximum Reaction Rate

We first assume a reaction in liquid phase:

$$B = D \tag{4}$$

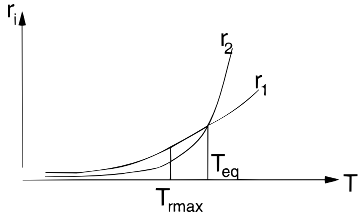

Figure 2. Forward and backward reaction rates r_1 and r_2 as a function of temperature T. The figure is drawn rather than calculated in order to enlarge important points.

with the reaction rates

$$r_1 = A_1 \mathrm{e}^{-E_1/RT} C_B \qquad r_2 = A_2 \mathrm{e}^{-E_2/RT} C_D \tag{5}$$

for the forward and backward reactions, r_1 and r_2. E_1 and E_2 are the activation energies for the forward and backward reaction, and A_1 and A_2 are the frequency factors. We will prove here that the temperature of the maximum reaction rate for all possible concentrations will be found in an almost constant distance, $\Delta(1/T)$, away from the equilibrium temperature. An illustration of the behavior of the reaction rates (eq 5) with respect to the temperature T is given in Figure 2.

Reaction 4 is at equilibrium when $r_1 = r_2$. Thus, for a mixture at equilibrium, the relation between C_B, C_D, and T_{eq} is

$$\frac{1}{T_{\mathrm{eq}}} = \frac{R}{E_2 - E_1}\left(\ln\left(\frac{A_2}{A_1}\right) + \ln\left(\frac{C_D}{C_B}\right)\right) \tag{6}$$

The temperature of the maximum reaction rate for the same concentrations C_B and C_D is easily found by differentiation of the net reaction rate $r_1 - r_2$ with respect to T^{-1}:

$$d(r_1 - r_2)/\mathrm{d}T^{-1} = 0 \tag{7}$$

Equation 7 can be further reduced to

$$A_1 C_B - \left(\frac{E_1}{R}\right)\mathrm{e}^{-E_1/RT} = A_2 C_D - \left(\frac{E_2}{R}\right)\mathrm{e}^{-E_2/RT} \tag{8}$$

and taking the logarithms and rearranging give

$$\frac{1}{T_{\mathrm{r,max}}} = \frac{R}{E_2 - E_1}\left(\ln\left(\frac{A_2 E_2}{A_1 E_1}\right) + \ln\left(\frac{C_D}{C_B}\right)\right) \tag{9}$$

We assume in the following that the kinetic parameters (A_1, A_2, E_1, E_2) can be regarded as constants between the temperatures $T_{\mathrm{r,max}}$ and T_{eq}. The difference between the temperature of the maximum reaction rate, $T_{\mathrm{r,max}}$ and the equilibrium temperature, T_{eq}, can now be found directly by subtracting eq 6 from eq 9, resulting in

$$\frac{1}{T_{\mathrm{r,max}}} - \frac{1}{T_{\mathrm{eq}}} = \frac{R}{E_2 - E_1}\left(\ln\left(\frac{E_2}{E_1}\right)\right) \tag{10}$$

For elementary reactions, $E_2 - E_1$ is equal to the negative enthalpy change of the reaction, $-\Delta H$. The ΔH, E_1, and E_2 of reaction generally exhibit some temperature dependency and are weakly dependent upon the concentrations. In many cases, however, they will be approximately constant over the temperature and concentration range of interest. For exothermal reactions with Arrhenius type rate expressions as in eq 5, the result of (10) provides a direct method for maximizing reaction rates in non-isothermal, rate-controlled chemical reactors with *one* single reaction. Furthermore, the result is easy to apply since the only required information is the equilibrium line and the activation energies.

A temperature of maximum reaction rate for exothermal reactions exists because a temperature decrease for this type of reactions implies both increasing driving forces and reduced kinetics. At a certain temperature these two effects are equal, and thus there exists a temperature of maximum reaction rate. For endothermal reactions there is no temperature of maximum reaction rate since both driving force and kinetics increase when the temperature increases.

More Complex Reactions

It is straightforward to generalize the result of (10) for any reaction:

$$n_1B_1 + n_2B_2 + ... = m_1D_1 + m_2D_2 + ... \tag{11}$$

with a reaction rate of the form

$$r = A_1 e^{-E_1/RT} f_1(C_{B_1}, C_{B_2}, ...) - A_2 e^{-E_2/RT} f_2(C_{D_1}, C_{D_2}, ...) \tag{12}$$

In order to determine the equilibrium temperature, we again set the net reaction rate, r, equal to zero. The temperature of the maximum reaction rate is similarly found by differentiating eq 12 with respect to T^{-1} and setting $dr/dT^{-1} = 0$. For a particular concentration of reactants and products, the difference between the inverse of the temperatures thus becomes

$$\frac{1}{T_{r,max}} - \frac{1}{T_{eq}} = \frac{R(\ln(E_2/E_1))}{E_2 - E_1} \tag{13}$$

Hence, the conclusions drawn above are valid also for more complex reaction mechanisms on the form of (12). The trajectory of the maximum reaction rate will still be found in a constant distance, $\Delta(1/T)$, away from the equilibrium line, and its exact location can be found from the activation energies in the rate expression.

Gas-Phase Reaction at Constant Pressure

For gas-phase reactions in reactors with constant pressure, the mathematical relationship between the temperature of the maximum reaction rate and the equilibrium temperature depends on the experimental basis of the rate coefficients. There are two common Arrhenius type rate expressions used for gas-phase reactions like (11):

$$r = k_1 P_{B_1}^{n_1} P_{2_1}^{n_2} ... - k_2 P_{D_1}^{m_1} P_{D_2}^{m_2} ... \tag{14}$$

which is perhaps the most common (see, e.g., ref 7), and

$$r = k'_1 C_{B_1}^{n_1} C_{B_2}^{n_2} ... - k'_2 C_{D_1}^{m_1} C_{D_2}^{m_2} ... \tag{15}$$

which is the one used by Schön and Andresen.[3] These can both describe the same reaction, but there is a major difference between them with regard to the temperature dependency when the reaction is carried out at constant pressure. In eq 14 only the rate coefficients themselves will vary with temperature. (The partial pressures are merely the product of mole fractions and total pressure and are not influenced by a varying temperature.) Thus, for reaction rates based on partial pressures in (14), the relationship between the temperature of the maximum reaction rate and the equilibrium temperature becomes exactly the same as in eq 13 for any given partial pressure of reactants and products.

In eq 15 also the concentrations vary with temperature since the number of moles per volume changes with changing temperature. The relationship between the maximum reaction rate and the equilibrium temperature therefore must reflect these changes and becomes somewhat more complex. The complete derivation for this case is given in Appendix 1.

We thus conclude that eq 13 with rate expression 14 generalizes the numerical results obtained by Månsson and Andresen,[2] Dybkjaer and Gam,[1] and Schön and Andresen[3] by providing an analytical answer to their problem. According to eq 13, the difference between the two inverse temperatures should then mainly be related to the variation in the enthalpy of reaction ($-\Delta H = E_2 - E_1$ for elementary reactions) over the composition space. This is in agreement with the results presented by Schön and Andresen who report an 8% standard deviation in the distance ($1/T$) as the ammonia synthesis proceeds from high to low temperatures (at constant pressure). In the same temperature interval, the enthalpy of reaction varied from -55.9 kJ/mol at 1200 K to -48.1 kJ/mol at 400 K. This interpretation is further supported by Schön and Andresens' results for the reaction $N_2O_4 = 2NO_2$. For this system they reported a 4.2% standard deviation in the optimal $\Delta(1/T)$, while ΔH varies similarily less, from 21.6 to 20.7 kJ/mol.[8]

In a plug-flow reactor, any volume change of reaction ($\sum n_i \neq \sum m_i$) will speed up or slow down the gas flow. Thus, the temperature as a function of spatial coordinate will be affected. The parameters in eq 14, however, will not be affected, and relation 13 still holds true. In applying eq 13 over large temperature and concentration ranges, however, one should be aware that the kinetic expression may change if the temperature, pressure, and/or concentrations vary largely.

Gas-Phase Reaction in a Constant Volume

For a gas-phase reaction in a vessel with constant volume, the variation of temperature will affect not only the kinetic constants but also the pressure of the gas. Considering again the two forms of the rate expression (14, 15), we easily see that, in the pressure based equation, both the kinetic coefficients and the partial pressures will be temperature dependent. In the concentration based rate expression, however, only the kinetic coefficients will exhibit temperature dependency. Reducing the temperature of a reactive mixture from the equilibrium temperature to a lower temperature for instance (without allowing it to react) will change neither the amount of moles nor the volume of the reactor. Only the pressure will fall. Thus for concentration based kinetic coefficients, and for a given concentration of reactants and products, the relationship between the temperature of the maximum reaction rate and the equilibrium temperature will be

$$\frac{1}{T_{r,max}} - \frac{1}{T_{eq}} = \frac{R(\ln(E'_2/E'_1))}{E'_2 - E'_1} \tag{16}$$

where E_1' and E_2' are the activation energies associated with the kinetic expression given by (15). This expression is then equivalent to (13).

For the pressure based rate expression (14), however, the relationship between the inverse temperatures is somewhat more complex, and the derivation is given in Appendix 2. Again, the pressure based rate expression can always be replaced by a concentration based rate expression as long as the kinetic coefficients are known.

Thus, the result of (13) is still valid for activation energies belonging to eq 15, while activation energies determined on a pressure basis must be used according to Appendix 2. As is shown in the appendix, however, the difference is rather marginal.

In general, a volume change of reaction ($\sum n_i \neq \sum m_i$) may imply major pressure changes during the course of operation. Such pressure changes may affect the size of the activation energies E_1' and E_2' in eq 15 and hence also in the result (16). The pressure changes will also change the equilibrium temperature of the reactive mixtures, but relation 16 between the temperature of the maximum reaction rate, and the equilibrium temperature will not be much affected unless the reaction mechanism itself changes.

Maximum Reaction Rates at a Constant Thermodynamic Driving Force

The optimization principle equipartition of forces was derived by the use of linear phenomenological equations. These are only valid near equilibrium for chemical reactions. Thus, one should expect that constant thermodynamic driving forces according to eq 1 would only be able to predict optimal combinations of (low) entropy production rate and (high) conversion near equilibrium. However, for elementary reactions, $E_2 - E_1$ can be replaced by $-\Delta H$ in eq 13, and a rearrangement of (13) gives an expression with a right hand side equal to eq 2 when the reactor is operated at temperatures T_{op} equal to the temperatures of the maximum reaction rate, $T_{\text{r,max}}$:

$$R\left(\ln\left(\frac{E_2}{E_1}\right)\right) = -\Delta H\left(\frac{1}{T_{\text{r,max}}} - \frac{1}{T_{\text{eq}}}\right) \tag{17}$$

In most cases, the left side $R(\ln(E_2/E_1))$ will be close to constant. Thus, in a reactor with constant pressure, the trajectory of the maximum reaction rate calculated from eq 13 can also be calculated from eqs 1 and 2 by choosing the proper driving force $\Delta G/T = R(\ln(E_2/E_1))$. Unless there are large variations in the activation energies, the equipartition of forces principle[4,6] can therefore be applied also near its boundary condition of the maximum reaction rate and not only close to equilibrium for elementary, exothermic reactions occurring at constant pressure. Whether it can be applied far from equilibrium *in general* remains to be seen.

Conclusions

We have derived an analytical relationship between the equilibrium temperature and the temperature of the maximum reaction rate for exothermal reactive mixtures with Arrhenius type rate equations. The result implies that the trajectory of the maximum reaction rate is approximately parallel to the equilibrium line in a conversion versus inverse temperature diagram. The trajectory can be calculated from knowledge of the equilibrium line and the activation energies only. Thus, future optimization of temperature profiles in chemical reactors have been simplified. The constant distance between the two curves is also equivalent to an approximately constant driving force, $\Delta G/T$, for elementary reactions. Thus, we have also shown that the recently developed optimization principle called equipartition of forces can be applied near maximum reaction rates for exothermic elementary reactions occurring at constant pressure.

List of Symbols. A = affinity of reaction; A_i = Arrhenius' frequency factors; B, D = molecules; C = concentration; E_i = activation energies; ΔG = change in Gibbs energy for a reaction; ΔH = change in enthalpy for a reaction; k_i = kinetic coefficients; P = pressure; R = gas constant; T = absolute temperature; l = phenomenological coefficient; m_i, n_i = stochiometric coefficients; r = reaction flux/rate.

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Appendix 1: Concentration Based Rate Expressions for Reactions Occurring at Constant Pressure

For rate expressions based on concentrations (15), both the kinetic coefficients and the concentrations will vary with variations in pressure. Assuming ideal gas law, the concentrations C_i are

$$C_i = P_i/RT \tag{18}$$

while the concentrations at the equilibrium temperature are

$$C_{i,\text{eq}} = \frac{P_{i,\text{eq}}}{RT_{\text{eq}}} = C_i\frac{T}{T_{\text{eq}}} \tag{19}$$

since $P_{i,\text{eq}} = P_i$ at constant pressure and given mole fractions. Thus, reaction rate 15 becomes

$$r = A'_1 e^{-E'_1/RT} f_1(C_{B_1,\text{eq}}, C_{B_2,\text{eq}}, ...)(T_{\text{eq}}/T)^N - A'_2 e^{-E'_2/RT} f_2(C_{D_1,\text{eq}}, C_{D_2,\text{eq}}, ...)(T_{\text{eq}}/T)^M \tag{20}$$

where

$$N = \sum n_i \tag{21}$$

$$M = \sum m_i \tag{22}$$

Taking the differential $\mathrm{d}r/\mathrm{d}T^{-1}$ equal to zero gives

$$A_1' e^{-E'_1/RT} f_1(C_{B_1,\text{eq}})\left(\frac{T_{\text{eq}}}{T}\right)^N\left[-\frac{E'_1}{R} + NT\right] = A'_2 e^{-E'_2/RT} f_2(C_{D_i,\text{eq}})\left(\frac{T_{\text{eq}}}{T}\right)^M\left[-\frac{E'_2}{R} + MT\right] \tag{23}$$

Taking the logarithm and rearranging

$$\frac{1}{T_{\text{r,max}}} = \frac{R}{E'_2 - E'_1}\left(\ln\left(\frac{A'_2 f_2(C_{D_i})(T_{\text{eq}}/T)^M}{A'_1 f_1(C_{B_i})(T_{\text{eq}}/T)^N}\right) + \ln\left[\frac{(E'_2/R) - MT_{\text{r,max}}}{(E'_1/R) - NT_{\text{r,max}}}\right]\right) \tag{24}$$

Equation 24 was not solved explicitly for $T_{\text{r,max}}$ since that would hinder the comparison with the equilibrium temperature. The equilibrium temperature is derived in the same way, giving the difference

$$\frac{1}{T_{\text{r,max}}} - \frac{1}{T_{\text{eq}}} = \frac{R}{E'_2 - E'_1}\ln\left[\frac{(E'_2/R) - MT_{\text{r,max}}}{(E'_1/R) - NT_{\text{r,max}}}\right] \tag{25}$$

between the inverse temperature of the maximum reaction rate and the inverse temperature of equilibrium.

When there is a volume increase associated with the reaction ($M > N$), the fraction on the right side of eq 25 will decrease if $M/N > E_2/E_1$. Thus $T_{\text{r,max}}$ calculated according to (25) will be higher than if it was calculated according to (13). (For exothermic reactions E_2 is always larger than E_1.)

For $N = M$ or $M/N < E_2/E_1$, the total fraction on the right side of eq 25 will be increased. In such cases $T_{r,max}$ calculated according to (25) will be lower than if it was calculated according to (13).

Appendix 2: Pressure Based Rate Expressions for Reactions Occurring in a Constant Volume

Consider reaction 11 to be a gas-phase reaction in a vessel with fixed volume.

Reaction rate 14 can then be written

$$r = A_1 e^{-E_1/RT}(\gamma_{B_1} y_{B_1})^{n_1}(\gamma_{B_2} y_{B_2})^{n_2} ... P_t^N - A_2 e^{-E_2/RT}(\gamma_{D_1} y_{D_1})^{m_1}(\gamma_{D_2} y_{D_2})^{m_2} ... P_t^M \quad (26)$$

where P_t is the total pressure in the vessel. We assume that ideal gas law can be applied and that all activity coefficients $\gamma_i = 1$. The temperature of maximum reaction rate is again found from $dr/dT^{-1} = 0$, which gives

$$A_1 e^{-E_1/RT} f_3(y_{B_i})\left(-\frac{E_1}{R}\right)\left(-P_t^N - N P_t^N \frac{\ln T}{T}\right) = A_2 e^{-E_2/RT} f_4(y_{D_i})\left(-\frac{E_2}{R}\right)\left(-P_t^M - M P_t^M \frac{\ln T}{T}\right) \quad (27)$$

where

$$f_3(y_{B_i}) = y_{B_1}^{n_1} y_{B_2}^{n_2} ... \quad (28)$$

$$f_4(y_{D_i}) = y_{D_1}^{m_1} y_{D_2}^{m_2} ... \quad (29)$$

Taking the logarithms and rearranging gives

$$\frac{1}{T_{r,max}} = \frac{R}{E_2 - E_1}\left(\ln\left(\frac{A_2 f_4(y_D) P_t^M}{A_1 f_3(y_B) P_t^N}\right) + \left[\frac{(E_2/R) + (M \ln T_{r,max}/T_{r,max})}{(E_1/R) + (N \ln T_{r,max}/T_{r,max})}\right]\right) \quad (30)$$

while the equilibrium temperature is

$$\frac{1}{T_{eq}} = \frac{R}{E_2 - E_1}\left(\ln\left(\frac{A_2 f_4(y_D) P_t^M}{A_1 f_3(y_B) P_t^N}\right)\right) \quad (31)$$

Equation 30 was not solved explicitly for $T_{r,max}$ since that would hinder the comparison with (31). As can be seen, the inverse distance between the temperature of equilibrium and the temperature of the maximum reaction rate is still similar to (13) but not equal.

$$\frac{1}{T_{r,max}} - \frac{1}{T_{eq}} = \frac{R}{E_2 - E_1} \ln\left[\frac{(E_2/R) + (M \ln T_{r,max}/T_{r,max})}{(E_1/R) + (N \ln T_{r,max}/T_{r,max})}\right] \quad (32)$$

When $N = M$, the same (positive) number is added to the numerator and the denominator on the right side of eq 32, the total fraction will be reduced. Thus, $T_{r,max}$ calculated according to (32) will be higher than if it was calculated according to (13).

When there is a volume reduction associated with the reaction ($N > M$), the denominator will increase more than the numerator, the fraction will be reduced, and $T_{r,max}$ must be higher than according to eq 13.

When there is a volume increase associated with the reaction ($M > N$), however, the fraction on the right side of eq 32 will increase if $M/N > E_2/E_1$, thereby contributing to a reduced $T_{r,max}$ as compared with eq 13.

The importance of this deviation term is significant when the activation energies are similar in size (e.g. when $\Delta H = E_2 - E_1$ is small). For a hypothetical reaction with a low enthalpy change of reaction ($E_2 = 40$ kJ/mol, $E_1 = 30$ kJ/mol, $M = 2$, and $N = 4$), the additional term varied from 1.2 K at an equilibrium temperature of 400 K up to 4.5 K at equilibrium temperatures around 1500 K. Exchanging the values of M and N in the last case reduced the size of the deviation term by more than 60%.

For large enthalpies of reaction, however, the difference between (13) and (32) appears to be insignificant. For a reaction with $E_2 = 170$ kJ/mol, $E_1 = 60$ kJ/mol, $M = 2$, and $N = 4$, the additional term in eq 32 amounts to a maximum 0.3 K over a large temperature range (400 K $< T_{eq} <$ 1200 K).

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