

# Thermodynamic Analysis and Thermodynamic Efficiency of Chemical Reactors

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In this paper, conditions of minimal dissipation for processes occurring in chemical reactors with a given duration and a given degree of transformation are obtained. It is demonstrated that the derived entropy production can be used to construct the space of realizable (thermodynamically feasible) regimes of a chemical reactor.

## 1. Introduction

The degree of transformation achievable in a chemical reactor depends on the kinetics and duration of the process, the conditions under which it is run, and the available controls. Finite-time thermodynamics (FTT) methods<sup>1–3</sup> make it possible to study the influence of these factors. They also allow us to construct the thermodynamically realizable area in the state space of the process, where the reactor can operate without violating thermodynamic constraints.

These methods were initially applied to heat engines,<sup>4–7</sup> yielding the limiting power and the maximal efficiency as functions of power. It turns out that the thermodynamically realizable area here is determined by heat exchange kinetics. The same methodology was then used to study mass transfer processes, separation processes, throttling, crystallization, and other processes.<sup>8,9</sup>

In this paper, we will apply the general FTT approach to processes with chemical transformations. There are, in general, three steps: (1) Thermodynamic balances (for mass, energy, and entropy) for the system are constructed. They link external flows with changes in the system's composition and internal energy and with the entropy production in it, if the system is nonhomogeneous or if it includes chemical reactors. (2) The problem of finding the minimal possible entropy production (minimal average entropy production) in the system, subject to various constraints (on the process's kinetics, its duration, the rate of particular flows, etc.), is solved, giving the minimal entropy increment  $\Delta S_{\min}$  or the minimal entropy production  $\sigma_{\min}$  as functions of these constraints. (3) The inequality

$$\sigma(B) \geq \sigma_{\min}(B) \quad (1)$$

determines the realizable area in the space of constraints, described by the vector  $B$ . Only in this area can the system operate without violating the laws of thermodynamics. If the duration of the process is unconstrained and, therefore, its rate (e.g., the power of a heat engine) is unconstrained, then  $\sigma_{\min} = 0$ . In this case, the boundary of the area singled out by (1) represents a reversible process. If  $\sigma_{\min} > 0$ , then the realizable area shrinks.

The most important and difficult of the above steps is the second one. It requires the solution of an optimal control

problem. The accuracy of the estimate of  $\sigma_{\min}$  can be increased here by taking into account more factors, but this can make the corresponding optimal control problem much harder.

In the first part of this paper, we will use this approach for a mixing reactor, and in the second part, we consider a pipe displacement reactor. We assume that the reaction rates obey the law of mass actions and that all mixtures are near ideal solutions. Consequently, the chemical potential of the  $i$ th component has the form<sup>10</sup>

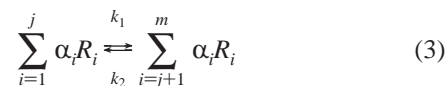
$$\mu_i = \mu_{i0}(T, P) + RT \ln x_i \quad (2)$$

where  $x_i$  is the molar fraction of the  $i$ th component in the mixture,  $R$  is the universal gas constant, and  $T$  and  $P$  are the mixture's absolute temperature and pressure, respectively.

## 2. Realizability Area for a Periodic Mixing Reactor

**2.1. Thermodynamic Balances.** We consider periodic process in a chemical mixing reactor with constant volume and at constant temperature. There is no heat exchange with the environment (adiabatic process). The mixture is a single-phase near ideal solution. Its chemical potential can be calculated using (2).

The stoichiometric equations for the reaction here have the form



where  $\alpha_i < 0$  for  $i \leq j$  and  $\alpha_i > 0$  for  $i > j$ . The reaction rate  $W$  is determined by the law of mass actions

$$W(x, T) = k_1(T) \prod_{i=1}^j x_i^{\alpha_i} - k_2(T) \prod_{i=j+1}^m x_i^{\alpha_i} = W_1(x, T) - W_2(x, T) \quad (4)$$

We assume that the local equilibrium hypothesis holds, that is, the system is in instantaneous equilibrium at each time and, therefore, its thermodynamic description is valid. We further assume for simplicity that input and output substances are delivered and removed reversibly. If not, we would need to take into account changes in free energy when the initial components are mixed and when the output mixture is separated.

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Mass balances for the  $i$ th component and for the total number of moles are

$$\frac{dN_i}{dt} = \frac{d(Nx_i)}{dt} = \alpha_i W(x, T), \quad N_i(0) = N_{i0} \quad i = 1, \dots, m \quad (5)$$

$$\frac{dN}{dt} = W(x, T) \sum_{i=1}^n \alpha_i = W(x, T) \alpha_\Sigma, \quad N(0) = N_0 \quad (6)$$

The energy balance is

$$-\frac{d}{dt} \sum_{i=1}^m N_i h_i = 0 \quad (7)$$

and the entropy balance is

$$\frac{d}{dt} \sum_{i=1}^m N_i s_i - \sigma = 0 \quad (8)$$

Here,  $h_i$  and  $s_i$  are the molar enthalpy and molar entropy for the  $i$ th component and  $\sigma$  is the reaction's entropy production.

The chemical potential of the  $i$ th component (molar Gibbs energy) is the difference between enthalpy  $h$  and  $Ts$ :

$$\mu_i = h_i - Ts_i, \quad i = 1, 2, \dots, m \quad (9)$$

If we multiply the entropy balance (eq 8) by  $T$ , subtract it from the energy balance (7), and take into account (9), we get

$$-\frac{d}{dt} \sum_{i=1}^m N_i \mu_i + T\sigma = 0 \quad (10)$$

In terms of the degree of transformation  $\zeta$ ,

$$x_i(\zeta) = \frac{N_i}{N} = \frac{N_{i0} + \alpha_i \zeta}{N_0 + \alpha_\Sigma \zeta} \quad (11)$$

Substitution of  $\mu_i(x_i)$  from (2) into (10) and differentiating yields

$$\sigma = \frac{W(x, T, P) A(x, T, P)}{T} \quad (12)$$

where  $A(x, T) = -\sum_{i=1}^m \alpha_i \mu_i(T, P, x_i)$  is the reaction's chemical affinity.

For the reaction's rate (4) and its chemical potential (2), we get

$$A = RT \ln \frac{W_1(x, T, P)}{W_2(x, T, P)} = RT \ln \frac{W + W_2}{W_2} \quad (13)$$

The degree of transformation  $d\zeta$  in turn depends on the reaction's rate via the equation

$$\frac{d\zeta}{dt} = W(x, P, T), \quad \zeta(0) = 0 \quad (14)$$

Since  $\sigma = d\Delta S/dt$ , if the degree of transformation is a monotone function of time, then  $d\Delta S/d\zeta = A(x, T, P)/T$ . If the reaction's chemical affinity is also nonnegative, then the reaction's entropy increment is a monotone function of  $\zeta\tau = \bar{\zeta}$ . Thus, minimizing dissipation corresponds to minimizing the duration subject to the given degree of transformation or to maximizing the degree of transformation subject to a given duration.

**2.2. Minimal Dissipation Problem.** After taking into account (12) and (13), the problem of minimal entropy production in this system takes the form

$$\Delta S = \int_0^\tau \sigma(t) dt = R \int_0^\tau W \ln \frac{W + W_2(x, T, P)}{W_2(x, T, P)} dt \rightarrow \min \quad (15)$$

subject to the given degree of transformation

$$\zeta_\tau = \int_0^\tau W dt = \bar{\zeta} \quad (16)$$

and subject to conditions (11) and (14), which determine  $x(\zeta)$ . The reaction rate  $W(t)$  can be used as the control here. This makes the problem much simpler, because we do not consider how to implement the control program  $W(t)$  (e.g., by controlling the initial composition, establishing an additional convective feed of some of the components  $i < j$ , varying the pressure, etc.). Since the aim here is to estimate the reactor's maximal performance, we neglect the influences arising from how the control is implemented (e.g., by establishing addition intermediate feeds) on the balance equations. Note that the concentrations  $x(\zeta)$  enter the model only through  $W_2$ , which depends on  $x_i$  for  $i > j$ .

For the optimal process, the degree of transformation is a monotonic function of  $t$ . Therefore, we can use  $\zeta$  instead of  $t$  as the problem's independent variable.

After the substitution

$$dt = \frac{d\zeta}{W} \quad (17)$$

and after expressing  $x$  in terms of  $\zeta$  from (11), we get

$$\Delta S = R \int_0^{\bar{\zeta}} \ln \frac{W + W_2(\zeta, T, P)}{W_2(\zeta, T, P)} d\zeta \rightarrow \min \quad (18)$$

subject to

$$\int_0^{\bar{\zeta}} \frac{d\zeta}{W} = \tau \quad (19)$$

The problem's Lagrange function is

$$L = \ln \frac{W + W_2(\zeta, T, P)}{W_2(\zeta, T, P)} + \frac{\lambda}{W}$$

Here,  $\lambda$  is the Lagrange multiplier. The first-order condition of optimality for  $L$  on  $W$  gives

$$\frac{\partial L}{\partial W} = 0 \rightarrow \frac{W^2}{W + W_2(\zeta, T, P)} = \frac{W^2}{W_1(\zeta, T, P)} = \lambda = \text{Const } \forall \zeta \quad (20)$$

Therefore, the condition of minimal dissipation for an isothermal periodic process in a reactor of ideal mixing is that the ratio of the square of the total reaction rate to the direct reaction rate is a time-independent constant.

From (20), we get

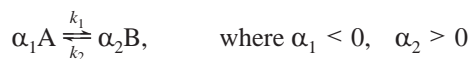
$$W^*(\zeta, T, P) = \frac{\lambda}{2} \pm \sqrt{\frac{\lambda^2}{4} + \lambda W_2(\zeta, T, P)} \quad (21)$$

For the solution to be physically possible, we must have  $W^* > 0$ , so we can drop the minus sign in (21).

The term  $\lambda$  is to be found from condition (19) by solving the following equation

$$\int_0^{\bar{\xi}} \frac{d\xi}{\frac{\lambda}{2} + \sqrt{\frac{\lambda^2}{4} + \lambda W_2(\xi, T, P)}} = \tau \quad (22)$$

**2.3. Example.** Consider a reaction where one component is consumed and another is created:



The reaction rate is

$$W = W_1 - W_2 = k_1 x_1^{-\alpha_1} - k_2 x_2^{\alpha_2} \quad (23)$$

Therefore

$$N_1(t) = N_{10} - \alpha_1 \xi(t), \quad N_2(t) = N_{20} + \alpha_2 \xi(t) \quad (24)$$

After taking into account (24), the rate of the inverse reaction becomes

$$W_2(\xi) = k_2 \left( \frac{N_{20} + \alpha_2 \xi}{N_{10} + N_{20} + (\alpha_2 - \alpha_1) \xi} \right) \quad (25)$$

The minimal entropy production problem here takes the form

$$\Delta S = R \int_0^{\bar{\xi}} \ln \left( \frac{W}{W_2} + 1 \right) d\xi \rightarrow \min_W \quad (26)$$

Its solution (the optimal reaction rate) with accuracy up to the constant  $\lambda$  is

$$W^* = \frac{\lambda}{2} + \sqrt{\frac{\lambda^2}{4} + \lambda W_2} \quad (27)$$

Here,  $\lambda$  is to be found from the condition of fixed duration

$$\int_0^{\bar{\xi}} \frac{d\xi}{\frac{1}{2}\lambda + \sqrt{\frac{\lambda^2}{4} + \lambda W_2}} = \tau \quad (28)$$

If

$$N_{10} = N_{20} = \frac{1}{2}, \quad \alpha_1 = 2, \quad \alpha_2 = 1,$$

$$k_2 = 1, \quad \bar{\xi} = \frac{1}{2}, \quad \tau = 1$$

then (28) can be rewritten as

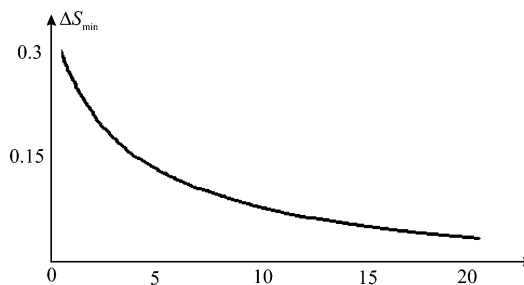
$$\int_0^{0.5} \frac{d\xi}{\lambda^2 + \sqrt{\lambda^2 + 4\lambda \left( \frac{0.5 + \xi}{1 - \xi} \right)}} = 0.5 \quad (29)$$

After replacing the independent variable  $\xi$  with  $t$

$$t = \sqrt{\lambda^2 + 4\lambda \left( \frac{0.5 + \xi}{1 - \xi} \right)}$$

this conditions becomes

$$\int_{\sqrt{\lambda^2 + 2\lambda}}^{\sqrt{\lambda^2 + 8\lambda}} \frac{\lambda t dt}{(t + \lambda)(t^2 - \lambda^2 + 4\lambda)^2} = \frac{1}{24} \quad (30)$$



**Figure 1.** Dependence of the minimal entropy production in a chemical reactor on the process duration.

Integrating (30) using Ostrogradski's formula yields

$$\lambda = 0.23$$

Substitution of  $\lambda$  into (27), yields the integrand for (26) that depends only on  $\xi$

$$\Delta S_{\min} = 0.24$$

After repeating these calculations for different  $\tau$ , we obtain  $\Delta S_{\min}(\tau)$ , as shown in Figure 1. The realizable area for the reactor lies above this graph. The boundary corresponds to the maximal degree of transformation and the given duration of the process. This maximal degree of transformation can be found by substituting the reaction rate from (21) into (14). The entropy increment in a real reactor can be calculated from the amounts of input and output mixtures at  $t = 0$  and  $t = \tau$  and their compositions. If this calculated entropy lies significantly higher than this boundary, then the productivity of the reaction can be increased by approaching the conditions of minimal dissipation (eq 20). Deviation from a constant on the left-hand side of (20) arises when the reactor operates in a thermodynamically nonoptimal way.

### 3. Pipe Displacement Reactor

We consider a pipe reactor with a mixture whose composition and temperature change from section to section but is homogeneous in each section. The reaction rate  $W$  obeys (4) and stoichiometric condition (3) holds. The constants for direct and inverse reaction rates are defined as

$$k_i = k_{i0} e^{-E_i/RT}, \quad i = 1, 2 \quad (31)$$

where  $E_i$  is the activation energy for the  $i$ th reaction.

Let us write down the thermodynamic balances for the mixture's elementary volume in the  $l$ th section. For the mass balance, we get

$$\frac{d(Nx_i)}{dl} = \alpha_i W(x, T, P), \quad \frac{dN}{dl} = \alpha_\Sigma W(x, T, P) \quad (32)$$

$$N(0) = N_0, \quad N_i(0) = N_{0i}, \quad i = 1, \dots, n$$

For the energy balance, we get

$$\frac{d(Nh)}{dl} = q(T, T_0), \quad h(0) = h_0 \quad (33)$$

and for the entropy balance

$$\frac{d(Ns)}{dl} = \frac{q(T, T_0)}{T_0} + \sigma, \quad s(0) = s_0 \quad (34)$$

where  $\sigma$  is the entropy production due to the chemical reaction and heat transfer.

After expressing molar entropy  $s$  from (9) in terms of  $h$  and chemical potentials and substituting it in (33)–(34), we get

$$\sigma = W(x, P, T) \frac{A(x, P, T)}{T} + q(T_0, T) \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (35)$$

Here,  $q$  is the flow of heat supplied by the source with the temperature  $T_0$  and  $A$  is the chemical affinity of the reaction. Reduction of  $\sigma$  corresponds to the reduction of the heat flux  $q$ .

The entropy production in the reactor is found by integrating  $\sigma$  over the length of the reactor. The entropy production due to heat transfer is primarily determined by the average temperature. It is almost independent of the temperature profile. That is why we seek the optimal regime that minimizes entropy production due to the chemical reaction. Then, the entropy production in the reactor is

$$\bar{\sigma} = \int_0^L W(x, P, T) \frac{A(x, P, T)}{T} dl \quad (36)$$

In any section  $l$ , the concentration of the  $i$ th component is related to the degree of transformation in the following way

$$x_i(\xi) = \frac{N(0)x_{i0} + \alpha_i \xi}{N(0) + \alpha_\Sigma \xi} \quad (37)$$

Here,  $N(0)$  is the total number of moles entering the reactor and  $\xi(l)$  is the dependence of the degree of transformation on the reactor's length and obeys the equation

$$\frac{d\xi}{dl} = \frac{W(x, T, P)}{v}, \quad \xi(0) = 0 \quad (38)$$

where  $v$  is the velocity of mixture.

As we did above, we express the chemical affinity in terms of the direct and inverse reaction rates

$$A(x, T, P) = RT \ln \frac{W_1(x, T, P)}{W_2(x, T, P)} \quad (39)$$

We assume that the pressure  $P$ , the reactor length  $L$ , and the reaction mixture's velocity  $v$  are given.

The problem of maximizing the reactor performance is reduced to finding such dependence of the reaction mixture's temperature  $T(l)$  on  $l$  that  $\bar{\sigma}$  is minimal for the given degree of transformation  $\xi(L) = \bar{\xi}$ .

After replacing the independent variable  $l$  with  $\xi$ :

$$dl = d\xi \frac{v}{W(\xi, T, P)} = d\xi \frac{v}{W_1(\xi, T, P) - W_2(\xi, T, P)}$$

we get

$$\bar{\sigma} = v \int_0^{\bar{\xi}} R \ln \frac{W_1(\xi, T, P)}{W_2(\xi, T, P)} d\xi \rightarrow \min_{T(\xi)} \quad (40)$$

subject to

$$v \int_0^{\bar{\xi}} \frac{d\xi}{W_1(\xi, T, P) - W_2(\xi, T, P)} = L \quad (41)$$

Here, the variables  $x_i$  in  $W_i(x, T, P)$  ( $i = 1, 2$ ) are expressed in terms of  $\xi$  using (37).

The optimality condition for the problem (40)–(41) is given by the condition of stationarity in  $T$  of the Lagrange function  $L$

$$L = R \ln \frac{W_1}{W_2} + \frac{\lambda}{W_1 - W_2}$$

We obtain

$$\frac{dL}{dT} = 0 \rightarrow R \left( \frac{W_{1T}}{W_1} - \frac{W_{2T}}{W_2} \right) \frac{(W_1 - W_2)^2}{W_{1T} - W_{2T}} = \text{Const} \quad (42)$$

or

$$(W_1 - W_2) \frac{\frac{\partial}{\partial T} (\ln W_1 - \ln W_2)}{\frac{\partial}{\partial T} \ln(W_1 - W_2)} = \text{Const} \quad (43)$$

We denoted here partial derivatives of  $W_v$  with respect to  $T$  as  $W_{vT}$ , ( $v = 1, 2$ ).

Thus, the condition of minimal dissipation for the chemical transformation in a pipe reactor is reduced to finding a temperature profile  $T(\xi)$  for which the expression on the left side of equation (43) is constant.

For example, for a single-staged reaction where the rates  $W_1$  and  $W_2$  of the direct and inverse reactions are

$$W_1 = K_1(T)x_1^{-\alpha_1}, \quad W_2 = K_2(T)x_2^{\alpha_2}$$

and

$$K_i(T) = K_{i0} \exp(-E_i/RT), \quad i = 1, 2$$

condition 43 takes the form

$$\frac{[ay^\gamma x_1^{-\alpha_1}(\xi) - yx_2^{\alpha_2}(\xi)]^2}{\gamma ay^\gamma x_1^{-\alpha_1}(\xi) - yx_2^{\alpha_2}(\xi)} = \text{Const} = \lambda \quad (44)$$

where  $x_1(\xi)$  and  $x_2(\xi)$  are determined by (29) and  $y(T)$  is a function of temperature of the form

$$y(T) = K_{20} e^{-E_2/RT}, \quad \gamma = \frac{E_1}{E_2}, \quad a = \frac{K_{10}}{K_{20}}$$

After computing  $y(\xi, \lambda)$  from (44), one can then calculate the corresponding temperature profile with minimal dissipation

$$T^*(\xi, \lambda) = \frac{E_2}{R(\ln K_{20} - \ln y(\xi, \lambda))}$$

The parameter  $\lambda$  depends on  $\bar{\xi}$  and  $L$ . Substitution of  $T^*(\xi, \lambda)$  into (41) yields the equation for finding  $\lambda$ .

Therefore, the difference between the expression on the left-hand side (43), where all functions are known, and a constant for the real process gives a measure of how far the real process is from being thermodynamically optimal.

#### 4. Conclusion

In this paper, we consider simple kinetic mechanisms and hydrodynamic regimes for chemical reactors. It is demonstrated how the irreversibility of a process determines the thermodynamically realizable area in its state space. A similar approach can be used in more complex systems, such as catalytic reactions, segregation processes, biochemical reactors, etc.

However, for such systems, the computational difficulties are much greater.

A necessary condition for a process to operate at minimal dissipation is obtained. This condition requires that some function of the process's variables be constant, that is, have the same value at all times and in all sections of the reactor. This value is a function of external parameters. This condition can be used to construct an automatic control system which maintains the minimal dissipation of a process when external conditions change.

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