# Thermodynamic Analysis and Evaluation of the Feasibility Range of a Chemical Reactor

## A. M. Tsirlin*, Ni Min Kan**, and V. V. Trushkov*

*Institute of Program Systems, Russian Academy of Sciences,
ul. Sovetskaya 2, Pereslavl'-Zalesskii, Yaroslavl oblast, 152020 Russia*
*** Shanghai University, Shanghai, China*
*e-mail: tsirlin@sarc.botik.ru*
Received March 15, 2005

**Abstract**—The conditions of minimal irreversibility of finite-time processes performed in chemical reactors to a given conversion are determined. The estimated entropy production allows one to find the feasibility range of a chemical reactor.

The conversion attainable in a chemical reactor depends on the time, kinetics, and conditions of the process and control possibilities. By methods of finite-time thermodynamics [1–3], the effect of each of the factors can be evaluated and the feasibility range of the reactor can be found.

The first objects for which this problem was solved were heat engines [4–7]. For them, by methods of finite-time thermodynamics, the limiting power and the maximal efficiency as a function of the power were found. The feasibility range of the heat engines depended on the heat-transfer kinetics. Further, these methods were used to investigate heat transfer, mass transfer, separation, etc. [8, 9].

Let us present the general scheme of using methods of finite-time thermodynamics for studying processes involving chemical transformations.

(1) For a system to be explored, thermodynamic balance equations (for mass, energy, and entropy) are written. These equations relate external fluxes to changes in the internal energy and composition of the system and also to the entropy production in the system if the system is nonuniform or there are chemical transformations in it.

(2) The problem of the minimum possible entropy increase (the minimal average entropy production in the system) is solved under some or other constraints (e.g., on the process kinetics or time, the intensity of one flux or another, etc.) to find $\Delta S_{min}$ or $\sigma_{min}$ as a function of these constraints.

(3) The inequality

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

determines the feasibility range of the thermodynamic system under the constraints characterized by the vector B.

When the process time is infinite and, hence, the flux intensity can be arbitrarily low, then $\sigma_{min} = 0$. In this case, the boundary of the range determined by inequality (1) is given by reversible processes. At $\sigma_{min} > 0$, the feasibility range is narrower.

The most important and complex step of the general scheme is step (2) because it requires one to solve an optimal control problem and the greater the number of real factors taken into account, the more difficult it is to solve the problem of minimal dissipation but, at the same time, the more accurate the estimate of $\sigma_{min}$.

According to the scheme proposed, we will consider initially a batch reactor and then a tubular continuous reactor. We will assume that the reaction rate obeys the mass action law and mixtures of reactants are near-ideal solutions; therefore, the chemical potential of the $i$th component in a mixture can be written as [10]

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

where $x_i$ is the mole fraction of the $i$th component and $\mu_{i0}$ is the standard chemical potential of the $i$th component.

## FEASIBILITY RANGE FOR A BATCH REACTOR

### Thermodynamic Balances

Let us consider the process in a batch chemical reactor at constant temperature without heat exchange with the environment. Let the reaction mixture be a near-ideal single-phase solution. Since the mixture is near-ideal, the chemical potentials can be found from expression (2).

The stoichiometric reaction equation has the form

$$\sum_{i=1}^{j} \alpha_i N_i \xrightleftharpoons[k_2]{k_1} \sum_{i=j+1}^{m} \alpha_i N_i, \tag{3}$$
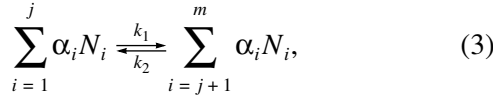
where $k_1$ and $k_2$ are the rate constants for the forward and reverse reactions, respectively, and the coefficients $\alpha_i < 0$ at $i \le j$ and $\alpha_i > 0$ at $i > j$. The reaction rate $W$ is determined by the mass action law:

$$
\begin{aligned}
W(x, T) &= k_1(T) \prod_{i=1}^{j} x_i^{\alpha_i} - k_2(T) \prod_{i=j+1}^{m} x_i^{\alpha_i} \\
&= W_1(x, T) - W_2(x, T).
\end{aligned} \tag{4}
$$

The following thermodynamic balance equations can be written:

the mass balance equations for the $i$th component and the total number of moles, respectively,

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

$$\frac{dN}{dt} = W(x, T) \sum_{i=1}^{m} \alpha_i = W(x, T)\alpha_\Sigma, \quad \begin{aligned} N(0) &= N_0, \\ N_i(0) &= N_{i0}; \end{aligned} \tag{6}$$

the energy balance equation,

$$\frac{d}{dt} \sum_{i=1}^{m} N_i h_i = 0; \tag{7}$$

and the entropy balance equation,

$$\frac{d}{dt} \sum_{i=1}^{m} N_i s_i - \sigma = 0. \tag{8}$$

The chemical potential (molar Gibbs free energy) can be expressed as the difference of the enthalpy $h$ and the product $Ts$:

$$\mu = h - Ts. \tag{9}$$

Multiplying entropy balance equation (8) by $T$, subtracting the product from energy balance equation (7), and taking into account expression (9), we obtain

$$\frac{d}{dt} \sum_{i=1}^{m} N_i \mu_i + T\sigma = 0. \tag{10}$$

Let us introduce the conversion $\zeta$ by the equation

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

Substituting $\mu_i(x_i)$ in form (2) into Eq. (10) and differentiating, we find

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

where $A(x, T, P) = -\sum_{i=1}^{m} \alpha_i \mu_i (T, P, x_i)$ is the chemical affinity of the reaction.

For reaction rate (4) and chemical potential (2), the chemical affinity of the reaction is represented as

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

In turn, the conversion is related to the reaction rate by the equation

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

### Problem of Minimal Dissipation

Let us find the minimum of the entropy increase of the system, which, with allowance for expressions (12) and (13), is written as

$$
\begin{aligned}
\Delta S &= \int_{0}^{\tau} \sigma(t)\, dt \\
&= R \int_{0}^{\tau} W \ln \frac{W + W_2(x, T, P)}{W_2(x, T, P)}\, dt \longrightarrow \min,
\end{aligned} \tag{15}
$$

at a given conversion $\bar{\zeta}$,

$$\int_{0}^{\tau} W\, dt = \bar{\zeta}, \tag{16}$$

under conditions (11) (defining the vector $x(\zeta)$) and (14). As a control parameter, the reaction rate $W(t)$ can be chosen. This significantly simplifies the problem since the ways of changing $W$ (by varying the initial composition or the pressure, providing convective feed of one initial component or another ($i < j$), etc.) fall beyond the scope of the formulation of the problem. Since our purpose is to evaluate the limiting possibilities of the reactor, we ignore the fact that one or another way of changing $W$ (e.g., by feeding reactants) affects the balance equations. Note that the concentrations in the vector $x(\zeta)$ are involved in the problem through the function $W_2$, which depends on $x_i$ at $i > j$.

The problem can be solved more simply if we note that the conversion $\zeta$ in the optimal process is a monotonic function of time $t$ and, therefore, can be used instead of $t$ as an independent variable.

Making the change of variable

$$dt = \frac{d\zeta}{W} \tag{17}$$

and expressing $x$ through $\zeta$ from formula (11), we obtain

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

under the condition

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

Bearing in mind that the universal gas constant $R$ does not affect the optimality conditions, we can write the Lagrangian function of this problem in the form

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

The requirement that this function should be stationary in $W$ leads to the condition

$$\frac{\partial F}{\partial W} = 0 \longrightarrow \frac{W^2}{W + W_2(\zeta, T, P)}$$

$$= \frac{W^2}{W_1(\zeta, T, P)} = \lambda = \text{const} \quad \forall \zeta. \qquad (20)$$

The condition of minimal dissipation at a given conversion and a fixed time of the isothermal process in a well-stirred batch reactor is that the ratio of the square of the total reaction rate to the forward reaction rate at each moment of time should be maintained constant.

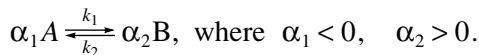From condition (20), the optimal reaction rate $W^*$ is obtained:

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

According to the physical meaning of the process, $W^* > 0$, and only the plus sign can be retained in front of the root in expression (21).

$\lambda$ is found from condition (19):

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

**Example.** Let us consider a reaction in which one substance is consumed and one substance forms:

$$\alpha_1 A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \alpha_2 B, \quad \text{where} \quad \alpha_1 < 0, \quad \alpha_2 > 0.$$

The reaction rate is

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

and thus

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

The reverse reaction rate with allowance for expressions (24) can be expressed as

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

The entropy increase according to expression (18) is

$$\Delta S = R \int_0^{\bar{\zeta}} \ln \left( \frac{W}{W_2} + 1 \right) d\zeta \longrightarrow \min_W. \qquad (26)$$

The optimal reaction rate up to a constant $\lambda$ is

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

$\lambda$ determines the given process time

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

Let us take

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

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

and rewrite expression (28) in the form

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

Since $t$ and $\zeta$ are related by the expression

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

we have

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

Having found integral (30) by the Ostrogradsky method, we then calculate the Lagrange multiplier $\lambda^*$ corresponding to the optimal conditions: $\lambda^* = 0.23$. After substitution of $\lambda^*$ into expression (27), the integrand in expression (26) will depend only on $\zeta$. Calculating this integral, we obtain $\Delta S^* = 0.24$.

Performing similar calculations at other process times $\tau$, we obtain the function $\Delta S^*(\tau)$, the graph of which is shown in the figure. Above the graph is the feasibility range of the reactor. The boundary of the range corresponds to the maximum attainable conversion at a given process time. To find this conversion, it is necessary to substitute the reaction rate found from condition (21) into Eq. (14). The process output at a given conver-
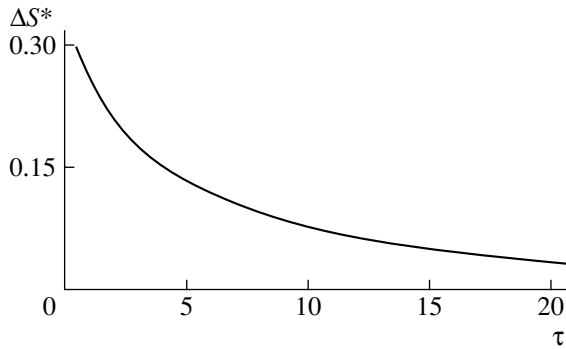
Minimal entropy increase in a chemical reactor versus process time.

sion is inversely proportional to $\tau$. If the entropy increase in a real reactor that is found from the amounts and compositions of the products at the moments of time $t = 0$ and $t = \tau$ is represented by a point lying much higher than the boundary, then the output can be increased by approaching condition (20) of minimal dissipation. The deviation of the left-hand side of equality (20) from the constant indicates the moments of time at which the operating conditions of the reactor are far from the thermodynamically optimal conditions.

## A TUBULAR CONTINUOUS REACTOR

Let us consider the process in a tubular reactor containing a mixture that is uniform in each section but varies in composition and temperature from section to section. The reaction rate $W$ obeys law (4), and the stoichiometric ratio between the components meets condition (3). The rate constants for the forward and reverse reactions depend on temperature as

$$k_i = k_{i0}\mathbf{e}^{-\frac{E_i}{RT}}, \quad i = 1, 2, \tag{31}$$

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

From the thermodynamic balance equations for a volume element of the mixture in section $l$, we obtain

the mass balance equations,

$$\frac{d(Nx_i)}{dl} = \alpha_i W(x, P, T),$$

$$\frac{dN}{dl} = \alpha_\Sigma W(x, P, T), \tag{32}$$

$$N(0), \quad N_i(0) - \text{are given}, \quad i = 1, \ldots, n;$$

the energy balance equation,

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

and the entropy balance equation,

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

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

Let us express the molar entropy $s$ from expression (9) through the molar enthalpy $h$ and the chemical potentials and, after substituting into Eqs. (33) and (34), obtain the entropy production

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

where $q$ is the heat flux supplied from a source with temperature $T_0$.

The entropy production in the reactor is found by integrating $\sigma$ along the reactor length. The integral of the entropy production in the heat transfer is mainly determined by the average temperature and depends insignificantly on the temperature profile; therefore, it is necessary to determine the conditions of minimal entropy production in the chemical reaction, whereas the irreversibility of the heat transfer can be evaluated for the found solution as

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

In each section $l$, the concentration of the $i$th component is related to the conversion as

$$x_i(\zeta) = \frac{N(0)x_{i0} + \alpha_i\zeta}{N(0) + \alpha_\Sigma\zeta}. \tag{37}$$

Here, $N(0)$ is the total number of moles entering the reactor and $\zeta(l)$ is the conversion as a function of the coordinate of the section, which satisfies the equation

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

Here, $v$ is the velocity of the mixture.

Let us express, as above, the chemical affinity through the forward and reverse reaction rates:

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

The pressure $P$, the reactor length $L$, and the velocity $v$ of the reaction mixture are assumed to be given.

In this case, the problem of the limiting possibilities of the reactor is reduced to the determination of such a law of change in the temperature $T(l)$ of the reaction mixture that $\bar{\sigma}$ attains a minimum at a given conversion

$$\zeta(L) = \bar{\zeta}.$$

Let us write this problem, changing the argument $l$ to $\zeta$:

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

We obtain

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

under the condition

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

where the functions $W_\nu(\zeta, T, P)$ are obtained from the functions $W_\nu(x, T, P)$ by changing the variables $x_i$ to $\zeta$ according to expression (37).

Let us write the condition for the optimality of problem (40), (41) as a condition that the Lagrangian function F of this problem is stationary in $\bar{T}$, denoting the partial derivative of $W_\nu$ with respect to $T$ as $W_{\nu T}$:

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

$$\frac{dF}{dT} = 0 \Rightarrow R \left( \frac{W_{1T}}{W_1} - \frac{W_{2T}}{W_2} \right) \frac{(W_1 - W_2)^2}{W_{1T} - W_{2T}} = \text{const}, \quad (42)$$

or, in another form,

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

Thus, the condition of minimal dissipation in the chemical transformation process in a tubular reactor is the choice of such a temperature profile $T(\zeta)$ that the left-hand side of equality (43) is constant. For example, for a single-step reaction in which the forward and reverse reaction rates $W_1$ and $W_2$ are written as

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

where

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

expression (43) takes the form

$$\frac{[a y^\gamma x_1^{-\alpha_1}(\zeta) - y x_2^{\alpha_2}(\zeta)]^2}{\gamma a y^\gamma x_1^{-\alpha_1}(\zeta) - y x_2^{\alpha_2}(\zeta)} = \text{const} = \lambda, \quad (44)$$

where $x_1(\zeta)$ and $x_2(\zeta)$ are found from Eq. (29) and $y(T)$ is a function of temperature of the form

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

Having found exactly or approximately $y(\zeta, \lambda)$ from condition (44), one can calculate the law of change in

the temperature that corresponds to the minimal dissipation:

$$T*(\zeta, \lambda) = \frac{E_2}{R[\ln k_{20} - \ln y(\zeta, \lambda)]}.$$

$\lambda$ depends on both $\bar{\zeta}$ and $L$ and can be found after substituting $T*(\zeta, \lambda)$ into condition (41).

Importantly, in a functioning reactor, for which the changes in all the functions in equality (43) are known, the deviation of the left-hand side of this equality from the constant characterizes the deviation from the minimal dissipation conditions.

## NOTATION

$A$—chemical affinity of a reaction;
$B$—vector of constraints imposed on a process;
$E$—activation energy;
$F$—Lagrangian function;
$h$—molar enthalpy;
$L$—reactor length;
$N$—number of moles;
$P$—pressure;
$R$—universal gas constant;
$s$—molar entropy;
$T$—absolute temperature;
$t$—current time;
$x$—mole fraction;
$W$—reaction rate;
$\alpha$—stoichiometric coefficient;
$\Delta S$—entropy increase;
$\zeta$—conversion;
$\lambda$—Lagrange multiplier;
$\mu$—chemical potential;
$\sigma$—entropy production;
$\tau$—process time.

## SUBSCRIPTS AND SUPERSCRIPTS

$i$—component;
min—minimal value;
$\nu = 1$, forward reaction; 2, reverse reaction;
*—optimal value.

## REFERENCES

1. Andresen, B., *Finite-Time Thermodynamics*, Copenhagen: Univ. Copenhagen, 1983, p. 189.
2. Salomon, P. and Nitzan, A., Finite Time Optimizations of a Newton's Law Carnot Cycle, *J. Chem. Phys.*, 1981, vol. 74, no. 6, pp. 3546-3560.
3. Tsirlin, A.M., *Metody optimizatsii v neobratimoi termodinamike i mikroekonomike* (Optimization Methods in Irreversible Thermodynamics and Microeconomics), Moscow: Fizmatlit, 2003.

4. Novikov, I.I., Nuclear Power Plant Efficiency, *At. Energ.*, 1957, no. 3, p. 409.

5. Orlov, V.N. and Rudenko, A.V., Optimal Control in Problems of the Limiting Possibilities of Irreversible Thermodynamic Processes, *Avtom. Telemekh.*, 1985, no. 5, pp. 27–41.

6. Amel'kin, S.A., Andresen, B., Salamon, P., Tsirlin, A.M., and Yumaguzhina, V.N., Limiting Possibilities of Thermomechanical Systems: Single-Source Processes, *Izv. Akad. Nauk, Energ.*, 1998, no. 2, pp. 118–126.

7. Amel'kin, S.A., Andresen, B., Salamon, P., Tsirlin, A.M., and Yumaguzhina, V.N., Limiting Possibilities of Thermomechanical Systems with Several Sources, *Izv. Akad. Nauk, Energ.*, 1999, no. 1, pp. 152–158.

8. Orlov, V.N. and Rozonoer, L.I., Evaluation of the Efficiency of Controlled Thermodynamic Processes on the Basis of the Energy, Mass, and Entropy Balance Equations, *X Vsesoyuznoe soveshchanie po problemam upravleniya* (X All-Union Conf. on Control Problems), Moscow: Nauka, 1986, pp. 187–189.

9. Tsirlin, A.M., Mironova, V.A., Amelkin, S.A., and Kazakov, V.A., Finite-Time Thermodynamics: Conditions of Minimal Dissipation for Thermodynamic Process with Given Rate, *Phys. Rev. E*, 1998, vol. 58, no. 1, pp. 215–223.

10. Prigogine, I. and Defay, R., *Chemical Thermodynamics*, London: Longmans Green, 1954. Translated under the title *Khimicheskaya termodinamika*, Moscow: Nauka, 1966.