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The theory and practice of energy saving in the chemical industry: some methods for reducing thermodynamic irreversibility in chemical technology processes

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Abstract

The causes of thermodynamic irreversibility in chemical reactions and other industrial chemical processes (in particular absorption, stripping, and heat transfer) and ways of reducing energy consumption have been examined. Some thermodynamic principles based on the Second Law of thermodynamics such as the so called “counteraction principle,” “driving force method,” “quasi-static method,” and the result some of practical methods for energy saving design are discussed. It is demonstrated that the possibilities for reducing energy consumption are substantially higher than often seems possible. The correctness and practical effectiveness of the above methods have been confirmed by many commercial examples, for instance the lead author was able to reduce heat consumption in more than 20 commercial CO_2 removal installations by changes in networks only, without changing the absorbent. The heat consumption was reduced to about 1/2 to 1/3 of that used with conventional flow sheets.

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1. Introduction.

The purpose of this paper is to counter the widespread viewpoint that thermodynamic irreversibility in processes involving chemical reactions ostensibly is inevitable and results in large energy resource losses [1]. It seems to the authors that this misconception and the lack of understanding

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Nomenclature

C	specific heat capacity;
E, e	Exergy;
ΔE_{ch}	change in “chemical” exergy;
ΔE_p	change in “pressure” exergy;
ΔE_t	change in “thermal” exergy;
F_h	area of heat transfer or mass transfer;
G	Gibbs energy, molar or volume flow rate;
$\bar{G}_i = \mu_i$	partial molal Gibbs energy, chemical potential of *i*-component;
H, $\bar{H}_i$	enthalpy, partial molal enthalpy;
K_e	chemical equilibrium constant;
K_h, K_m	heat transfer rate coefficient, mass transfer rate coefficient;
N	quantity of moles;
L	quantity of liquid;
M	mass flow rate;
P	pressure;
$P^*{}_i$	partial equilibrium pressure;
Q	quantity of substance mole/hour, kg/hour or m^3/hour;
R	universal gas constant;
S, $\bar{S}_i$	entropy, partial molal entropy;
T	Temperature;
T_0	ambient temperature;
V	Volume;
W	useful work;
$X_{i,}$	concentration of *i* component in liquid;
ΔY	the process driving force in any form;
Y_i	concentration of *i* component in gas mixture;
η_e	exergetic efficiency;
Φ	reflux ratio for stripping;

Subscripts

Rev	Reversible.

by many process designers of the Second Law methods for reducing exergy losses[1] are the main causes of non-optimal designs with excessive energy consumption.

Energy resource consumption has been shown to be the principal cost of many energy-intensive chemical processes, such as ammonia production [2–4]. As a result, the aim of modern energy-

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[1] To clarify, we note that different terms are used in the literature for exergy changes, such as exergy *losses*, *expenditures*,

intensive process design has been to reduce energy consumption [2–6]. In addition, as will be shown below, a reduction in energy consumption often results in a simultaneous decrease (not an increase) in capital cost.

In our opinion, most of the ideas in this report are so simple and evident that they should be of common knowledge to chemical process designers. It is thus difficult to understand why textbooks and monographs [7–12] don't present, in systematic form, the known rules for saving energy in the design of chemical processes. There are, however, many published papers that are devoted to the use of the Second Law for the reduction of energy consumption [13–23]. In particular, the ideas expressed in [19,20] are closest to the approach used in this paper. The theoretical basis is given by the well-known exergy method [10–12].

This paper is based partly on the senior author's book [24] and papers in [25–28] as well as on the many publications of different scientists. We would like to draw particular attention to the many excellent papers of Petliuk and Platonov devoted to energy saving chemical rectification designs, published as far back as 1964 [29,30].

2. Some thermodynamic fundamentals of energy saving in the chemical industry

2.1. Thermodynamic reversibility and the driving force of chemical processes

Thermodynamic reversibility requires that all process driving forces, such as temperature, pressure and chemical potential differences be zero at all points and times. Thus, the theoretical thermodynamically reversible chemical process must proceed along an equilibrium line that is in chemical equilibrium at each point of a reactor. Accordingly, the driving force for the process must be zero throughout the entire process: not just at the end. Such a theoretical process results in the production of the maximal amount of useful work, or in the consumption of the minimal amount of work.

Unfortunately, a reversible chemical process operates at an infinitesimal rate, and requires an infinitely large plant. To operate a chemical process in finite time and at finite cost, it is necessary to have finite driving forces, i.e., to expend some thermodynamic availability (exergy) and, as a result, to consume energy resources. The goal of the process designer is to expend this thermodynamic availability wisely while achieving the technological goals of the process. Too large a driving force expends more exergy than is necessary and wastes our energy resources, while too small a driving force requires excessive capital investment. In particular, the designer should avoid an apparatus that has too large a driving force in one part, and too small a driving force in another part. In such a case, both energy resources and capital are wasted.

The classical example of the thermodynamically reversible operation of chemical reactions is

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consumption, and *destruction.* We note that exergy expenditure in one part of a more complex system may be used to good advantage in another part of the system, or used to reduce capital costs, or used to provide a useful product outside the system. In accord with the objective of this paper to improve energy saving practices in industrial processes, we would most often use the term *exergy expenditure*.

the van't Hoff ideal-gas reaction equilibrium chamber [9], Fig. 1. This example has been used as a method for deducing the concept of the equilibrium constant. This model can also be used to derive the expression for the maximal useful work that can be produced as a result of a reaction. The chamber contains an equilibrium mixture of reaction components. Additional quantities of raw materials are supplied by transport through semi-permeable membranes, infinitely slowly and with infinitesimally small changes in pressure, concentrations and temperatures. The reaction products are removed in the same manner.

The maximal work W_{rev} associated with such a chemical reaction, say specifically the reaction shown in Fig. 1

$$\mathrm{nA} + \mathrm{mB} = \mathrm{hC} + \mathrm{jD} \tag{1}$$

carried out at constant temperature and pressure, can be expressed as

$$\Delta W_{\mathrm{rev,P,T}} = -\Delta G = RT\left(\ln K_{\mathrm{e}} - \ln\frac{P^{\mathrm{h}}_{\mathrm{C1}}P^{\mathrm{j}}_{\mathrm{D1}}}{P^{\mathrm{n}}_{\mathrm{A1}}P^{\mathrm{m}}_{\mathrm{B1}}} -\right) = -(\Delta H - T\Delta S) > 0 \tag{2}$$

The Gibbs energy (G) always decreases during a spontaneous chemical reaction, and the maximal obtainable work is equal to the decrease in Gibbs energy at the P and T of the reaction[2].

Our task is to use this change in Gibbs energy to recover the useful work to maximal extent, or, as will be shown later, to reduce the magnitude of the Gibbs energy change where possible.

As stated earlier, if a chemical reaction could be carried out reversibly, the process would produce the maximum quantity of useful work. To produce finite changes in a finite time, it is

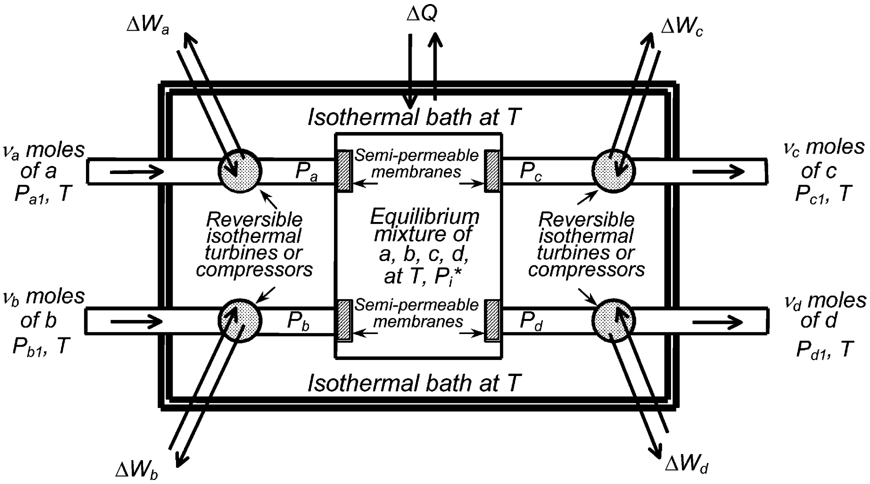

Fig. 1. A van't Hoff reaction chamber [9]

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[2] To expedite the analysis, we have focused on spontaneous reactions. That is, reactions running with a decrease of Gibbs energy and consequently with the possibility of obtaining useful work. For non-spontaneous reactions, which proceed with an increase in Gibbs energy, it is necessary to spend work to run them. One energy-saving possibility is to carry out such reactions by combining them together with spontaneous reactions. [31].

necessary, however, to have finite driving forces. Therefore, all actual processes, chemical or otherwise, must operate in a thermodynamically irreversible way.

The generalized driving force in a chemical reaction is the difference in partial Gibbs energies, i.e. chemical potentials:

$$\bar{G}_{\mathrm{i}} = \mu_{\mathrm{i}} = \bar{H}_{\mathrm{i}} - T\bar{S}_{\mathrm{i}} \tag{3}$$

The actual process driving forces are the differences in partial pressures ΔP_{i}, concentrations $\Delta x_{\mathrm{i}}, \Delta y_{\mathrm{i}}$ and temperatures ΔT.

Since chemical reactions are carried out irreversibly, a considerable part of the Gibbs energy change may not be utilized. It was mentioned above that there is a widespread misconception that these losses are large and inevitable [1]. We will show here that there are many technical methods for reducing the thermodynamic irreversibility of chemical reactions, as well as of mass and heat transfer processes.

We will first consider the expansion, from P_1 to P_2, of a compressed gas in a cylinder, as shown in Figs. 2 and 3 [7]. This is the mechanical equivalent of a spontaneous chemical reaction.

Fig. 2a represents the expansion against a counteracting external pressure that is continuously adjusted to precisely match the pressure of the gas in the cylinder as the gas expands from P_1 to P_2. The driving force for the expansion is zero at all points; thus, the process is reversible and the work recovered is the maximum possible. This reversible work is represented by the area under the P_1P_2 curve in Fig. 3. However, since the driving force is zero, such an expansion would take an infinite time and is not possible.

Another type of expansion is shown in Fig. 2b, where the gas expands against the constant

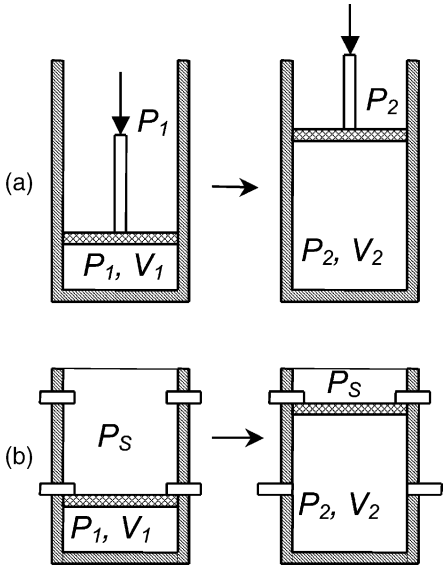

Fig. 2. Reversible and irreversible expansion work of a compressed gas [7]. (a) Reversible expansion $W_{\mathrm{R}} = \int_1^2 PdV$; (b) Irreversible expansion $W_{\mathrm{IR}} = P_{\mathrm{S}}(V_2 - V_1)$

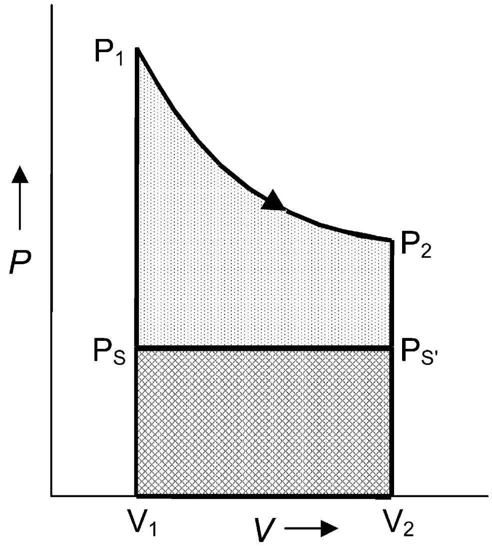

Fig. 3. Graphical integration of reversible and irreversible work [7].W_R=Area $V_1P_1P_2V_2$;W_{IR}=Area $V_1P_SP_{S'}V_2$

pressure of the surroundings, P_S, which is lower than P_1 or P_2. Since the driving force for the expansion, (P_{GAS}–P_S), is finite, the expansion is irreversible, but can proceed in a finite time. The work obtained, shown in Fig. 3 as the dark shaded area under the P_S line, is clearly less than the reversible work.

It is easily seen from Fig. 3, that the amount of work obtained from this irreversible expansion can be increased by increasing the counteracting pressure above the pressure of the surroundings, P_S.

If the counteracting pressure is increased beyond P_2, the gas cannot expand fully to V_2, but, depending on the geometry of the curves, the work obtained may continue to increase. Of course, if the counteracting pressure is increased further all the way to P_1 (the initial pressure of the compressed gas), the gas cannot expand at all and no work will be obtained. Thus, we see that there is an optimal value of counteracting pressure, somewhere between the pressure of the surroundings (P_S) and the initial pressure of the gas (P_1) that produces the maximum work for the irreversible expansion of the gas against a single counteracting pressure.

Analogously, it is clear from Fig. 3 that it is possible to use multiple stages of constant counteracting pressures to further increase the expansion work, and that the maximum value of work obtainable increases as the number of stages increases.

Thus, though it is never possible to recover the entire theoretical reversible expansion work, it is possible by proper design and operation to maximize the work obtained (i.e., minimize the exergy loss) for a given, or revised, expansion scheme.

Though the following discussion deals only with the expansion of a compressed gas, the conclusions for saving energy are of general applicability. Process energy can be saved by:

1. Applying a counteraction to reduce the driving force
2. Optimizing the process conditions
3. Using multiple stages

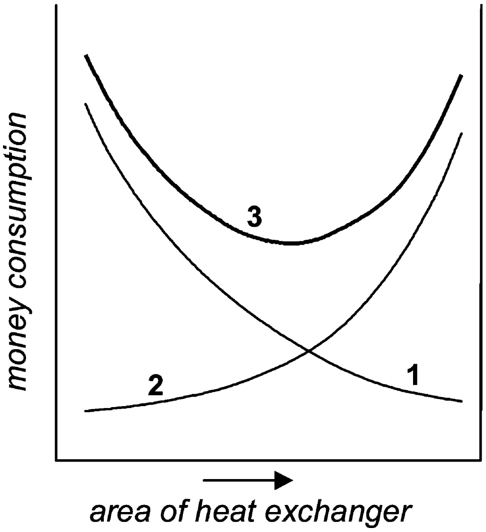

Fig. 4. The conventional task of optimum area of heat exchanger.1—Energy consumption cost; 2—Investment cost; 3—Sum of costs.

4. Other methods, as described later in this paper

It will also be shown that, analogously, there are optimal pressures, temperatures and reactant ratios for chemical reactions, corresponding to the minimal specific exergy losses, i.e., the exergy optimum for a given process flow sheet [26].

It is important to recall that there is a well-known conflict between our desire to reduce energy consumption (that is to reduce the driving force) and the opposite wish to increase the driving force in order to increase the rate of the process and, thereby, to decrease the capital investment. A balance between these two effects produces an economic optimum (see Fig. 4), but it is important to pay attention to some other aspects of conventional cost optimizations.

The monetary cost of energy resources used is based on the current market price for energy. Typically nowadays, monetary costing neglects the costs of current as well as future environmental and ecological problems for the country and the world.

Another factor is the influence of a change in capital investment at a given process stage on the investment at other stages. A simple example is demonstrated in Fig. 5 a and b. Stage 1 of

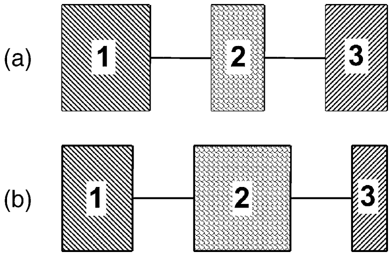

Fig. 5. The influence of heat consumption on capital investments at boiler *1*, constant-enthalpy process stage *2* and cooler *3*. (a) High heat consumption; (b) Low heat consumption.

this process is a boiler that produces steam for use in stage 2, which is a constant-enthalpy process (such as a distillation column which generally operates with essentially no enthalpy difference between feed and products). According to the First Law of thermodynamics, the heat produced at stage 1 and fed to the constant-enthalpy stage 2, is removed at stage 3—a cooler that generally discharges heat to the ambient. It is now assumed that the relative capital cost investments in the three stages of this process are depicted as in Fig. 5 a. If the driving force and energy consumption at stage 2 are reduced, the capital investment there is increased (in a distillation column this could be done by increasing the number of plates), as shown in Fig. 5 b. However, the capital investment at both stages 1 and 3 will be reduced because the amount of heat which needs to be supplied by the boiler and removed by the cooler is consequently decreased. In such cases, it may be possible to reduce both energy consumption and investment costs simultaneously.

There are other ways to reduce exergy losses and total investments simultaneously. Compare the simple examples of heat transfer with an extremely non-uniform ΔT driving force (Fig. 6 b), with that of a uniform driving force (Fig. 6 a). Due to the near-zero ΔT driving force at the right end of the heat exchanger in Fig. 6 b, the logarithmic mean driving force is near zero, and the heat exchange area must thus be very large. Furthermore, due to the large driving force at the left end of the exchanger, the exergy loss in the case of Fig. 6 b is also large because it is proportional to the large area between the two temperature profile lines.

The use of a uniform driving force (Fig. 6 a) allows, however, a reduction in exergy losses as well as a reduction of heat exchanger area. In general, changes in flow sheets that make driving forces more uniform can simultaneously reduce both exergy losses and capital investments.

Similarly, with chemical reactions, a chemical engineer may want to reach equilibrium at the exit of a reactor (state 2, Fig. 7). But if attention is not paid to the large driving force at the reactor inlet (state 1), irreversibility and exergy losses may be excessive. At the same time, since the mean driving force towards state 2 in this reactor is near zero, the reactor size and cost may also be excessive.

A general conclusion is that the art of the energy saving chemical engineer is to make driving forces small and uniform.

This issue is analyzed in more detail below.

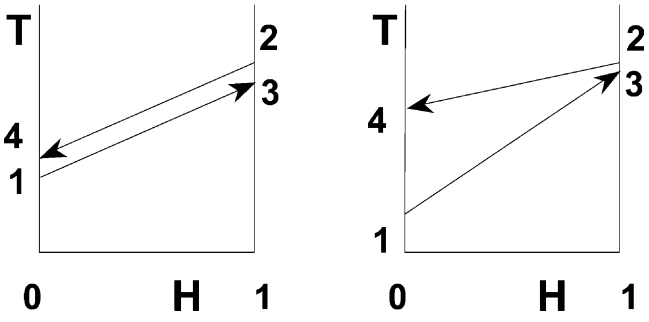

Fig. 6. The temperatures of streams during heat exchange a) The uniform driving force; b) The nonuniform driving force.

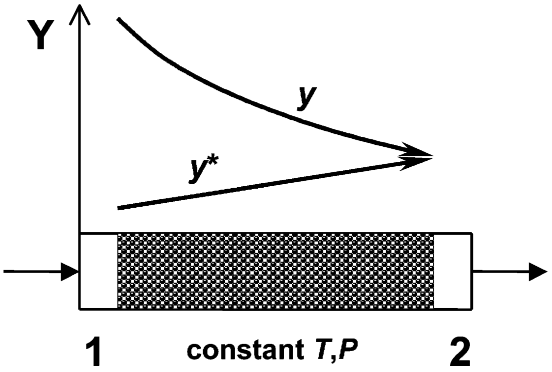

Fig. 7. The classical example of thermodynamically irreversible way of chemical reaction.y—concentration of a reagent; y∗—equilibrium concentration; 1—input of reagents; 2—outlet of reagents.

2.2. The Le Chatelier principle[3] and the "counteraction principle"

At first glance, the demands of the Second Law generate diametrically opposite consequences for the chemist-technologist and for the power engineer [26]. The chemist-technologist would like to increase the extent of reaction and, as a result, the yield of useful products. He/she wants, consequently, to increase the driving force of the process, i.e. to increase the absolute value of the decrease in Gibbs energy, $-\Delta G$. The classical Le Chatelier principle, which is a consequence of the Second Law, deals with this matter and is thus employed. To increase the *extent of reaction*, the Le Chatelier principle requires a reduction in pressure for a reaction that operates with an increase in volume, and an increase in pressure for reactions that operate with a decrease in volume. These pressure changes increase the $-\Delta G$ driving forces, thus driving the reactions further towards completion.

Analogously, the Le Chatelier principle requires a reduction in the temperature of exothermic reactions, and an increase in the temperature of endothermic reactions. Furthermore, to increase the yield of useful products, Le Chatelier's principle recommends an excess of one of the reactants.

The power engineer, on the other hand, would like to reduce the thermodynamic losses by applying a "counteraction" to reduce the magnitude of the $-\Delta G$ driving force: e.g., by increasing the temperature of exothermic reactions; reducing the temperature of endothermic ones; increasing the pressure of reactions that increase in volume; and reducing the pressure of reactions that decrease in volume.

The advanced process designer must try to integrate these opposite objectives. This would be possible if the process could be run in a manner approaching those shown in Fig. 2 a, 3 and in

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[3] To be more succinct, the Le Chatelier–Braun principle can be formulated as follows [7,9]: "A system in chemical equilibrium attempts to counteract any change in pressure, temperature or composition".

Fig. 8, where each process is run reversibly with a gradually decreasing counteraction such that $\Delta G_{ij} \rightarrow 0$ at all locations and times.

Let us analyze one of the examples of the opposite requirements of the Second Law, viz. the influence of the temperature on the technological and exergetical characteristics of an exothermic reaction.

First we examine an exothermic reaction operating at a constant temperature. The Le Chatelier principle requires a decrease in temperature to increase the yield and, thus, to increase the amount of heat released. On the other hand, we see from the Carnot relation, Eq. (4), that the exergetic value of a unit of heat increases as the temperature increases,.

$$W = Q(1-T_0/T) \tag{4}$$

where Q here is quantity of heat.

Thus, it is clear that for a constant-temperature exothermic reaction there is an optimal reaction temperature where the exergetic value of the heat released is maximal and, as a result, exergy losses are minimal. (This is discussed in more detail in Section 4 of this paper.)

However, instead of using a constant reaction temperature, the best way, in principle, is to vary the reaction temperature; start the reaction under the maximal temperature and then reduce it gradually, so that the reaction is complete at the reactor exit, (see Fig. 8 a). This method reduces the $-\Delta G$ driving force along the entire length of the reactor: at the entrance due to the high temperature, and at the exit due to the reduced concentration of the reactants. Thus, the heat of reaction can be recovered with maximal efficiency, while simultaneously running the reaction to completion [26].

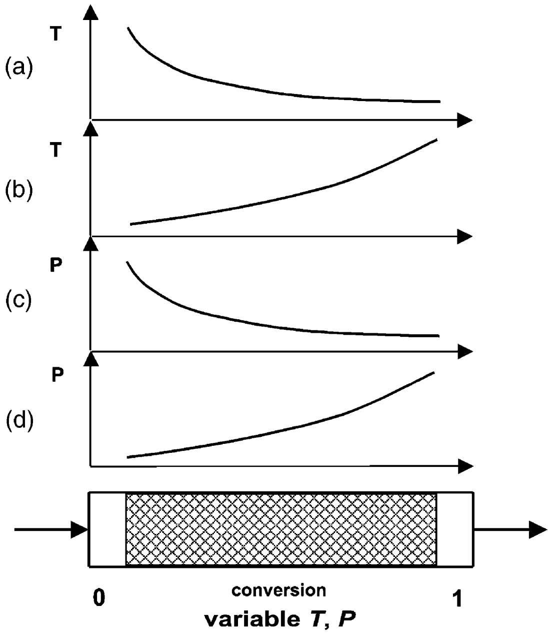


Fig. 8. Thermodynamic reversible ways of operating chemically reversible reactions by counteraction, that is with retarding, with maximal use of Gibbs energy and minimal energy consumption. a—exothermic reaction, b—endothermic reaction, c—reaction with volume increase, d—reaction with volume decrease.

Correspondingly, endothermic reactions (Fig. 8 b) should be started at a minimal temperature, and then the temperature should be increased gradually. In this manner, the $-\Delta G$ driving force is made low along the entire length of the reactor. It is noteworthy here that the initial heat required can be supplied as inexpensive low-temperature heat, while the more expensive higher temperature heat is needed only at the end, to run the reaction to completion.

Now we analyze chemical reactions that result in volume changes. The relationship between the changes in volume, pressure and Gibbs energy is:

$$\left[\frac{\partial(\Delta G)}{\partial P}\right]_{\mathrm{T}} = \Delta V \tag{5}$$

Eq. (5) shows that for a reaction in which volume increases ($\Delta V > 0$), a decrease in pressure causes a further decrease in ΔG (i.e., an increase in the absolute value of $-\Delta G$) and, accordingly, results in an increased product yield. Of course, this is exactly what the Le Chatelier principle predicts.

Unfortunately, the thermodynamic irreversibility, i.e., the exergetic loss, also increases with an increase in the magnitude of the $-\Delta G$ driving force. Thus, if we operate this reaction at a constant low pressure we can expect higher yields, but will also incur higher exergetic losses. Alternatively, if operated at a constant high pressure to reduce the exergetic losses, the yields are reduced.

The resolution of this conflict would be to run the reaction at a variable pressure as shown in Fig. 8 c. Use a high pressure as a counteraction at the start, and then gradually lower the pressure as the reaction proceeds to a high yield at the end of the reactor. In this manner the reaction can proceed with a reduced $-\Delta G$ driving force at all points, i.e., a reduced exergetic loss, without sacrificing yield. In the limit, as $-\Delta G \rightarrow 0$ at all locations and times, the reaction would be thermodynamically reversible.

This is completely analogous to the thermodynamically reversible expansion of a compressed gas, Fig. 2 a and 3.

Unfortunately, it would take an infinite time, even if it were possible to run the reaction at the appropriate continuously varying pressure. A compromise would be to run the reaction in a finite number of stages with each succeeding stage being at a lower pressure than the prior one. Though this multi-stage process cannot be thermodynamically reversible, it would lead to reduced exergetic losses. In practice, however, such a multi-stage reaction is sometimes difficult to accomplish. Thus, we may be limited to a one-stage constant pressure reaction and, if so, our task is to try to find the optimal process conditions. Note also that this is in accordance with our previous conclusion that there is an optimal pressure for the single-stage expansion of a gas.

At the beginning of the reaction, the conversion is near zero but the exergetic losses are a finite quantity. Therefore, at this point, the specific losses per unit of useful product are nearly infinite. If the reaction is carried out completely, the exergetic losses (reduction in Gibbs energy) are maximal. Therefore, an optimal conversion and optimal pressure, corresponding to the minimal exergy consumption per unit of reaction product, must exist. Some examples will be discussed later. It will be shown that the specific exergy loss per quantity of useful product is a good criterion for optimization (for the case when the capital costs are nearly constant and the influence of the change of conditions on the other stage parameters is negligible).

For a reaction that decreases in volume, Eq. (5) shows that an increase in pressure increases the magnitude of the $-\Delta G$ driving force, thus, increasing both the conversion (as predicted by the Le Chatelier principle) and the exergetic loss. For such a reaction to proceed in a thermodynamically reversible fashion, the pressure should start low and increase with the conversion as shown in Fig. 8d. The same final pressure is achieved with less compressor work by shifting the compression from the reactants (whose volume is larger) toward the products (whose volume is smaller). Similar arguments apply here as did in the preceding discussion of reactions that increase in volume. Here, however, the optimal pressure for a constant pressure reaction, may well be less than that suggested by the Le Chatelier principle.

Next we consider the effect of using an excess of one of the reactants to increase the yield of useful product. Unfortunately, increasing the excess of one reactant increases the magnitude of the $-\Delta G$ driving force, which thereby increases the exergy loss. In addition, there are exergy losses due to mixing that require the consumption of energy to separate the excess reactant from the products.

Rather than using an excess reactant, a better approach is to run the reaction to partial completion and then to recycle the unreacted feedstock. This can be expedient in spite of the energy cost of separating and recirculating the unreacted feedstock. This conclusion is in agreement with exergy analysis.

Accordingly, it is possible to say that when the well-known Le Chatelier principle (resulting from the Second Law) is used by chemists in order to run the reaction to completion, they are often forgetting the opposite Second Law requirement (the “counteraction principle”) needed to reduce the exergy consumption per unit of product.

At first glance, the “counteraction principle” appears to be a quasi “anti Le Chatelier principle” [25]. However, as we have shown here, both the “counteraction principle” and the Le Chatelier principle are based on the Second Law.

A more generalized conclusion follows from Fig. 8. Theoretically, if we want to eliminate thermodynamic losses in a reaction (or in a mass transfer process) we must transfer energy and matter at each point along the entire length of the reactor. In practice, to reduce thermodynamic losses, we often operate a series of reactors step by step, with energy and mass transfer at each step.

Examples of use of the “counteraction principle” in the chemical industry are discussed in Section 6.

2.3. A brief description of the “driving force method” and the “quasi-static method”

From “the counteraction principle” it is easy to arrive at “the driving force method”, which differs not in concept but in the details of practical usage. To use this method it is necessary at first to calculate the process operating and equilibrium lines, and then to compare them. The next step is to examine the driving forces, to find where they are too high, and then to search for methods to reduce them. This procedure is very useful in design.

The convergence of the above mentioned lines is a necessary (but not sufficient) way to reduce exergy consumption. Even perfect convergence, as discussed below, does not mean that the exergy consumption is an absolute minimum. In addition, changes in process temperature or pressure can change the characteristics of the equilibrium line. Therefore, we need to use the “counteraction principle” at each point along the equilibrium line.

From our experience, the use of the so-called “quasi-static method” is very productive. The main idea of this method is to calculate the conditions of the theoretical quasi-static process, which would run along the equilibrium line [32,33]. This calculation shows, for example, the temperature and other conditions for such a process needed to operate with zero driving force. The senior author used this method to reduce heat consumption in a chemidesorption process for the removal of CO_2 from a chemisorbent. More detailed results are given in Sections 7 and 8.

3. Some comments on the problem of reducing driving forces

3.1. Methods for reducing driving force: the useful, the useless, and the harmful

It is important to analyze the statement that the reduction in driving forces is the basis for energy saving methods, because there are many examples where reduction in driving forces gave the opposite results, or none. These examples, however, don’t invalidate the main thesis. The following statements would help to avoid mistakes.

1. The reduction in driving forces is a necessary but not sufficient requirement for a reduction in exergy consumption. It only makes exergy reduction possible, but not automatically. The reduction in driving forces must be accompanied by the recovery of useful work, otherwise it may be useless. To recover the useful work (or obtain similar positive results) it is often necessary to use great ingenuity.
2. It is also important that the decrease in driving forces in some stages of an industrial process does not lead to negative results at succeeding stages of the process.
3. A typical example of a harmful reduction in driving force is the addition of reagents with an apparatus which employs full mixing, instead of by displacement using plates. The driving force of the process in the apparatus with full mixing is low because the reactants are mixed with the reaction products. The rate of the process is also low, but the exergy consumption does not decrease: instead it increases, because the exergy required for the separation of the reaction products from the mixture increases.It is useful to note that in homogeneous gas phase reactions (except for membrane processes) the reactants and products inevitably flow in the same direction and can mix with a resulting exergy loss. The conclusion for this case is to try to run the reaction without mixing along the length of the reactor.
4. The reduction of driving force at one stage must not be attained by increasing the irreversibility at another stage. The example from [20], see Fig. 9, shows a decrease of the temperature difference in a heat exchanger as a result of the throttling of high-pressure steam. This would indeed reduce the exergy loss in the heat exchanger itself, but the throttling process used to attain this is extremely irreversible. The result is an unnecessary increase of the required heat transfer area.
5. Other well-known examples of the harmful reduction of driving forces include poor heat insulation, high hydraulic resistance, friction, etc.

3.2. The influence of the thermodynamic properties of working substances on the irregularity of driving forces and the design of energy saving networks

It is well known that the driving force is uniform for the simple case of heat transfer between streams which have identical flow heat capacities ($G_i c_i$) (see for example Fig. 6 a). In this case

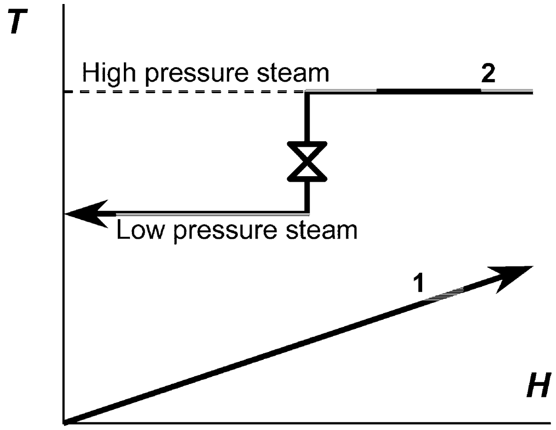


Fig. 9. The harmful losses in driving force of heat transfer between liquid (1) and steam (2) as the result or throttling of steam [19].

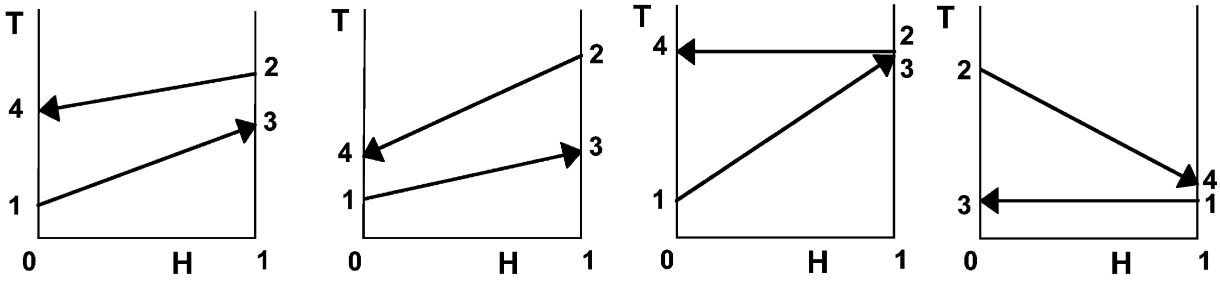
the driving force can be reduced by an increase in the heat transfer area, or the heat transfer coefficient. Nothing else is necessary. The exergy loss in such a case is:

$$\Delta Ex = \sum E_x^{\mathrm{out}} - \sum E_x^{\mathrm{in}} = (Ex_3 + Ex_4) - (Ex_1 + Ex_2) = Gc\left[(T_3 - T_1) + (T_4 - T_2) - T_0 \ln\frac{T_3T_4}{T_1T_2}\right] = -\frac{T_0K_hF_h\Delta T_t}{T_3 - T_1}\ln\frac{T_3T_4}{T_1T_2} \qquad (6)$$

If $T_3 = T_2$ and, then in this case also $T_4 = T_1$, and $\Delta T_t = 0$. In this case $\Delta Ex = 0$, but the heat transfer area is infinitely large. It is evident from Eq. (6) that if $\Delta T \neq 0$, exergy is always lost.

If the flow heat capacities of the two liquids are not the same, the typical behavior of driving forces is shown in Fig. 10. The exergy losses in such cases are:

$$\Delta Ex = -T_0G_1c_1 \ln\left[\frac{T_3T_4}{T_1T_2}\left(\frac{T_2}{T_4}\right)^{1\text{-}v}\right] \qquad (7)$$



(a) (b) (c) (d)

Fig. 10. The temperatures of streams during heat exchange at (a) $G_{1\text{–}3}\ c_{1\text{–}3} < G_{2\text{–}4}\ c_{2\text{–}4}$ and (b) $G_{1\text{–}3}\ c_{1\text{–}3} > G_{2\text{–}4}\ c_{2\text{–}4}$. (c) The temperatures of streams during heat exchange at condensation of pure saturated steam and heating of gas or liquid. (d) The temperature of streams during heat exchange at evaporation of pure liquid and cooling of gas or liquid.

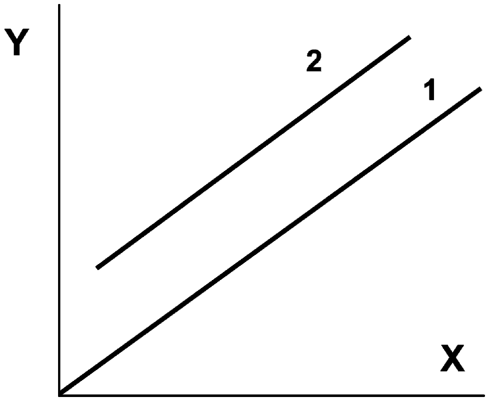


Fig. 11. The equilibrium (1) and operating (2) lines in gas absorption, where X, Y are the gas concentrations in liquid and gas phases, respectively.

where, $v = \frac{G_2c_2}{G_1c_1}$

It is seen that whenever the flow heat capacities of two streams differ, the exergy losses can never be equal to zero. This is true even if the difference in temperatures at one end of the heat exchanger is zero (because the difference at the other end cannot simultaneously be zero). This is also true if only one of the working substances is undergoing a phase change; for example condensation or evaporation of water (see Fig. 10 c,d).

Analogously, in absorption processes it is easy to reduce the irreversibility of physical absorption (Fig. 11) by reducing absorbent circulation, increasing the number of plates or the volume of packing, etc.

Many technological processes, perhaps most of them, are more complex and the problems can't be solved in such simple ways. If the driving force is irregular, an increase in the height of the absorber or of the heat transfer area can help approach equilibrium at one or two points, but the driving force in the other points may still be too large (see for example Figs. 12 and 13).

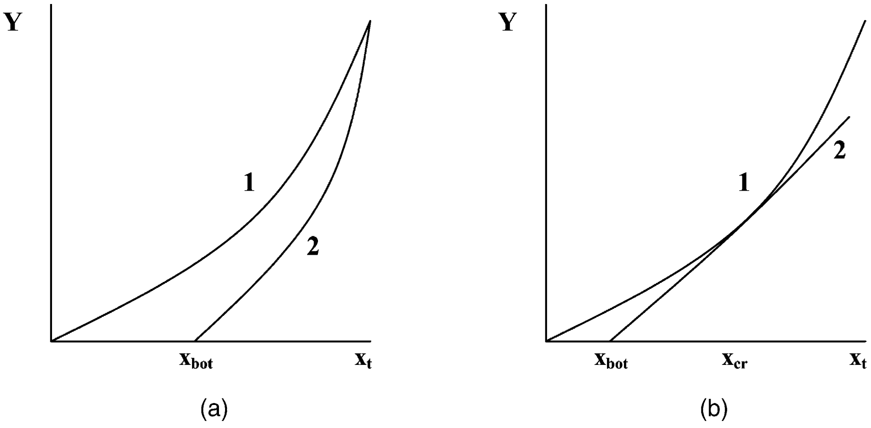


Fig. 12. The equilibrium (1) and operating (2) lines for nonisothermal chemidesorption and at equilibrium at the top of desorber, point x_t (a), and at equilibrium at the "critical" section, point x_{cr} (b)

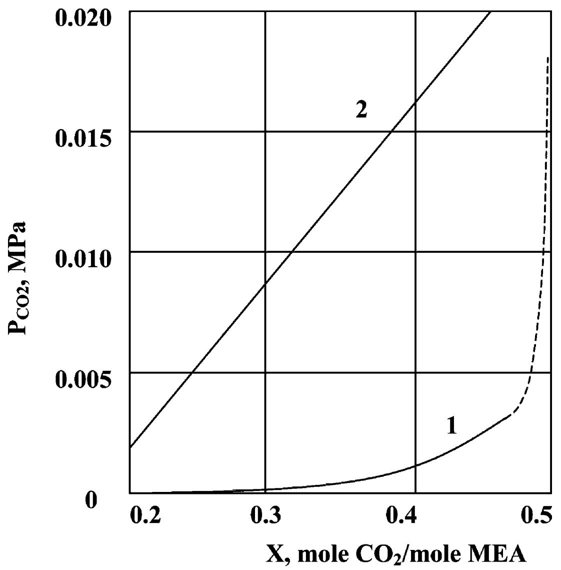


Fig. 13. The equilibrium (1) and operating (2) lines of CO_2 chemisorption by MEA (monoethanolamine) solution

Fig. 12 represents the CO_2 desorption process from monoethanolamine (MEA) solutions by adiabatic stripping with steam. In this example, it is impossible to approach equilibrium at both the top and the bottom of the desorber using a simple input of absorbent to the top of the column and removal of absorbent from the bottom. Equilibrium can be reached at only one point in the apparatus.

The same is true for absorption of CO_2 by MEA solutions, as shown by the equilibrium and operating lines in Fig. 13. It is seen that it is possible, in the limit, to approach equilibrium at the top or at the bottom of the absorber, but the driving force in the middle part will inevitably be high if the conventional simple design and normal process conditions are used. This is due to the peculiarity of this gas-liquid equilibrium. In such cases it is necessary to revise the flow sheets or, if possible, to change the working substances. Revised flow sheets are discussed in Sections 7 and 8.

4. Some comments on exergy analysis

Several Second-Law methods have been proposed to analyze and improve process efficiencies. These include the "entropy method" [31], the "driving force" method, the "quasi-static method" and, the currently popular, "exergy analysis" method [10,11].

Exergy (previously called thermodynamic availability) is a term that represents the theoretical optimal work that can be done as a result of the state of a system changing to that of an equilibrium state, generally that of the ambient. The exergy of a system is a function of changes in its thermophysical properties as well as of changes in its chemical composition. It is convenient to consider them separately.

The exergy of a flow system (not undergoing chemical change) is the maximum work that can be obtained by bringing the system into equilibrium with the ambient, $T_o, P_o, v_o = O$, $z_o = O$, and is represented by:

$$Ex = (H-H_0)-T_0(S-S_0) + mv^2/2 + mgz \tag{8a}$$

Since the kinetic and potential energy terms are often negligible, they are indeed often omitted from this equation.

Eq. (8a) defines the "physical" or "thermomechanical" exergy of the system. Conceptually, if the temperature of the system is greater than the ambient, work can be extracted by running a reversible heat engine between the system and the ambient at T_o. This reversible work is the system's "thermal" exergy. Also, if the system pressure is greater than the ambient (note that $H = U + PV$), work can be obtained by a reversible isothermal expansion to the ambient pressure, P_o. This reversible work is the system's "pressure" exergy.

When the state of a flow system changes from state 1 to state 2, the change in the maximum work obtainable (neglecting kinetic and potential energies) is, from Eq. (8a):

$$(Ex_2-Ex_1) = (H_2-H_1)-T_0(S_2-S_1) \tag{8b}$$

An increase in ΔE_X represents an increase in the amount of work that can be obtained if the system is brought reversibly to the ambient state, T_o, P_o.

As noted above, we can also add or remove a theoretical work equivalent as a result of chemical reactions, i.e., chemical exergy. Gibbs energy is the generalized driving force for isothermal chemical reactions. Thus, it is necessary to relate chemical exergy with the decrease in Gibbs energy at constant temperature.

The maximum work obtainable from an isothermal chemical reaction is equal to the decrease in Gibbs energy of the reaction. When carried out at ambient temperature and pressure the maximum work available is:

$$\Delta Ex_{ch} = -\Delta G_{To,Po} = -[(H_{prod}-H_{react})-T_o(S_{prod}-S_{react})] = G_{react}-G_{prod} \tag{9}$$

Values of standard Gibbs energies of formation, available in the literature, can be used in Eq. (9) to calculate the chemical exergy. Though the products of reaction are not in chemical equilibrium with the ambient, the effect usually is small enough to be ignored.

An isothermal chemical reaction operating at a temperature different from T_o can also contribute equivalent work, $-\Delta G_T$, to a system. As a result, even though it is not in thermal equilibrium with the ambient, such an isothermal reaction may also be considered to provide a chemical exergy input. Values of $-\Delta G_T$ can be calculated from $-\Delta G_{To}$ and heat capacity data or, alternatively, from experimentally-obtained equilibrium constants.

The second law efficiency of a chemical process can be simply expressed as:

$$\eta = (\text{work output})/(\text{work input}) \tag{10}$$

The work terms may be actual work (such as mechanical or electrical work), or potential work such as thermal exergy, ΔEx_T , pressure exergy, ΔEx_P, and chemical exergy, ΔEx_{ch}

Assuming that the work input for a chemical process is chemical exergy, the second law efficiency can be expressed in terms of exergy as:

$$\eta = \eta_e = (W + \Delta Ex_T + \Delta Ex_P)/(\Delta Ex_{ch}) \tag{11}$$

where the second law efficiency, η, is now called exergetic efficiency, η_e. Further discussion of exergy components and efficiencies can be found in [34].

Our objective here is not to do a detailed exergy analysis, nor to calculate exergy efficiencies. Rather, we want to explore directional changes in exergetic efficiencies as a result of directional changes in temperature and pressure. We will consider isothermal exothermic, isothermal endothermic, and isobaric reactions that change in volume.

4.1. Reversible exothermic processes

First we consider an exothermic chemical reaction in which the reactants and products enter and leave the plant at the ambient temperature, T_o and at the ambient pressure, P_o. In principle, this could be a fuel being oxidized reversibly in a fuel cell at T_o and P_o. Here, the chemical exergy input, $-\Delta G_{\mathrm{To,Po}}$, is recovered directly as an electrical work output. The work obtainable from such a reversible fuel cell is $-\Delta G_{\mathrm{To,Po}}$, and, in accordance with Eq. (11), the exergetic efficiency is 100%

It is important to note that, when an “exothermic” reaction is carried out reversibly, as in a fuel cell, the direction of heat transfer is not necessarily out from the system;

Take for example, a reversible fuel cell operating with carbon at constant ambient temperature and pressure, 298 °K, and 1 atm:

$$C + O_2 \rightarrow CO_2 \tag{12}$$

Heat must be added to the system to maintain a constant temperature of 298 °K. Thus, the “exothermic” oxidation of carbon is in fact, endothermic, when carried out reversibly.

On the other hand, for a reversible fuel cell operating at 298 °K with hydrogen,

$$H_2 + {}^1/{}_2O_2 \rightarrow H_2O \tag{13}$$

heat must be removed to maintain a constant temperature of 298 °K; i.e., it is exothermic.

Thus, when applied to reversible chemical reactions, the characterizations “exothermic” and “endothermic” must be used with care.

It is also important to note that the heat transferred in to, or out of, these reversible fuel cells is only a small fraction of the reversible work output, or of what we normally consider to be the “heat of reaction.” Also, since the heat transferred is at the ambient temperature, it has no Second Law value (i.e. zero thermal exergy) and, thus, has no effect on the work output.

To increase the reaction rate, it is often necessary to increase the temperature of the reaction. Thus, it is interesting to explore how increasing the reaction temperature, above T_o, affects the maximum work output of reversible and irreversible exothermic reactions.

For an exothermic reaction, the magnitude of $-\Delta G_{\mathrm{T,Po}}$ decreases as the reaction temperature, T, increases, resulting in a decrease in the extent of reaction. (Accordingly, the Le Chatelier Principle, which concerns itself only with extent of reaction, does not recommend an increased reaction temperature for exothermic reactions.) Indeed, as the reaction temperature is further increased we arrive at an “equilibrium” temperature, T_{eq}, where $-\Delta G_{\mathrm{Teq,Po}}$ becomes zero and where, therefore, the extent of reaction is also zero. Similarly, the reversible work obtainable, which is equal to $-\Delta G_{\mathrm{T,Po}}$, also continues to decrease with increasing reaction temperature till it becomes zero when the equilibrium temperature is reached.

Thus, unless it is necessary to increase the rate of reaction, it is best to operate a reversible exothermic process at the ambient temperature, T_o.

4.2. Irreversible exothermic processes

The ordinary combustion process (generally operated at ambient pressure) is an irreversible exothermic process. It does not produce work directly, but rather produces heat from which we hope to generate work. Thus, the exergetic efficiency, Eq. (11), reduces to:

$$\eta_e = (\Delta Ex_T)/(\Delta Ec_{ch}) \tag{14}$$

The maximum work that could be generated from such an irreversible oxidation process, is the work potential of the heat at the reaction temperature, T, relative to the ambient temperature, T_o, i.e., its thermal exergy, which is:

$$W_{max} = Q(T-To)/T = \Delta E\mathrm{x}_T \tag{15}$$

where Q is quantity of heat.

Note, from Eq. (15), that when an irreversible exothermic reaction is carried out at T_o, the maximum second law efficiency is zero. This is the exact opposite of the result for a reversible exothermic reaction, where T_o was the optimal reaction temperature.

Clearly, for the heat of reaction to have a positive thermal exergy, the reaction temperature, T, must be greater than T_o.

One might be tempted to conclude that the exergetic value of the heat of reaction would increase indefinitely as the combustion temperature increased; but this is not the case. As we have seen above, the extent of an exothermic reaction decreases as the temperature increases: eventually becoming zero at T_{eq}. At this equilibrium temperature, Q in Eq. (15) will be zero and, there will be no thermal exergy output. Thus, there must be a reaction temperature, greater than T_o, but less than T_{eq}, where the work effect is optimal and; therefore, where the exergy losses are minimal.

Thus, once again, we come to the conclusion that there is an optimum operating temperature, where the exergy losses for an actual chemical process are minimal.

4.3. Endothermic processes

An endothermic reaction can be considered to be an exothermic reaction that is run in the opposite direction. Hence, we can refer to the preceding discussion of exothermic reactions to gain insight into the optimal operation of endothermic reactions.

The endothermic reaction needs an exergy input for it to proceed. That exergy input could be an electrical work input to a reversible fuel cell running backwards as a reversible “electrolysis cell,” or the thermal exergy input used in a traditional endothermic process.

The extent of reaction of endothermic reactions increases as the temperature increases. Therefore, it would be advantageous to increase the reaction temperature. However, the reversible endothermic process can also operate quite well at the ambient temperature, T_o.

For the irreversible endothermic process, where heat is used as the exergy input, and chemical exergy is the work output, the exergetic efficiency is:

$$\eta_e = (\Delta Ex_{ch})/(\Delta Ex_T) \tag{16}$$

It is clear from Eq. (16) that operation at the ambient temperature, T_o, is not possible. The driving force for this process, the denominator in Eq. (16), is thermal exergy, not heat; and there is no thermal exergy in heat at T_o. However, if the reaction temperature is increased too much, the exergetic driving force of the heat added will be excessive.

Thus, for irreversible endothermic reactions, as was the case for irreversible exothermic reactions, the optimal operating temperature must be greater than T_o. Also, as before, we must conclude that there is a finite operating temperature at which exergy losses will be minimal.

4.4. Processes with volumetric changes

Now we want to consider, for chemical reactions whose volume changes, the effect of changing the pressure from the ambient, P_o, to a different pressure, P.

Significant volume changes can occur (for gas-phase reactions operating at constant temperature and pressure) when there is a difference between the number of moles of products, n_p, and the number of moles of reactants, n_r. The volume increases when $n_p > n_r$, and decreases when $n_p < n_r$.

Conceptually, the reactants and products of a reaction occurring at P_o, T_o, can each be reversibly and isothermally compressed, or expanded, between P_o, and a new reaction pressure, P. Assuming that the gases are ideal, and that the reaction is carried out at T_o, the difference between the work effects on the products and reactants is:

$$\Delta Ex_p = (n_p - n_r)RT_o \ln\frac{P}{P_o} \tag{17}$$

Note, from Eq. (17), that when $n_p = n_r$ (i.e, there is no volumetric change) the net work effect is zero. In exergy terms, this means that, regardless of the reaction pressure, P, the pressure exergy of the products is equal to the pressure exergy of the reactants. This result is in accordance with the well-known fact that pressure changes do not affect the thermodynamics of a constant volume reaction.

When $n_p > n_r$ (a volumetric increase), Eq. (17) shows that the net work-effect is positive when $P > Po$. The pressure exergy of the products exceeds the pressure exergy of the reactants. Thus, isothermal reactions that increase in volume are more thermodynamically efficient when run at higher pressures. Note that this is contrary to the Le Chatelier principle that recommends a decrease in pressure for reactions that increase in volume.

When $n_p < n_r$ (a volumetric decrease), Eq. (17) shows that the net work-effect is positive only when $P < Po$. Here, again, the pressure exergy of the products exceeds the pressure exergy of the reactants. Thus, isothermal reactions that decrease in volume are more thermodynamically efficient when run under vacuum. This, too, is opposite to the Le Chatelier recommendation.

The above conclusions are based on the theoretical exergetic impact of directional changes in operating pressures. In practice, however, since gas compressors and expanders must operate with exergy losses, we understand that there are limits to the actual thermodynamic improvements resulting from directional changes in operating pressures. These limits determine the thermodynamically optimum operating pressures for chemical processes operating with volumetric changes.

4.5. Exergy analysis results

The preceding discussion of chemical reactions from an exergetic efficiency viewpoint led to some interesting conclusions.

The intuitive characterizations of chemical reactions as “exothermic” and “endothermic” may not apply to reactions that are carried out reversibly. Also, apart from rate considerations, thermodynamically reversible isothermal chemical reactions (exothermic or endothermic) can be carried out efficiently at the ambient temperature, T_o.

On the other hand, irreversible exothermic and endothermic reactions must not be carried out at T_o, where, exothermic reactions have zero exergetic efficiency, and endothermic reactions have zero yield. For these irreversible isothermal reactions, there is an optimal finite operating temperature, $T_{opt} > T_o$, where exergy losses are minimal.

We also found that, from a theoretical viewpoint; reactions that increase in volume are more efficient when carried out at pressures higher than ambient, $P > P_o$; while reactions that decrease in volume are more efficient when carried out under vacuum, $P < P_o$. These conclusions, based on the increase of exergetic efficiencies, are opposite to those recommended by the Le Chatelier principle (whose aim is to increase the extent of reaction).

Many results of exergy analyses of chemical plants and their components and subprocesses have been published. These demonstrate [35] that 65–90% of the exergy losses are due to the thermodynamic irreversibility of chemical reactions, and only 10–20% of the exergy losses arise in the separation stages. To reduce exergy losses, it is thus generally more important to reduce the thermodynamic irreversibility of chemical reactions.

It was mentioned previously that it is possible to reduce exergy losses if the reactions are not run to completion. Such designs, however, require an exergy expenditure to separate and recycle the reagents; however, an optimal conversion, which corresponds to the minimal exergetic losses per unit of useful reaction product, must exist for every process [26]. Some examples are given in Section 6.

It is noteworthy that other methods of Second Law analysis of processes were developed considerably earlier than the exergy method, e.g., the rather useful “entropy method” [36].

5. Some information on the industrial processes discussed in this paper

Most of the examples in this Section show how the preceding methods can be used to find ways for reducing energy consumption in different stages of modern plants that produce ammonia from natural gas. The main process stages are shown schematically in Fig. 14. The natural gas under pressure up to 4 MPa is fed together with steam to the primary reformer, see Figs.14 and 27a. This apparatus has many tubes filled with catalysts. The endothermic reaction of methane with steam (Eq. (18)) operates in the tubes at temperatures up to 800 °C.

$$CH_4 + H_2O = CO + 3H_2 - 206.4 \quad kJ \tag{18}$$

To provide heat for the reaction and achieve this high temperature, natural gas is combusted in the intertube space of the primary reformer. Heat from the hot flue gas exiting the primary reformer is then recovered for other uses in unit 9. The gas leaving the primary reformer contains H_2, CO, CO_2, unreacted CH_4, H_2O and other impurities.

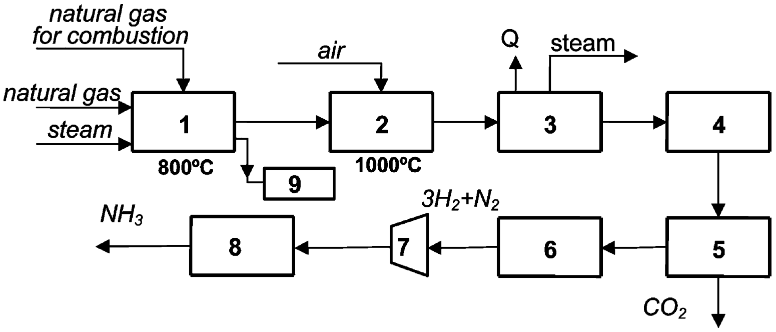


Fig. 14. The simplified flow sheet of conventional process of ammonia production.*1 The primary reforming (reaction 18), 2 The secondary reforming (reaction 19), 3 The reboiler for utilization of heat, 4 The CO conversion (reaction 20), 5 The CO_2 removal from synthesis gas (*Fig. 15*), 6 The fine synthesis gas purification from admixtures, 7 The compression, 8 The ammonia synthesis (reaction 21).*

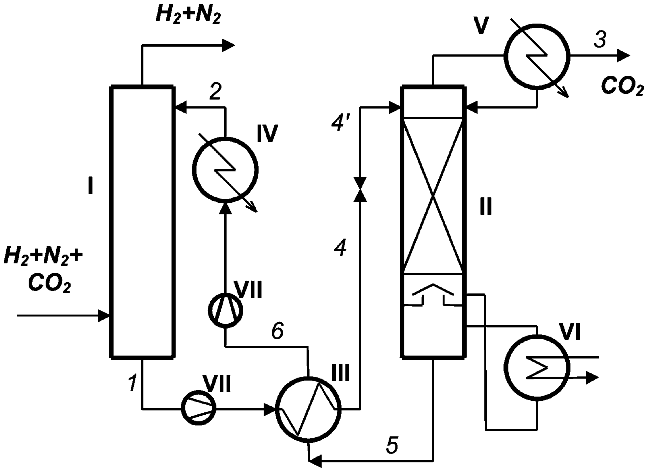


Fig. 15. Process flow diagram for CO2 recovery from gas by monoethanolamine (MEA) solutions. *I—absorber, II—regenerator, III—heat exchanger, IV—cooler of solution, V—cooler (condenser) for steam-gas mixture, VI—reboiler, VII—pumps*

The second unit in Fig. 14 is a secondary exothermic catalytic conversion of unreacted methane with air (Eq. (19)), operating at about 1000 °C.

$$CH_4 + 0.5O_2 = CO + 2H_2 + 35.6\ \text{kJ/mole} \tag{19}$$

The heat of conversion in the secondary reformer gas is used to produce high-pressure steam in unit 3. The 4th unit in Fig. 14 is the CO conversion (water-gas shift reaction) with steam:

$$CO + H_2O = CO_2 + H_2 + 41.0\ \text{kJ} \tag{20}$$

In modern practice, this CO conversion is usually accomplished in two stages (see Fig. 21).

The converted gas, which contains H_2, N_2, CO_2 and some impurities, then enters unit 5, Fig. 14, for CO_2 removal by absorption with a liquid absorbent (see Fig. 15). This is followed by unit

6 to remove impurities such as water vapor and trace quantities of carbon oxides; resulting in synthesis gas ($3H_2$+N_2). The synthesis gas is then compressed to about 30 MPa, and fed to the final unit (8 in Fig. 14) where ammonia is synthesized according to reaction (21):

$$N_2 + 3H_2 = 2NH_3 + 57\ \text{kJ/mole } NH_3 \tag{21}$$

6. Thermodynamic optimization of process conditions for chemical reactions based on the exergy concept and the counteraction principle

As discussed above, there are thermodynamically optimal reaction conditions for each chemically reversible reaction, which correspond to the minimal expenditure of exergy per unit of useful reaction product [26]. Thus, the best criterion for process optimization can be the maximal exergy efficiency (Eqs. (16) and (17)), or the minimal specific exergy expenditure per unit of useful products as follows:

$$\Delta ex_S = \frac{\Delta Ex}{Q_{PR}} \tag{22}$$

where Q_{PR}=the quantity of useful reaction products.

6.1. Methane reforming

It is seen that methane reforming (Eq. (18)) proceeds with an increase in volume. We can therefore expect that an increase in pressure will decrease the yield of CO and H_2, but, in accord with the counteraction principle, we also expect a reduced exergy expenditure. This leads to the existence of an optimal “counteracting” operating pressure that results in a minimal specific exergy expenditure.

Calculations were made assuming that:

- Equilibrium reaction conditions are reached at the exit of the converter
- The second stage of the process, i.e. conversion with air, is run with an O_2:CH_4 ratio of 0.6.
- The preheated natural gas enters at 450°C, and the converted gas exits at 1000 °C

With the above operating conditions fixed, then the equilibrium methane concentration after the first stage is a function of the reaction pressure.

It is seen from Fig. 16, that there are optimal operating pressures corresponding to the minimal specific exergy expenditures (Eq. (22)). The value of the optimal pressure depends on the H_2O:CH_4 ratio, i.e., *steam/gas* ratio. These results are close to commercial operating conditions. Interestingly, Fig. 16 also shows that the optimal operating pressure increases as the *steam:gas* ratio decreases.

This result is to be expected. The relative effect of the volume increase, due to Eq. (18), is diluted (by unreacted reagents) when the feedstock deviates from the stoichiometric *steam/gas* ratio of 1. Thus, to decrease the specific exergy expenditure (Eq. (22)), the optimal “counteracting”

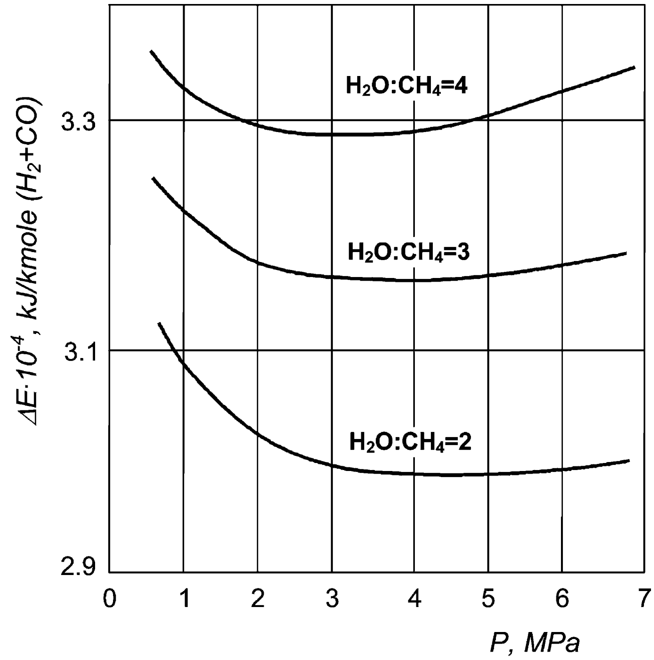


Fig. 16. Effect of pressure on specific exergy expenditure in methane reforming.

operating pressure should increase as the steam/gas ratio approaches the stoichiometric ratio, and vice versa. This is precisely the effect shown in Fig. 16.

It was said above that the exergy expenditure approaches a maximum as a chemical reaction approaches completion, in this case to 0% CH_4 in the reaction products. To reduce the specific exergy expenditure, the reaction should thus be run so that there will be a non-zero concentration of CH_4 in the reaction products. This is shown in Fig. 17, where equilibrium conditions at the outlet of the first stage reactor (the primary CH_4 reformer) are assumed. The calculation was made for $P = 1$ MPa, H_2O:CH_4 ratio $= 4$, and a temperature of 820 °C. It is seen that the optimal methane concentration is about 4 to 7%. The conclusion from this analysis is that it is preferable to run the methane reforming reaction, Eq. (18), under “soft” conditions, rather than to run it to completion.

This conclusion is in accord with some modern trends in ammonia production, i.e. incomplete methane conversion. Such processes require the use of new gas purification methods, such as the so-called “pressure swing adsorption,” with the associated complex separation of impurities such as methane, carbon monoxide and dioxide, water vapor, and the nitrogen in excess of the stoichiometric concentration [4].

6.2. Water-gas shift conversion

Now we analyze the water-gas shift conversion of carbon monoxide with steam (Eq. (20)). This reaction is exothermic. Raising the “counteracting” temperature would result in more efficient

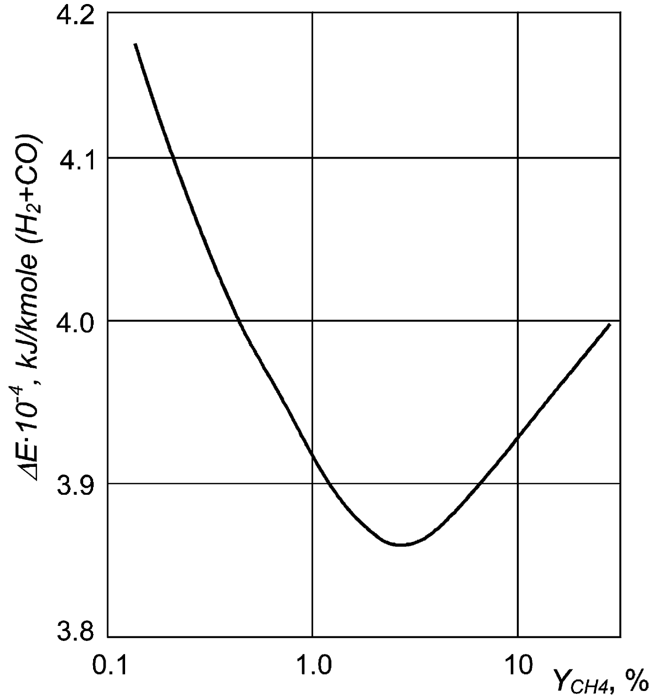


Fig. 17. Specific exergy expenditure per kmole of product H_2+CO in reaction (20) as a function of concentration of CH_4 (Y_{CH4}) in reaction products.

use of the reaction heat, but would also decrease conversion. Again, an optimal temperature thus exists, corresponding to minimal specific exergy expenditures (Eq. (22)).

Note, that, since there is no volume change in the shift reaction (Eq. (20)), we do not expect pressure to be a significant process variable with respect to exergetic efficiency.

There are, however, two additional process variables that can affect the exergetic efficiency of the water gas shift process: the CO concentration at the outlet of the reactor, and the *steam:gas* ratio, *r*, at the reactor inlet. Thus, in addition to an optimal temperature, we can also expect that there is an optimal outlet CO concentration as well as an optimal inlet *steam:gas* ratio.

Fig. 18 shows the effect of temperature on specific exergy expenditure for a series of outlet CO percentages. This figure, based on calculations assuming that the reactor outlet is at thermodynamic equilibrium, shows that the optimal temperature is lower than 400 °C. This is close to the actual temperature at the first stage of commercial shift processes.

In Fig. 18, each point on a constant % CO curve represents a different inlet *steam:gas* ratio. The effects of *steam:gas* ratio and outlet % CO are shown in Fig. 19 (where each point on a curve represents a different temperature). The optimal conditions are a *steam:gas* ratio of 0.35 and an exit CO concentration near 5%.

It was stated above, that an excess of one of the reagents results in increased exergy expenditure, but it increases conversion. It is seen from Fig. 20 (where each point on a curve represents a different exit CO concentration), that there is an optimal *steam:gas* ratio where the specific exergy

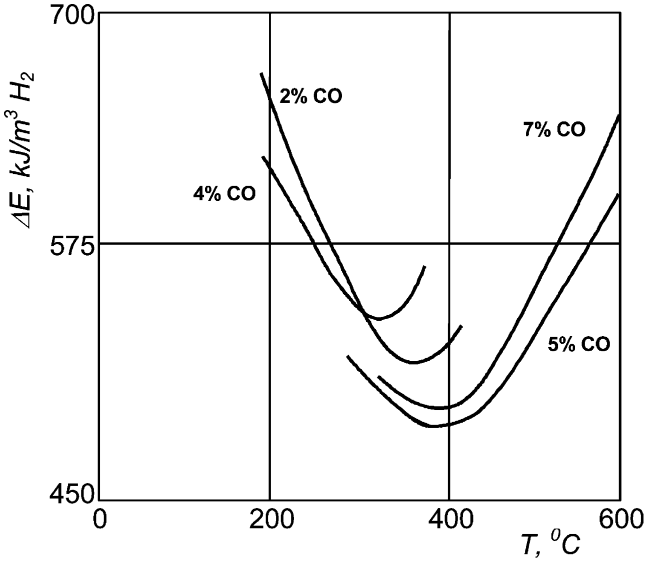


Fig. 18. Dependence of specific exergy expenditure in reaction (20) on temperature at the outlet of the reactor at different CO concentration in reaction product.

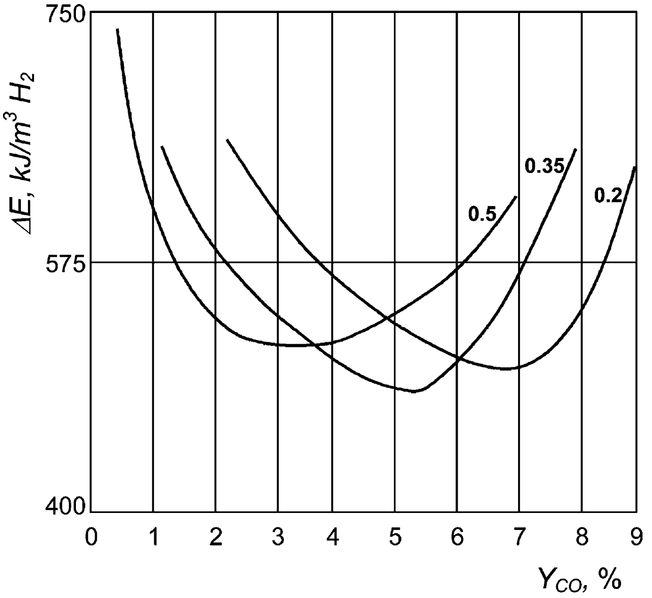


Fig. 19. Specific exergy expenditure per m^3 H_2 produced by reaction (20) as a function of Y_{CO} concentration of reacted CO in reaction products, at different steam:gas ratios (numbers on lines).

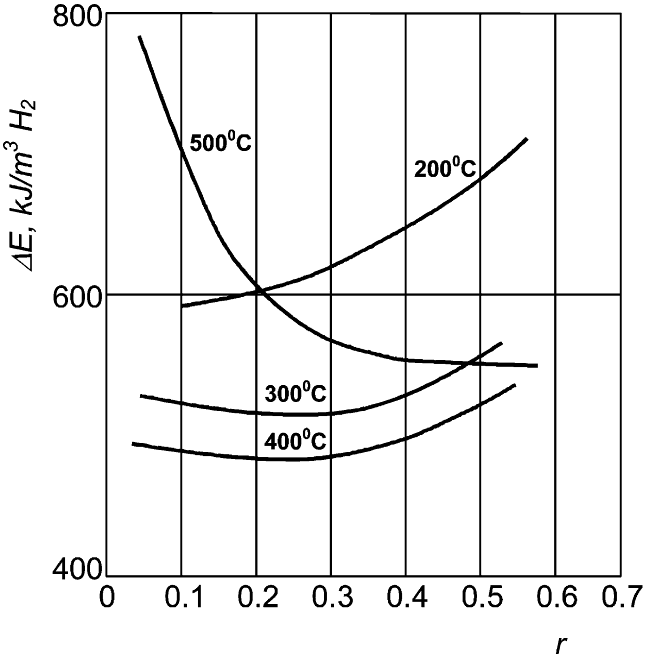


Fig. 20. Dependence of specific exergy expenditure per m^3 H_2 produced by reaction (20) on the ratio (*r*) *steam:gas* at different temperatures.

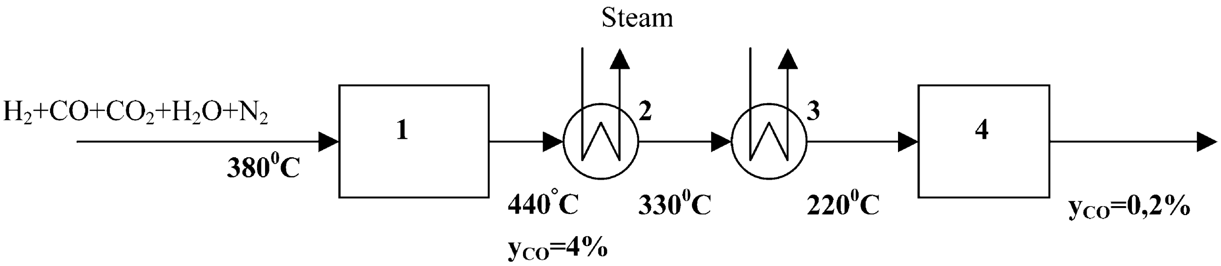


Fig. 21. Two stage CO conversion by steam (reaction 20). 1—high temperature conversion; 2, 3—utilization of heat of converted gas; 4—low temperature conversion.

expenditures are minimal. This value is near 0.25 at 300–400 °C, and is lower than generally used in practice.

Some conclusions can be drawn from these calculations about the possibility of further reduction of energy resource usage. The first conclusion is to use a conventional two-stage CO shift reactor, with a high temperature in the first stage and a reduced temperature in the second stage (Fig. 21). The high-temperature heat of reaction from the first stage is used to produce steam, or is recovered for other purposes, while increased conversion is achieved as a result of the lower temperature in the second stage.

However, the best design can be developed on the basis of the *Linde* idea of the use of a heat exchanger combined with the reactor (see Fig. 22) to integrate the reaction with the extraction of its heat of reaction. This allows a gradual decrease in the temperature of the working medium from the start to the end of the reactor. In this way it is possible to use the reaction heat with maximal efficiency within the reactor and to run the reaction to completion, as was previously suggested in Fig. 8.

6.3. Ammonia synthesis

One other commercial example of use of the reaction heat is the three-stage ammonia synthesis (see Fig. 23). In this example the exothermic synthesis, Eq. (21), is run at three different gradually reduced temperatures, while the high temperature reaction heat from the first stage is used to

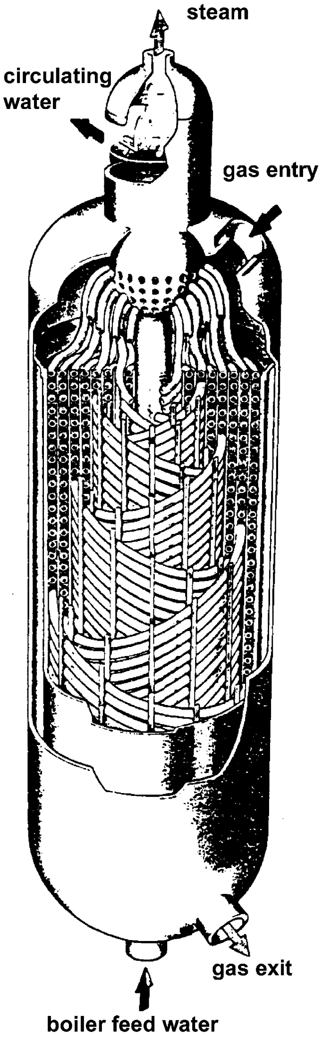


Fig. 22. Linde isothermal reactor of CO conversion by steam with removal of reaction heat from the reactor.

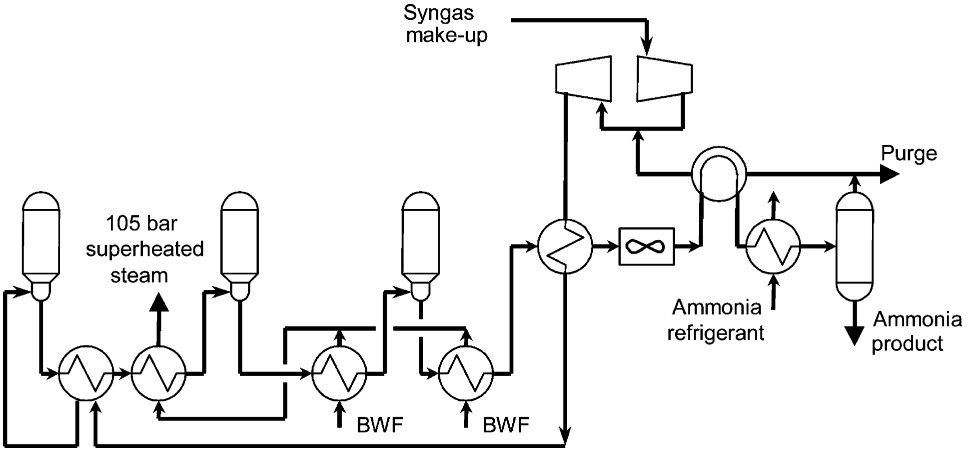


Fig. 23. Flow diagram of Braun three-reactor ammonia synthesis.

produce superheated high-pressure steam (see Fig. 23). This process has been proposed to replace the classical one-stage ammonia synthesis [3].

The ammonia synthesis reaction results in a decrease in volume, and is carried out at high pressure to achieve the increase in extent of reaction predicted by Le Chatelier's Principle. In the traditional design, the reactants are compressed prior to reaction. However, as shown in Fig. 8, a reaction that decreases in volume can be carried out more reversibly by starting at a low pressure and ending at a high pressure. Thus, in theory, the 3-stage ammonia synthesis would be more energy efficient if the initial pressure were low, and then increased, step by step, in the succeeding stages. This would reduce the overall energy of compression without compromising the extent of the reaction at the final stage. However, since compression work also increases as the temperature of a gas increases, the effective implementation of compression between stages to save energy is not such a simple matter with an exothermic reaction.

Other Second Law recommendations for use of the reaction heat can be stated briefly:

- It is better to remove the reaction heat by a medium that has minimal flow heat capacity, because the entropy increase and the consequent exergy expenditure are inversely proportional to the flow heat capacity.
- It is especially better to remove the reaction heat by constant temperature phase transformation of a working medium, or by mixed media at controlled phase transformation temperatures, because under such conditions the increase in entropy is not as high.
- It is better to remove the reaction heat directly from the reactor where the temperature is maximal and in direct contact with a required process heat sink, if possible. A good way is to evaporate part of the liquid while running liquid phase reactions. For example, liquid cyclohexane is oxidized by air in one of the steps in the industrial production of caprolactam. The heat of reaction is removed by evaporation of part of the liquid cyclohexane. This heat is then recovered, by condensing the cyclohexane vapor, to preheat other process steams. This approach is more effective than removing the reaction heat across a heat exchanger wall to a cooling medium.

7. Some examples of use of the analysis based on the “driving force method”

7.1. Methane reforming

The conventional steam/methane reforming process is shown in Fig. 27a. The primary reaction (Eq. (18)) is endothermic, and the required heat is supplied by the combustion of methane by air.

Changes in methane concentration along the primary reactor are shown in Fig. 24. It is seen that the CH_4 concentration (line 2) decreases continuously along the tube, nearly approaching the equilibrium concentration at the end. It is also seen that the equilibrium concentrations (line 1), corresponding to the real temperatures in tubes, are substantially lower than the operating concentrations except at the reactor outlet. This picture allows us to conclude that it is desirable to reduce the temperature at the start of the process by reducing the quantity of combusted gas in the inter-tube area. The extent to which the temperature can be reduced is seen from Fig. 25, where the real (line 2) and equilibrium (line 1) temperatures of this process are shown.

Different methods of reducing the driving force during steam methane reforming in tubular reactors are used in commercial practice, although the authors believe that good engineering can be applied to develop other methods. One of the realized versions is demonstrated in Fig. 26 [5]. It is a so-called Pre-Reformer. Briefly, the mixed raw materials, i.e. methane and steam are pre-heated, and the first stage of reaction is realized adiabatically without combustion of natural gas for heating. It is seen that the temperature in the early stage of reforming is lower than that in conventional primary reforming. This partial modernization of the classical process has reduced the consumption of natural gas for combustion by 5–10%.

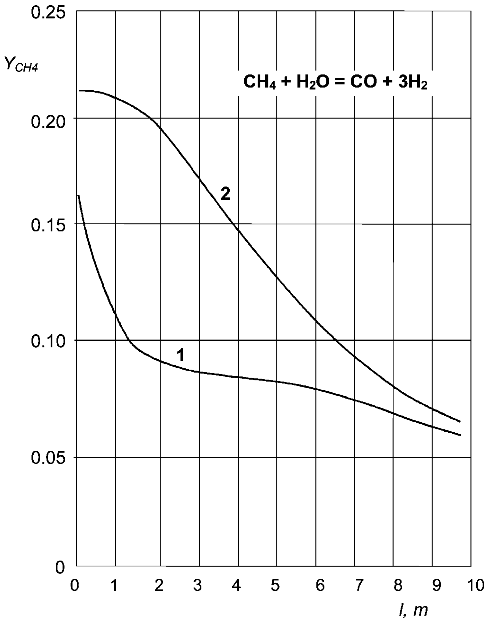


Fig. 24. The concentrations of methane in tube steam methane converter along tubes1—the equilibrium line; 2—the operating line.

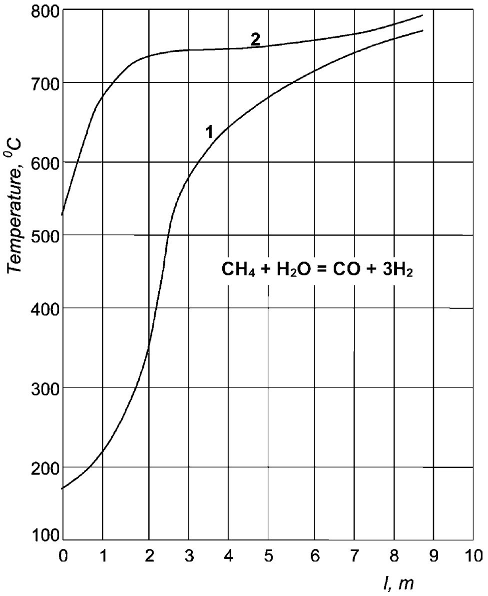


Fig. 25. The temperatures in tube steam methane reformer along tubes1—the equilibrium line; 2—the operating line.

Significantly better results have been obtained by development in Russia of the so-called “Tandem” process (Fig. 27 b), or autothermal reforming [4], and similar versions. The previous exergy analysis of the conventional process [24] of the steam catalytic conversion of methane in tubular reactors showed that the main exergy losses are the result of the thermodynamic irreversibility of methane combustion, and of the high difference between the burning gas temperature and the temperature inside the tube. There are also large losses in the utilization of the heat in the flue gas leaving the main part of the tubular furnace.

The new Tandem process (Fig. 27 b) has reduced losses. The secondary reformer operates at a higher temperature since the residual methane is oxidized with enriched air. The heat from the secondary reformer is at a high enough temperature to be used directly in the primary reformer. Thus there is no need to produce steam with its associated exergy loss, to recover heat from the secondary reformer, as is done in the conventional process (Fig.14, unit 3).

A heat balance analysis of the flow sheet for the Tandem process (Fig. 27 b) shows that ordinarily it is impossible to completely supply the primary endothermic reformer 1 with heat from the exothermic secondary reformer 2. Thus, non-conventional design decisions must be employed particularly for synthesis gas produced for ammonia synthesis, which requires a stoichiometric $(H_2+CO):N_2$ ratio of 3:1. The Tandem process, used commercially for more than a dozen years, uses two non-conventional design decisions:

1. The CH_4 concentration from the primary converter is increased, and a small quantity of O_2 is added to air in the secondary converter.
2. When used to produce synthesis gas for the synthesis of ammonia, it is necessary to use cryogenic, or pressure swing adsorption (PSA), to achieve the required $(H_2+CO):N_2$ ratio of 3:1, or to remove excess CH_4.

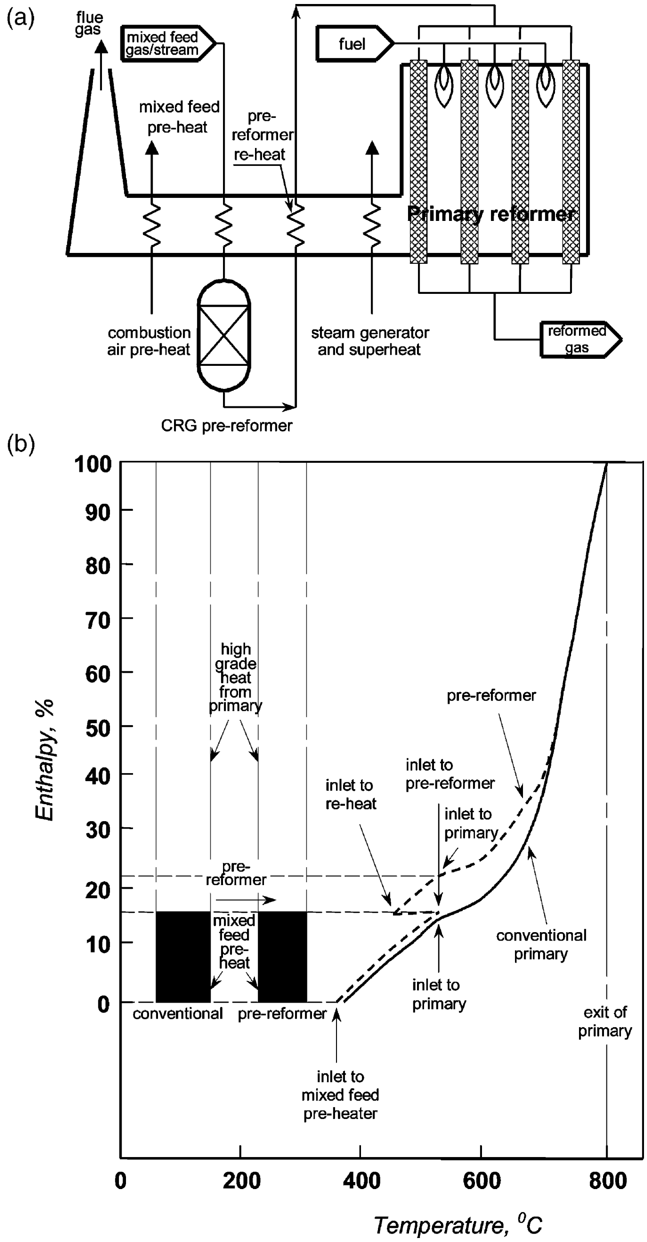


Fig. 26. Steam reforming of methane with combustion of natural gas in furnace and with(a) Pre-Reforming; (b) Basic concept of Pre-Reformer [5].

By the way, this process is an excellent example of the combination of reduced energy resources consumption, lower capital costs, and less contamination of the environment. Many calculations have shown that the major capital costs are in primary reforming. The tubes in the new Tandem Process operate with a low pressure difference across the tube wall compared with the classical

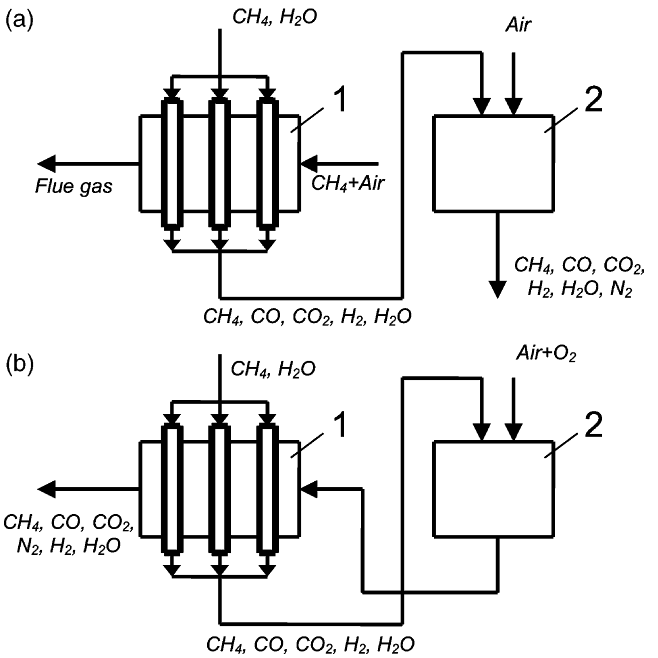


Fig. 27. The networks of steam methane reforming for ammonia production:(a) The conventional process; 1—the primary reforming with combustion of natural gas, 2—the secondary reforming(b) The Tandem process; 1—the primary reforming, 2—the secondary reforming.

version (Fig. 27a), and their cost is low. This new process uses much less fuel and, as a result, operates with reduced contamination of the environment by nitrogen oxides, carbon dioxide, and so on.

7.2. Removal of CO_2 from synthesis gas

The driving force method has been used with success to reduce heat consumption in the removal of carbon dioxide from synthesis gas by absorption with aqueous monoethanolamine (MEA) solution [25,26,32,33,37].

The flow sheet of the conventional version of the CO_2 removal process is shown in Fig. 15. CO_2 is removed from the synthesis gas by solutions of MEA in water. The gas mixture to be purified enters the bottom of absorber *I*. The MEA is regenerated by using heat in regenerator *II* to strip the CO_2 out. The cooled regenerated MEA solution enters the top of the absorber. The saturated MEA absorbent removed from the absorber bottom is preheated in heat exchanger *III* by the regenerated MEA absorbent leaving the bottom of desorber *II*.

Analysis of the equilibrium and operating lines of a chemidesorption unit (see Fig. 12) shows that equilibrium can be reached at only one point of a chemidesorber of conventional design (with a single feed of spent absorbent entering the top, Fig. 15), even if it were of infinite height. Thus, the driving force at other points in the desorber can never approach zero, resulting in excessive expenditure of exergy.

The same is especially true for CO_2 absorption by MEA (Fig. 13), where the great irreversibility (excessive driving force) is in the middle and bottom parts of the column.

These conclusions as well as the results of quasi-static analysis generated the ideas that led to the revision of the flow sheets for MEA gas purification, which were incorporated in many large ammonia plants in Russia. The first version (Fig. 28) is the flow sheet [33,37] with three streams of rich solution entering regenerator *II*, and the use of two streams of regenerated absorbent entering absorber *I*. The equilibrium and operating lines of such a multiflow desorption process are shown in Fig. 29.

A second revised flow sheet fully integrates the stripping process and heat transfer (Fig. 30)

At first glance the designs shown in Figs. 28 and 30 are different. But the main idea is the same, i.e., to approach the theoretical limit of adding and removing all streams of energy and substances along the entire height of the columns.

The commercial result of this analysis was that the heat consumption at more than 20 new plants (without substitution of absorbent) was reduced to 1/2 or 1/3 of the heat used in the conventional process.

Calculations show that similar designs can be used for the modification of MDEA (methyldiethanolamine) gas purification plants, which would then operate with as little as one half the heat consumption of the best commercial plants.

It seems that these examples confirm the fruitfulness of this analysis for the reduction of energy consumption.

Similar deductions can be made from the quasi-static analysis (see below).

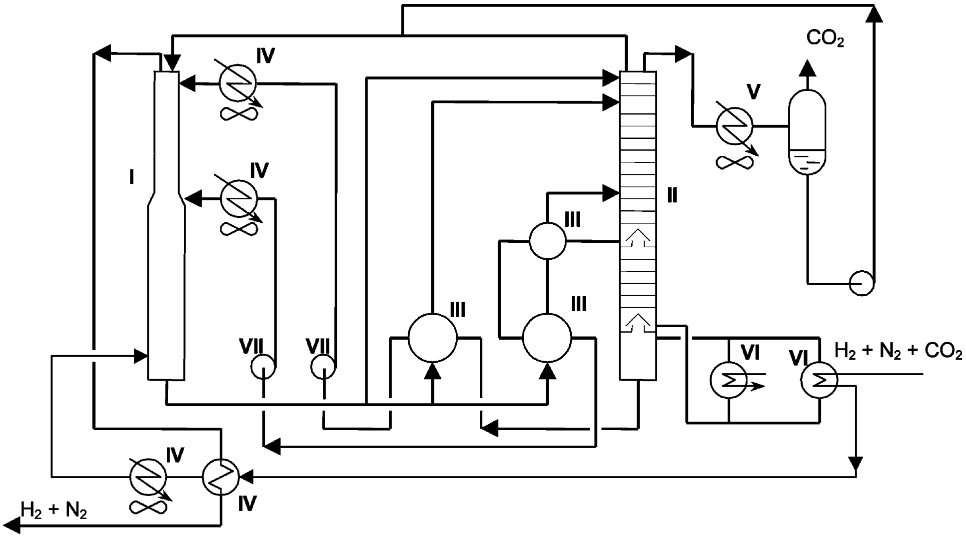


Fig. 28. Process flow diagram for purification of gas from CO_2 with MEA solution in 1500 MTPD ammonia plant with three flows of saturated solution and two flows of regenerated solutions [33].*I —absorber, II—regenerator, III—heat exchanger, IV—cooler, V—cooler (condenser) for steam-gas mixture, VI—reboiler, VII—pumps*

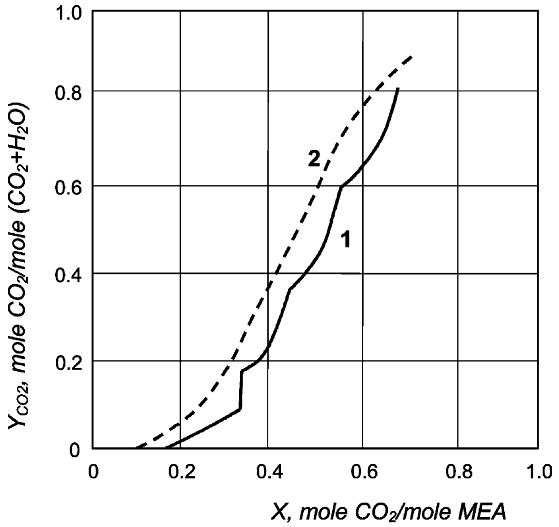


Fig. 29. The equilibrium (1) and operating (2) lines of multiflow CO_2 desorption from MEA solution (one version).

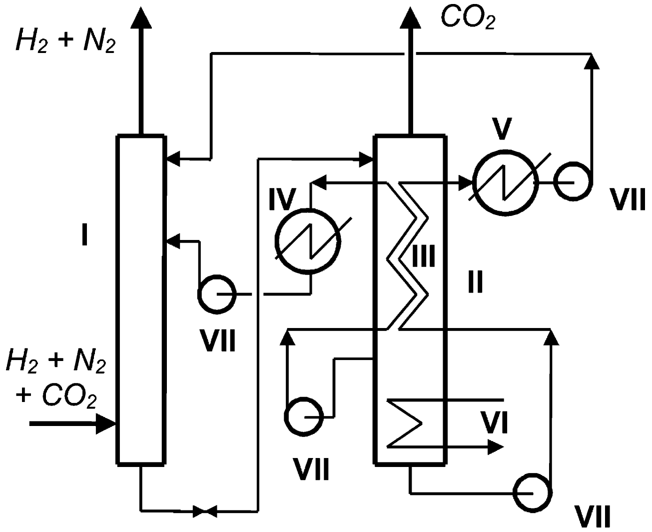


Fig. 30. Process flow diagram for purification of gas from CO_2 with MEA solution in 1500 MTPD ammonia plant with integration of solution regeneration and heat recuperation [37].*I—absorber, II—regenerator, III—heat exchanger, IV—cooler of solution, V—cooler (condenser) for steam-gas mixture, VI—reboiler, VII—pumps*

8. Some examples of use of the quasi-static method

The analysis of the theoretical quasi-static version of industrial processes [32,38] can give very important guidance for:

- calculating the best, i.e. limiting energy characteristics of a process;

- determining the technological conditions of such a process;
- understanding which methods can be used to improve the commercial process;
- calculating the optimal operating conditions for a given processes flow sheet.

8.1. Chemisorption of CO_2

To start, let us analyze a typical example of a countercurrent heterogeneous exothermic reaction: chemisorption of CO_2 by an aqueous MEA solution in a conventional absorber with a standard flow sheet (Fig. 15). When operated without heat removal or supply to the absorber, the temperature of the absorbent (see Fig. 31, line 1) increases from the top to the bottom of the absorber due to the heat of reaction. However, if we could run the absorption (see Fig. 31, line 2) along the equilibrium line, that is, in a quasi-static way with zero driving force, the temperature change is just the opposite. The temperature of the quasi-static process is considerably higher than the real temperature and must decrease, not increase, from the top to the bottom of the absorber. This insight led to a revised flow sheet for CO_2 removal by MEA, with high temperature absorption at the top part of the absorber, removal of hot absorbent from the middle part of the column, recovery of part of the heat of absorption, and then reinjection of the absorbent at a lower temperature into the absorber.

8.2. Desorption of CO_2

Additional unexpected and fruitful results were obtained from the quasi-static analysis of the desorption of CO_2 and H_2S from various chemisorbents such as MEA, DEA (diethanolamine),

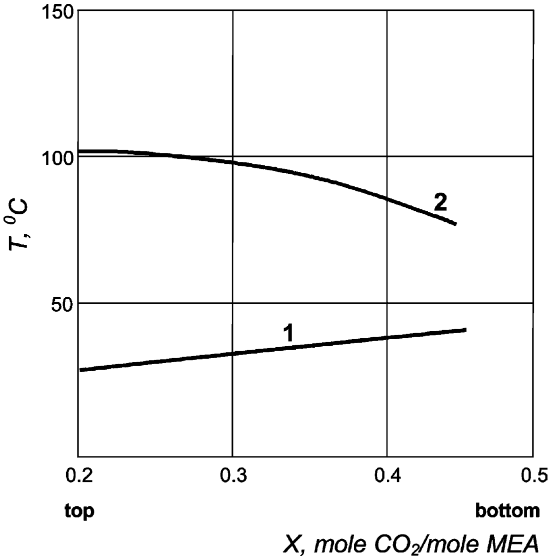


Fig. 31. Change in temperature of absorbent during CO_2 absorption by MEA solution from the top to the bottom of absorber as a function of absorbent saturation.1—the real process, 2—the quasi-static process.

nonaqueous MEA solutions and so on. The method of calculation and the results, with detailed mathematical analysis, are described in the author's papers and book [32,33,38].

We now discuss the most important results: the calculation of the minimal specific quantity of heat (per mole or cubic meter of CO_2) that is necessary to generate stripping vapor in each section of the desorber, assuming of course, that there is equilibrium in each section (Fig. 32). The main calculation equation is very simple:

$$q_{\mathrm{str,i}} = \frac{Q_{\mathrm{str,i}}}{G_{\mathrm{CO_2,total}}} = r\frac{G_{\mathrm{CO_2,i}}\ P^*_{\mathrm{abs(P,x),i}}}{G_{\mathrm{CO_2,total}}P^*_{\mathrm{CO_2(P,x),i}}} = r\frac{(x_i - x_2)\ P^*_{\mathrm{abs(P,x),i}}}{(x_1 - x_2)P^*_{\mathrm{CO_2(P,x),i}}} \qquad (23)$$

The quantity, $q_{str,i}$ is proportional to the product of the CO_2 fraction desorbed in the part of the desorber that is lower then this *i*-section, and the ratio of the equilibrium pressure of absorbent (water is often the diluent for MEA) to the equilibrium CO_2 pressure. The symbol, *r*, is the latent heat of vaporization of water.

Let us analyze in detail the curves shown in Fig. 34. The feed to the top of the desorber has a CO_2 concentration of 0.4 mole CO2/mole MEA. Each curve is for a different concentration of regenerated absorbent leaving the bottom of the desorber. The curves show the minimal quantity of heat needed to generate the stripping steam required at each *i*-section of the desorber, to operate at an infinitesimal rate, from a given $x_{i,CO2}$ concentration in the *i*-section down to the final CO_2 concentration in the regenerated absorbent. It is seen that for regeneration to a bottom CO_2 concentration greater than 0.25, the largest heat requirement (about 3200 kJ) must be supplied at the top of the desorber. Therefore, in this case the process calculation can be developed based on the assumption that equilibrium at the top of the desorber can be achieved as a limit, in an infinitely high desorber.

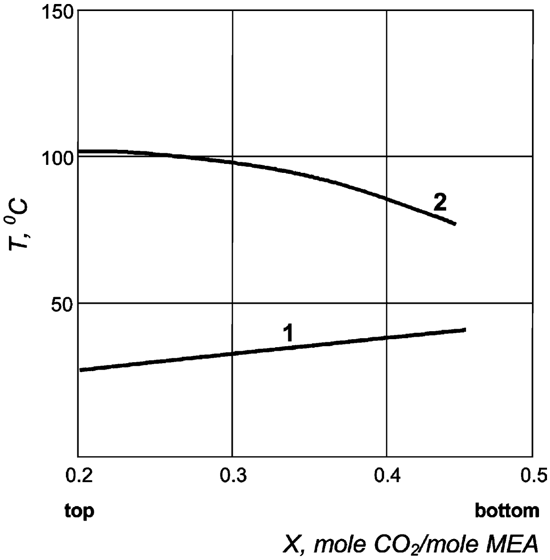


Fig. 32. Specific heat consumption $q_{str,\,i}$ (Eq. (23)) for production of stripping steam during regeneration of 15% MEA solution. Abscissa is current CO_2 concentration along the height of the apparatus. Numbers on the curves are CO_2 concentrations in regenerated solution (pressure of regeneration 0.18 MPa).

However, as is seen from Fig. 34**,** the attempt to further reduce the bottom CO_2 concentration, results in a striking increase in the minimum heat requirement: to 16,000 kJ for a bottom CO_2 concentration of 0.05 mole CO2/ mole MEA.

It is to be expected that the amount of stripping vapor increases as the bottom CO_2 concentration decreases: approaching infinity as the bottom CO_2 concentration approaches zero. However, the nature of the curves in Fig. 34 reflect the peculiarity of the vapor-liquid equilibrium for aqueous MEA solutions, whose equilibrium partial pressure, P^*_{CO2}, decreases rapidly.

This analysis allowed, as a result (see the details in [33]), calculation of the optimal conditions for MEA regeneration, and a reduction in the heat consumption at operating commercial units. Also, this analysis led to new ideas for changes in the flow sheet that were additional to those obtained from the previous driving-force analysis.

The dependence of the minimal reflux ratio, P_{H2O}/P_{CO2}, on the CO_2 concentration in a regenerated aqueous MEA absorbent was calculated, and is shown in Fig. 33. The minimum reflux ratio is constant for high CO_2 concentration in the lean solution, but increases rapidly for CO_2 concentrations below about 0.17. Correspondingly, the minimal heating requirements to regenerate lean solution would also increase rapidly as the CO_2 concentration decreased below this level. It is important to point out that these results were obtained for a desorber where thermodynamic equilibrium is achieved (one with infinite height and ideal mass transfer rates). Thus, these results are reflections of the inherent thermodynamic properties of the CO2/aqueous MEA system, and are not characteristics of an actual desorption apparatus (number and efficiency of plates, or volume and efficiency of packing). These results, originally published in Russian in 1968 [32]

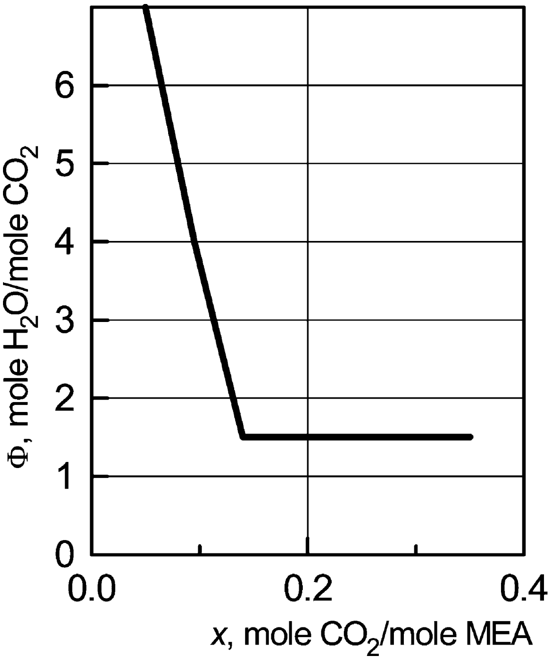


Fig. 33. The dependence of reflux ratio ϕ on the x concentrations of CO_2 in regenerated aqueous 15% MEA solution under pressure 0.18 MPa at quasi-static stripping.

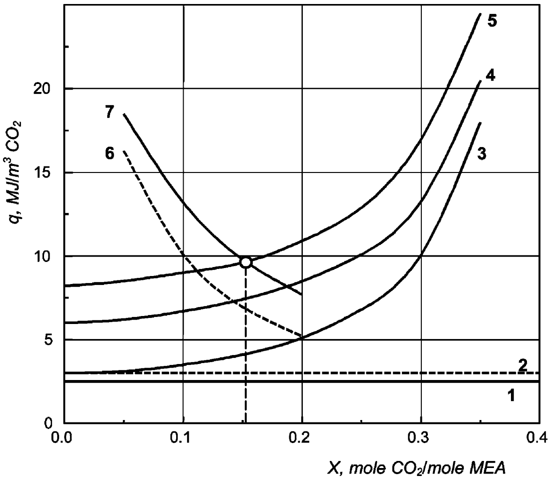


Fig. 34. Dependence of the minimal heat consumption *q* for MEA purification of gas from CO_2 on the x-concentration of the CO_2 in regenerated solution at P_{str}=0.18 MPa, *t*=15 °C. The CO2 concentration in the rich absorbent is 0.4 mole CO_2/mole MEA.1—□*H* —heat of absorption; 2—q_{str} under equilibrium conditions at the top of stripper; 3—heat for heating of absorbent; 4—1+3; 5—1+2+3—complete heat consumption; 6—q in “critical section”; 7—complete heat consumption if it is limited by equilibrium in the “critical section”.

explain why it is difficult to regenerate MEA solutions to very low CO_2 concentrations. The same analysis was also applied to other similar processes that desorb H_2S and CO_2 from various absorbents. The results of the calculation confirming the existence of the optimal desorption conditions corresponding to the minimal specific heat consumption are shown at Fig. 34. A more detailed explanation of the reasons for this minimum is given below.

It is known that for the simple flow sheet (Fig. 15) the heat consumption can be calculated approximately as follows:

$$Q = G_{\mathrm{CO_2}}\Delta H + Lc\Delta t_{\mathrm{h}} + G_{\mathrm{CO_2}} r \frac{P_{\mathrm{H_2O}}}{P_{\mathrm{CO_2}}} \tag{24}$$

where $\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{CO_2}}} = \Phi$Then, because $G_{CO2}=L\cdot\Delta x$, $\Delta x=x_1-x_2$, the specific heat consumption (per 1 m^3 of CO_2):

$$q = \Delta H + \frac{c\Delta t_{\mathrm{h}}}{\Delta x} + r\Phi \tag{25}$$

The first part of Eqs. (24) and (25) is the thermodynamic heat for gas desorption (approximately equal to its heat of absorption). The second part is for heating the liquid absorbent further, following the recovery of available process heat. The lower the CO_2 concentration, x_2, in the lean solution, the larger is the absorptivity of the absorbent, ΔX, and the lower is the specific heat required to heat the absorbent (Eq. (25)). But, the third part of Eqs. (24) and (25) is the heat of desorption of water from the critical section of the desorber, which, as is seen from Fig. 34 (line 6), increases when the CO_2 concentration in the lean solution is reduced. This is the physical background, leading to the existence of a thermodynamically based optimal gas concentration in the lean solution, that results in a minimal heat consumption for the conventional flow sheet (Fig. 15)

This result was confirmed many times at operating plants, and, by stripping only down to the optimal CO_2 concentration, led to a reduction in heat consumption.

However, when fine gas purification is needed, it may be necessary to strip to a lower than optimal CO_2 concentration. Using the conventional flow sheet (Fig. 15), this would require an increase in heat consumption. However, this increase in heat consumption can be avoided by revising the flow sheet to use two streams of lean absorbent, each of different CO_2 concentration (Figs. 28 and 30). This allows an increase in the absorptivity of the solution and achieves the fine gas purification without increasing the reflux ratio.

It seems that this method of analysis can be used more extensively than it is used now.

9. Conclusions

We have shown here that appropriate use of Second Law concepts can help one understand how to reduce energy consumption in the chemical industry

The main concepts used in this paper are generalized in the chart of Fig. 35. It is seen that the

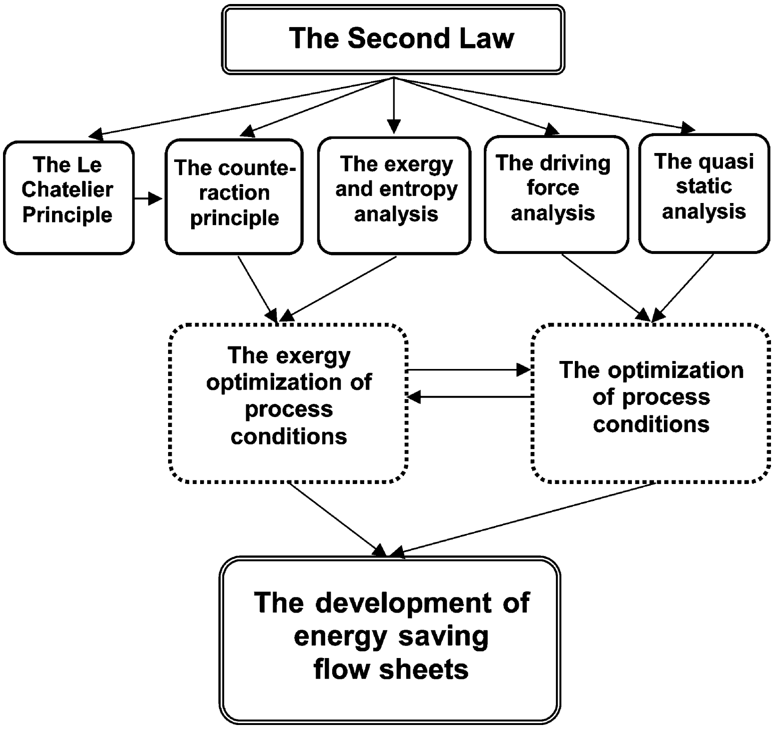


Fig. 35. Some consequences of the Second Law and methods of analysis based on them.

"driving force analysis" and the "quasi-static analysis" are consequences of the Second Law, but are not connected with exergy analysis.

The "counteraction principle", also a consequence of the Second Law, was used with exergy analysis and Le Chatelier's principle, to optimize energy usage. At the exergetic optimum for a given flow sheet, the optimum extent of reaction, excess reagent concentrations, temperature, and pressure, are fixed. However, after finding these optimum conditions, the designer should not be complacent but, rather, should try to create a new flow sheet that further reduces excessive driving forces, to arrive at an improved exergetic optimum.

Finally, a summary of the definitions of the methods proposed here are given below:

9.1. The "Counteraction principle"

The *counteraction principle* is the Second Law requirement that: to make maximal use of the Gibbs energy of chemical reactions and similar processes, i.e., to minimize exergy expenditures, it is necessary to retard the reactions, i.e., to conduct them under conditions that are COUNTER to the conditions favorable to increasing the species conversion.

9.2. The "Driving force method"

The *driving force method* consists of the analysis of driving forces of a process at all points in a chemical process apparatus, and the development of the engineering methods to change process conditions and flow sheets in order to reduce the driving force and, consequently, to reduce thermodynamic irreversibility.

9.3. The "Quasi-static method

The *quasi-static method* consists of the examination of the process conditions of a theoretical limiting quasi-static process that could be run with zero driving force along the equilibrium line, followed by comparison of such a fictitious but conceivable process with a real one, to discover engineering techniques that allow a real process to approach this quasi-static one.

Brief recommendations that are reflections of this paper, and were published in similar form previously [27], are listed below.

10. 12 Second Law of Thermodynamics commandments for reducing energy consumption

1. The driving force of a process must approach zero at all points in a reactor, at all times. Try to change the driving force to a uniform one.
2. Wherever possible, retard a process at the start, then gradually remove the retarding function.
3. If the reaction is exothermic it is necessary to raise (not to lower!) the temperature. If the reaction is endothermic, it is necessary to lower (not to raise!) the temperature. It is better to conduct the exothermic processes in a low flow-heat-capacity medium. It is better to remove reaction heat by phase change of the cooling medium, or by endothermic reactions, rather than by sensible heating of a cooling medium.

4. If the reaction is conducted in the gas phase and the volume increases, it is necessary to raise (not to reduce!) the pressure. If the gas volume decreases, it is necessary to reduce (not to increase!) the pressure[4].
5. It is not necessary to carry out chemical reactions up to their completion. It is better to recycle the unreacted streams.
6. Do not mix streams of different temperatures, different compositions, or different pressures. If possible, don't mix anything!
7. Remember that the increase in the process rate often leads to an increase in energy resource consumption.
8. Select the lowest temperature heat sources.
9. The best chemical reactor is a counter-current one with plug flow.
10. Investigate the conditions of quasi-static processes to discover methods for reducing energy resource consumption.
11. The best process is the one in which energy and species enter and leave along the full length of the apparatus.
12. A chemical process cannot be thermodynamically reversible if it has a stoichiometric excess; however, real processes can operate with minimal exergy expenditures at optimal stoichiometric excesses that are functions of the flow sheet.

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[4] At first glance, Commandments 3 and 4 appear to contradict Le Chatelier's principle but they are based on the Second Law and follow from Le Chatelier's principle, which is also a consequence of the Second Law.

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Corrigendum

Corrigendum to "The theory and practice of energy saving in the chemical industry: Some methods for reducing thermodynamic irreversibility in chemical technology processes" [Energy, 28 (2003) 55-97]☆

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The authors apologize for the many editorial-type errors in the paper discovered by them after its publication, mostly to do with nomenclature and the misplacement of one figure. While the content of the paper was correct, the following clarifications would help the readers understand it better.

Page 55 Abstract lines 4 and 5: replace "…the result some of practical…" with "…the results of some of the practical..."

Page 55 footnote. Change to fax +7 095 114 59-00, e-mail address to leites@rol.ru

Page 56: Replace the Nomenclature with

Nomenclature

c, C, c_i	specific heat
ex	specific exergy
Ex	exergy
Ex_{ch}	"chemical" exergy
Ex_P	"pressure" exergy
Ex_T	"thermal" exergy

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F_h	area of heat transfer or mass transfer
g	acceleration of gravity
G	Gibbs energy, or molar or volume flow rate
$\bar{G}_i = \mu_i$	partial molal Gibbs energy, chemical potential of *i*-component
h	number of moles of species C, Eq. (1)
H	enthalpy
$\bar{H}_i$	partial molal enthalpy
ΔH	change in enthalpy
j	number of moles of species D, Eq. (1)
K_e	chemical equilibrium constant
K_h, K_m	heat transfer rate coefficient, mass transfer rate coefficient
n	quantity of moles; number of moles of species A, Eq. (1)
L	quantity of liquid
m	number of moles of species B in Eq. (1); mass in Eq. (8a)
P	pressure
P_{GAS}	current gas pressure
$P^*{}_{abs(P,x),i}$	equilibrium absorbent vapor pressure (here water); under conditions in stripper corresponding to the boiling temperature under *P* and at *x* – CO_2 concentration in absorbent in stripper in *i*-section
$P_{CO2(P,x),i}$	equilibrium CO_2 pressure corresponding to the boiling temperature under *P* in stripper and *x* – CO_2 concentration in *i*-section
P_S	pressure of the surroundings
$P^*{}_i$	partial equilibrium pressure
q	the minimal specific heat consumption for CO_2 stripping (*str*) in *i*-section (*i*) attributed to 1 cubic meter of total quantity of CO_2 desorbed in all stripper (G_{CO2}, total)
Q	quantity of substance mole/hour, kg/hour or m^3/hour; in Eq. (4) – amount of heat
Q_{PR}	quantity of useful reaction products, Eq. (22)
$Q_{str,i}$	the minimal total heat consumption for CO_2 striping in regenerator (stripper, desorber)
r	the specific heat of vaporization of water (or other stripping agent)
R	universal gas constant
S,$\bar{S}_i$	entropy, partial molal entropy
T, t	temperature
T_0	ambient temperature
U	internal energy
V, v	volume, specific volume
W	useful work

X_i, x_i	concentration of species *i*, CO_2 concentration in liquid in *i* section of desorber
x_1, x_2	correspondingly CO_2 concentration in liquid in the top of desorber (1) and in the bottom (2)
y_i, Y_i	concentration of species *i*
Y_{CO2}	CO_2 concentration in gas mixture
z	height

Greek

Δ	Subtraction operator, e.g. $\Delta Ex_P = Ex_{P2} - Ex_{P1}$, change in “pressure” exergy, where subscript 1 is the initial state of the system and 2 a later state of the system
Δex_s	specific exergy expenditure, Eq. (22)
$\Delta T_h = T_6 - T_1$	in Fig. (15)
$\Delta T_t = \frac{(T_4-T_1)-(T_2-T_3)}{1\mathrm{n}\frac{T_4-T_1}{T_2-T_3}}$	Log mean temperature difference
ΔW	amount of work obtained during a chemical reaction
Φ	reflux ratio for stripping
η, η_e	second law (exergy) efficiency
ν	$= \frac{G_2c_2}{G_1C_1}$ on page 69; velocity on page 71

Subscripts and abbreviations

bot	bottom
ch	chemical
cr	(“critical”) – the section of desorber (stripper) where the driving force of desorption is minimal
r,R, rev	reversible
Ir, IR	irreversible
i, j	species, or current states of a system, or a stream index
opt	optimal
p, prod	products
P	pressure
r, react	reactants
str	stripping
t	in Fig. 12 – top
0	ambient parameter

Page 58 Fig. 1: species a, b, c, d in the figure should be denoted as A, B, C, D for consistency with Eqs (1) and (2)

Page 66 line 17 from top: add the word “but” before “they”

Page 71 line one: replace: “…T_o,P_o,v_o = O, z_o = O,…” with: “…T_o, P_o, and where $v_o = 0$, z_o = 0…”

Page 73: in Eq. (15) replace *To* with T_o

Page 76. Add to caption of Fig. 14: in “reaction N”, the number N always refers to the Eq. number in the text.

Page 78, 10th line under Fig. 16: replace “…under “soft” conditions, rather than to run it to completion”, with “… at lower steam/gas ratios, and to stop it short of completion.”

Page 79, in caption of Fig. 17: change from “20” to “18”.

Page 89, in caption of Fig. 29: change “1” to “2”, and “2” to “1”.

Page 91, line 5 after Eq. (23): change from “34” to “32.”

line 11 after Eq. (23): change from “3200” to “3800”.

replace Fig. 32 with the figure below.

Page 92, first and 6th line from top: replace “34” with “32”.

Page 93, in caption to Fig. 34: replace □ with Δ. In the first line of the caption, after “CO_2” add: “for the flow sheet shown in Fig. 15”.

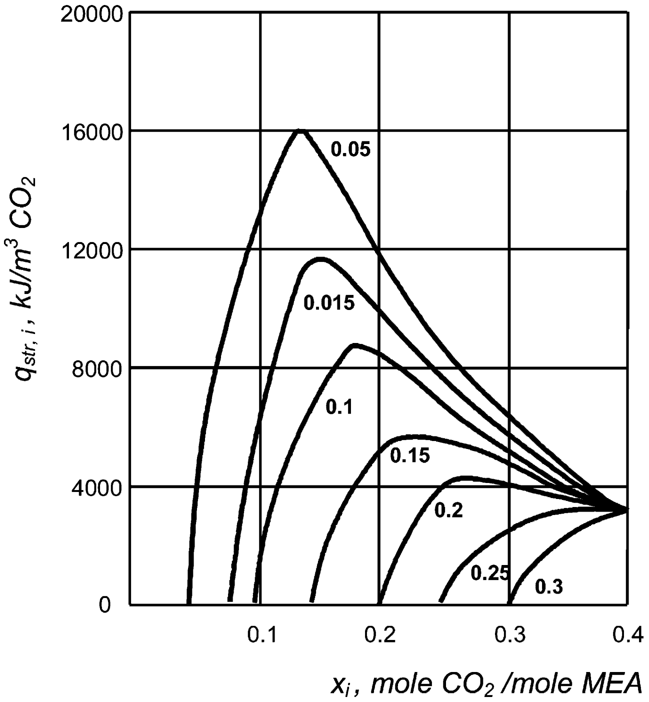

Fig. 32. Specific heat consumption $q_{str,i}$ (Eq. (23)) for production of stripping steam during regeneration of 15% MEA solution. Abscissa is current CO_2 concentration along the height of apparatus. Numbers on the curves are CO_2 concentrations in regenerated solution (pressure of regeneration 0.18 MPa)