

# Thermodynamics Analysis of Processes. 1. Implications of Work Integration

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This paper describes a new technique to analyze processes with a positive change in the Gibbs free energy,  $\Delta G$ , based on the second law of thermodynamics. In particular, the application of a two-stage process, consisting of an endothermic high-temperature first stage and an exothermic low-temperature second stage, has been investigated. This paper considers chemical reaction processes as heat engines and that by the appropriate flow of heat at a specific temperature (and, hence, with a specified exergy level) work can be added or removed from a process. The technique also investigates the integration of such processes in terms of work flows. The technique is useful in the early stages of the design process as well as for retrofitting. It helps identify opportunities and set targets for the process. The method does not require detailed information regarding the process and is based only on thermodynamic properties of the system.

## 1. Introduction

Chemical processes are usually characterized in terms of flows of mass and energy. Therefore, in the development of processes that are cost- and energy-efficient, there is a growing need to integrate processes in terms of mass and energy. In light of this, two branches of process integration have been developed: mass integration and energy integration. Energy integration is a systematic methodology for analyzing the energy flows within a process to identify targets and determine the optimal system for a minimum consumption of energy. For example, pinch analysis is an energy integration tool for designing heat-exchanger networks.<sup>1</sup> Mass integration aims at systematically identifying performance targets for the mass flows in a process. The synthesis of a mass-exchange network has been successfully applied to waste recovery and separation problems.<sup>2</sup>

The use of thermodynamic methods, especially the second law analysis, has proved to be a valuable tool in process synthesis and integration.<sup>3,4</sup> In particular, the application of the second law to processes involving chemical reactions, first introduced by Denbigh<sup>5</sup> and then considered by numerous researchers, reveals that chemical reactors usually are the main cause of thermodynamic inefficiency because of the irreversible manner in which reactions occur. Although present day technology does not allow for reactions to be carried out reversibly, not all of the exergetic losses are inevitable; it is possible to reduce the irreversibility of chemical processes. One possibility is to carry out chemical processes under a “prescribed degree of irreversibility”,<sup>5</sup> i.e., the consumption of a specific amount of exergy to account for technological constraints. Glavic et al.<sup>7</sup> performed a thermodynamic analysis of reactors in order to heat integrate the reactors into the process. De Ruyck<sup>8</sup> also proposed a way in which to include chemical reactions in composite curve theory by defining a

“reversible temperature”. Hinderdrink et al.<sup>9</sup> investigated the exergy losses associated with chemical reactions and suggested ways in which the exergy losses can be minimized. Leites et al.<sup>10</sup> also suggested various methods of reducing exergetic losses, and in turn energy losses, for chemical reactions and other chemical processes.

This paper will investigate the specific case of processes that have positive Gibbs energy changes (which means the process requires work) and explore the possibilities of saving energy by considering the second law analysis.

## 2. Positive Gibbs Energy Change of Reaction

**2.1. Significance.** The production of many industrial chemicals, such as methanol and ammonia, by direct routes (i.e., by a single-step isothermal process) is infeasible because these reactions possess a positive change in the Gibbs energy. A positive  $\Delta G$  has the following significance to a designer: first, it signifies a small equilibrium conversion and, second, that work must be supplied to a steady-state isothermal system. Several methods of overcoming the positive  $\Delta G$  and thus overcoming small equilibrium conversion have been suggested.<sup>4,11</sup> One of these methods suggests staging of the overall reaction; i.e., the feed is first converted into intermediates at certain operating conditions, and thereafter these intermediates are reacted to the desired product under different operating conditions. Usually, one of stages runs an endothermic reaction and the other stage an exothermic one.

**2.2. Staging Reactions.** The procedure of “staging reactions” can be examined using the synthesis method approach suggested by May and Rudd<sup>12</sup> for the development of Solvay Clusters. Consider a reaction with a positive change in the Gibbs energy:



To carry out this reaction under practical conditions, consider a two-stage route



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The Gibbs energy difference of both stages should be less than a small positive number,  $\epsilon$  ( $\epsilon < 42$  kJ/mol), to ensure a reasonable equilibrium conversion.<sup>12</sup>

Therefore, for reaction 1

$$\Delta G = G_Z - (G_A + G_B) > \epsilon \quad \text{at all temperatures} \quad (2)$$

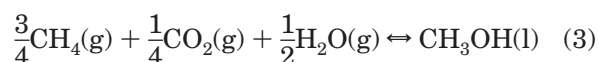
and for reactions 1a and 1b

$$\Delta G_{1a} = (G_X + G_Y) - (G_A + G_B) \leq \epsilon \quad \text{at conditions } T_1 \quad (2a)$$

$$\Delta G_{1b} = G_Z - (G_X + G_Y) \leq \epsilon \quad \text{at conditions } T_2 \quad (2b)$$

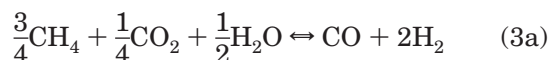
These inequalities can be plotted on a temperature–free energy curve to determine the temperatures of each reaction that satisfy these criteria.

**2.3. Synthesis of Methanol.** Consider, for example, the production of methanol by the following overall reaction:



Reaction 3 has a large positive standard Gibbs energy change (84.8 kJ/mol), is endothermic (36.8 kJ/mol), and has a negative entropy change (−161.0 J/mol·K). Therefore, the Gibbs energy difference is positive at all temperatures, becoming more positive as the temperature increases.

The reaction can be accomplished by using a two-stage process as outlined below. The first stage is the production of synthesis gas by reforming methane (gas phase)



Although reaction 3a has a large positive standard Gibbs energy change (113.8 kJ/mol), the enthalpy (164.9 kJ/mol) and entropy (171.3 J/mol·K) changes are both positive; therefore, the Gibbs energy difference is positive at low temperatures and negative at high temperatures. This implies that this reaction would be run at high temperatures.

The second stage requires the conversion of the synthesis gas to methanol



The enthalpy (−128.2 kJ/mol) and entropy (−332.5 J/mol·K) changes are both negative; therefore, the Gibbs energy change is negative at low temperatures but becomes positive at high temperatures. This implies that this reaction would be carried out at low temperatures.

The approach outlined in section 2.2 can be applied to the methanol synthesis example in order to determine how the two-stage process helps to overcome the positive change in the Gibbs energy. This will be discussed in the paragraphs that follow.

Figure 1 shows three lines (lines a–c). Line a represents the sum of the Gibbs free energy of the reactant (including the corresponding stoichiometric coefficients) in reaction 3a. Line b represents the sum of the Gibbs free energy of the products of reaction 3a (which is the

same as that of the reactants of reaction 3b). Line c represents the Gibbs free energy of the product (reaction 3b), in this case methanol.

The objective is to have  $\Delta G \leq \epsilon$  at the reaction conditions for both reactions 3a and 3b, as explained in section 2.2. These criteria are shown in Figure 1.

Figure 1 forms a ladder-like plot, with each jump corresponding to a reaction. It is clear that the two stages must be run at different conditions, with reaction 3a operating at a high temperature ( $T \geq T_1$ ) and reaction 3b carried out at a low temperature ( $T \leq T_2$ ).

Figure 1 also gives information regarding the enthalpy change of reaction at a temperature equal to absolute zero, assuming that the Gibbs energy change varies linearly with temperature. This requires assumption of a constant enthalpy change of reaction ( $\Delta H$ ) as well as a constant entropy change of reaction ( $\Delta S$ ). It is clear from Figure 1 that reaction 2a is endothermic, so energy must be added to drive the reaction, and that reaction 2b is exothermic, so energy must be removed.

Therefore, by carrying out the reaction in two stages, one can achieve a reasonable conversion at industrially attainable temperatures.

This paper will use the second law analysis to further explain this concept and explore the possibilities of such an arrangement.

### 3. Second Law Analysis

**3.1. Background.** The exergy analysis is a combination of the first and second laws of thermodynamics. The analysis of a process in terms of exergy proves to be useful because it provides quantitative information about irreversibilities and exergy losses in the process. In this way, the thermodynamic efficiency can be quantified, areas of poor efficiency can be identified, and targets can be determined in order that processes can be designed and operated to be more efficient. Exergy can be defined as the maximum amount of work that can be obtained from a system during a reversible change from a given state to the environmental (reference) state<sup>13</sup> and can be represented by  $B$ :

$$B = H - T_0 S \quad (4)$$

where  $H$  is the enthalpy,  $S$  is the entropy, and  $T_0$  is the temperature of the environment (reference state) taken to be 298.15 K. The kinetic and potential terms are neglected.

Changes in exergy,  $\Delta B$ , from state 1 to state 2 is therefore given by

$$\Delta B = (H_2 - H_1) - T_0(S_2 - S_1) \quad (5)$$

For a steady-state flow process as shown in Figure 2, the exergy balance can be represented by the following mathematical description:<sup>14</sup>

$$I = \sum_i (mB)_i - \sum_o (mB)_o + \sum_r Q_r(1 - T_0/T_r) + \sum W_s \quad (6)$$

where  $W_s$  is the shaft power,  $m$  represents the mass of the streams entering (i) or leaving (o),  $Q$  is the rate of heat transfer from the energy reservoir  $r$ , and  $T_r$  is the temperature of the reservoir.  $I$  is the irreversibility rate or the exergy loss associated with the process.

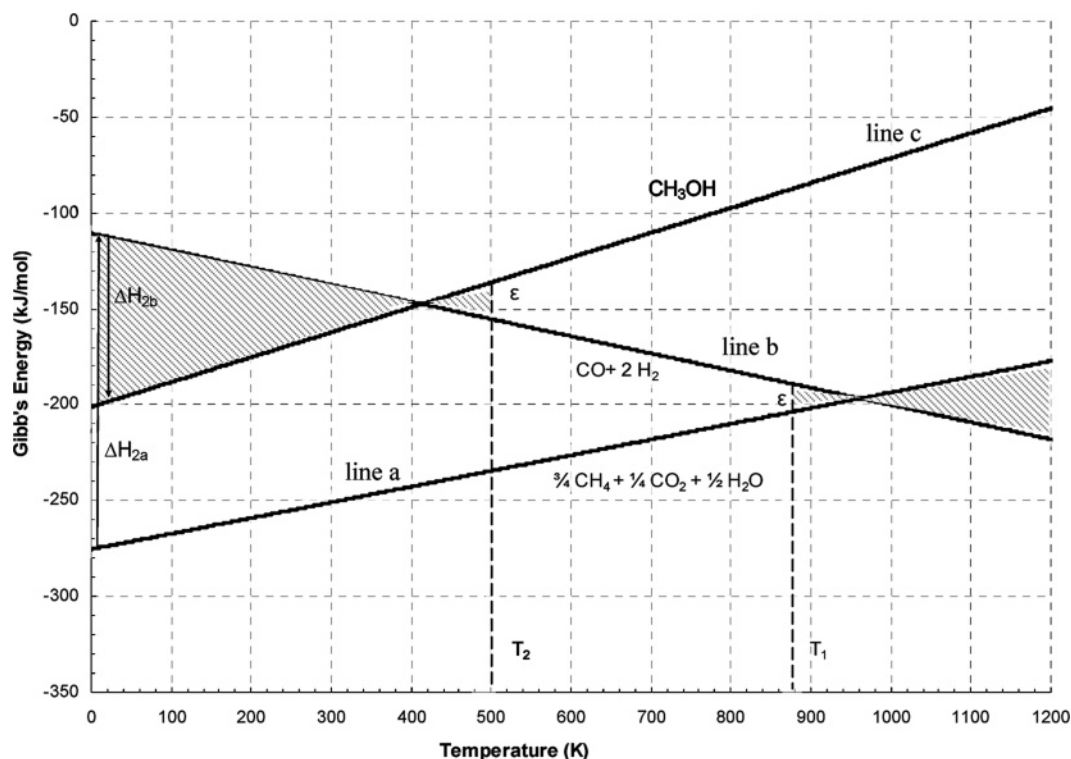


Figure 1. Gibbs energy-temperature plot for the synthesis of methanol using a two-stage route.

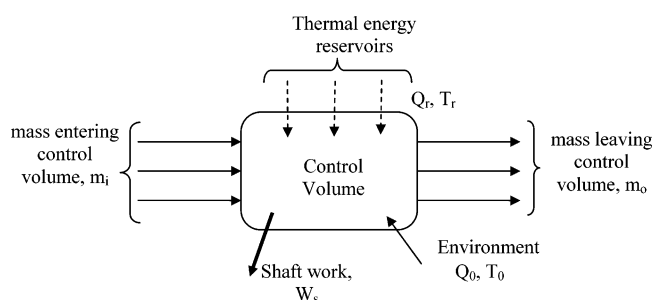


Figure 2. Exergy balance for an open control volume at steady state.

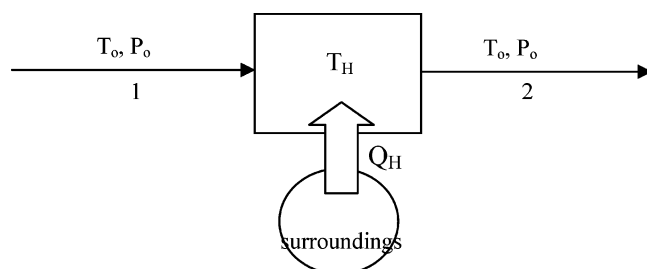


Figure 3. Schematic diagram of an isothermal endothermic reactor.

**3.2. Black-Box Exergy Analysis of a Reactive System. 3.2.1. Endothermic Reactions.** Consider an endothermic reactor, as shown in Figure 3.

Figure 3 shows an *endothermic reaction* carried out at a temperature  $T_H$ . The heat required for the reaction is  $Q_H$ . The product and reactant streams are assumed to enter and leave the *process* (defined as a “black box” between the input and output streams) at a temperature  $T_o$  and pressure  $P_o$ .

Applying eq 6, but replacing mass ( $m$ ) with moles ( $n$ ), to the system shown in Figure 3 gives

$$I_{\text{endo}} = (nB)_1 - (nB)_2 + Q_H(1 - T_o/T_H) \quad (7)$$

Substituting for the availability function,  $B$ , and rearranging give

$$I_{\text{endo}} = (n_1\hat{H}_1 - n_2\hat{H}_2) - T_o(n_1\hat{S}_1 - n_2\hat{S}_2) + Q_H(1 - T_o/T_H) \quad (8)$$

Noting that  $H_2 - H_1 = \Delta H_{\text{endo}}$  (the enthalpy change of the endothermic reaction), that  $S_2 - S_1 = \Delta S_{\text{endo}}$  (the entropy associated with the endothermic reaction), and that  $Q_H$  is equal to the enthalpy change of reaction at  $T_o$  (i.e.,  $Q_H = \Delta H_{\text{endo}}$ ) as given by the energy balance (first law balance), the equation can be simplified further to give

$$I_{\text{endo}} = T_o(\Delta S_{\text{endo}} - \Delta H_{\text{endo}}/T_H) \quad (9)$$

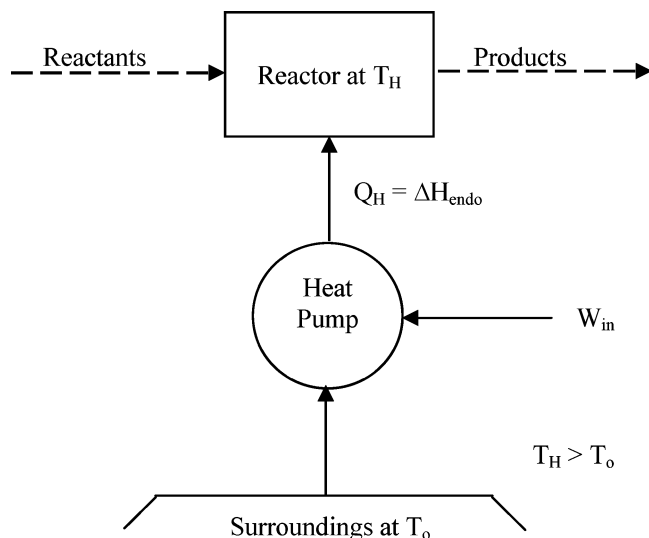
To keep the derivation simple, it is assumed that  $\Delta H_{\text{endo}}$  and  $\Delta S_{\text{endo}}$  are not functions of temperature (i.e., they remain constant). This assumption can be modified, which leads to the algebra becoming more complex, but this will not affect the approach or interpretation of the derivation.

Equation 9 is an expression for the irreversibility or lost work of an isothermal endothermic reactor. It is clear that the irreversibility is dependent on the temperature of the reactor and that, by varying the temperature, one may be able to reduce the irreversibility of the reaction.

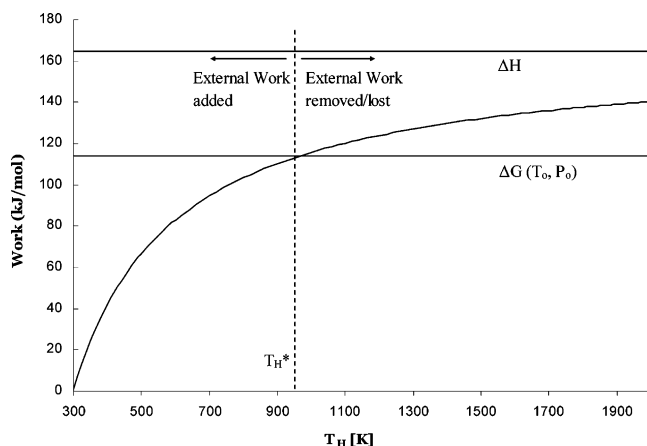
Equation 9 can also be expressed in terms of the Gibbs energy change of the endothermic reaction (because  $\Delta G_{\text{endo}} = \Delta H_{\text{endo}} - T_H\Delta S_{\text{endo}}$ ) as derived by Denbigh:<sup>5</sup>

$$I_{\text{endo}} = -\Delta G_{\text{endo}} \frac{T_o}{T_H} \quad (10)$$

Equations 9 and 10 apply to a reactor where heat is being supplied from the surroundings at the reaction



**Figure 4.** Endothermic reactor as a reservoir of a Carnot heat pump.



**Figure 5.** Work required for reaction 2a as a function of temperature.

temperature. Therefore, to reduce the irreversibility associated with the reaction, there is a need to reduce the change in the Gibbs energy of the reaction,  $\Delta G_{\text{endo}}(T_H)$ .

An alternative view is that the reactor could be considered in terms of a Carnot engine, as shown in Figure 4.

To supply a quantity ( $Q_H$ ) of heat to the reaction at temperature  $T_H$ , work ( $W$ ) is required. The work can be related to the temperature of the reactor ( $T_H$ ), the temperature of the surroundings ( $T_o$ ), and the heat required ( $Q_H$ ) by the second law:

$$W_{\text{in}} = Q_H(1 - T_o/T_H) \quad (11)$$

Equation 11 is useful in relating the temperature of the reactor to the amount of work required to supply the necessary heat of reaction (because  $Q_H = \Delta H_{\text{endo}}$ ).

Consider reaction 3a, which is endothermic. A plot of the work input as a function of the reaction temperature,  $T_H$ , is shown in Figure 5.

The work required increases as the temperature of the reactor increases and asymptotes to the heat of reaction ( $\Delta H_{\text{endo}}$ ). At a certain temperature,  $T_H^*$ , the work required is equal to the standard Gibbs energy change of the process,  $\Delta G(T_o, P_o)$  (which is equivalent

to the change in the exergy of the process,  $\Delta B$ ). This corresponds to the temperature at which the reaction is carried out reversibly and with a minimum work input. This can be proven by setting  $I_{\text{endo}} = 0$  in eq 7, which gives

$$\Delta B = \Delta G(T_o, P_o) = W = Q_H(1 - T_o/T_H^*) \quad (12)$$

Also, considering eqs 9 and 10, the reversible temperature of the endothermic reaction,  $T_H^*$ , is obtained when the Gibbs energy change of the endothermic reaction,  $\Delta G_{\text{endo}}(T_H) = 0$ ; thus, the reversible temperature,  $T_H^*$ , is given by

$$T_H^* = \Delta H_{\text{endo}}/\Delta S_{\text{endo}} \quad (13)$$

Under the assumption that  $\Delta H_{\text{endo}}$  and  $\Delta S_{\text{endo}}$  are constant, the reversible temperature,  $T_H^*$ , will be constant. The reversible temperature was also defined by Shinnar<sup>4</sup> and De Ruycck.<sup>8</sup>

If the reaction is carried out at a temperature greater than  $T_H^*$ , the work term is larger than the exergy change,  $\Delta G(T_o, P_o)$ , and therefore there is a loss of work (this corresponds to the irreversibility or a potential to recover work from the stream). If the reaction is carried out below  $T_H^*$ , the work term is less than the exergy change; therefore, external work has to be supplied to meet the requirements of the process, as shown in Figure 5.

**3.2.2. Exothermic Reactions.** A similar second law analysis can be performed for an exothermic reaction carried out at temperature  $T_C$ , while the streams enter and leave the process at temperature  $T_o$ . The irreversibility of an exothermic reactor can be expressed as

$$\begin{aligned} I_{\text{exo}} &= T_o \left( \Delta S_{\text{exo}} - \frac{\Delta H_{\text{exo}}}{T_C} \right) \\ &= -\Delta G_{\text{exo}} \frac{T_o}{T_C} \end{aligned} \quad (14)$$

Again, the entropy change of the exothermic reaction  $\Delta S_{\text{exo}}$  and the enthalpy change of the exothermic reaction  $\Delta H_{\text{exo}}$  were assumed to be constant.

Just as the endothermic reactor could be thought of in terms of a heat pump, the exothermic reactor could be considered as the “hot reservoir” of a heat engine, as shown in Figure 6.

In order for work  $W_{\text{out}}$  to be produced, the heat source  $Q_C$ , which is equal to the heat of the exothermic reaction ( $\Delta H_{\text{exo}}$ ) is taken from the reactor temperature  $T_C$  and heat is released to the surroundings at the temperature of the surroundings,  $T_o$ . The work produced can be expressed in terms of  $T_C$  and  $T_o$  as follows:

$$W_{\text{out}} = Q_C(1 - T_o/T_C) \quad (15)$$

Equation 15 gives an expression for the maximum work that could be obtained from the reaction if the heat of reaction was recovered and converted to work.

Equation 15 is plotted in Figure 7 for reaction 3b, which is exothermic.

Again, a reversible temperature for the exothermic reaction,  $T_C^*$ , can be defined where the exergy change



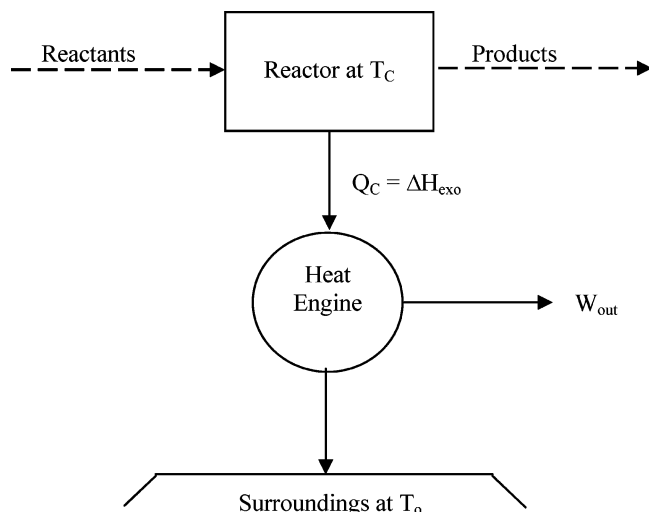


Figure 6. Exothermic reactor in terms of a heat engine.

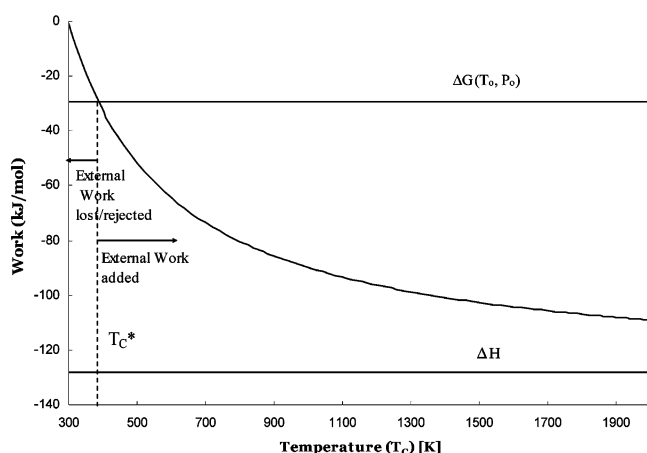


Figure 7. Work obtained from reaction 2b as a function of temperature.

for the exothermic process  $[\Delta G(T_o, P_o)]$  equals the work produced by the exothermic reactor, i.e.

$$\Delta B = \Delta G(T_o, P_o) = W = Q_C \left( 1 - \frac{T_o}{T_C^*} \right) = \Delta H_{\text{exo}} \left( 1 - \frac{T_o}{T_C^*} \right) \quad (16)$$

In this case,  $T_C^*$  is the ratio of the enthalpy change to the entropy change for the exothermic reaction, i.e.

$$T_C^* = \Delta H_{\text{exo}} / \Delta S_{\text{exo}} \quad (17)$$

At temperatures below the reversible temperature,  $T_C^*$ , the work term is smaller than the change in the exergy for the process, i.e.,  $\Delta G(T_o, P_o)$ ; thus, heat is rejected to the surroundings, and work is lost (irreversibility or an opportunity to recover work from the stream). When the temperature of the exothermic reaction is higher than the reversible temperature, the magnitude of the work term is larger than the change in exergy for the process, thus implying that work must be externally supplied in order to meet the work requirements for the process.

**3.2.3. Discussion.** Sections 3.2.1 and 3.2.2 discussed how the work required/ released by a reaction is related to the heat of the reaction. Of particular importance is the relationship between the minimum (or maximum)

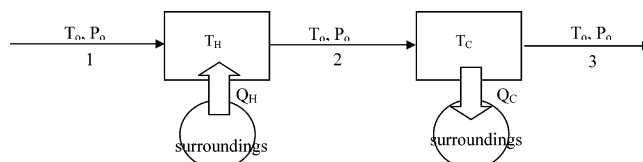


Figure 8. Schematic diagram of the two-stage process.

work and the heat of the reaction as given by eqs 12 (endothermic reaction) and 16 (exothermic reaction). One is able to get an indication of the temperature at which the reaction should be carried out in order to reduce irreversibilities. It should be noticed that the heat and work requirements can be matched only in cases when  $\Delta G(T_o, P_o)$  is less than  $\Delta H$  because

$$\frac{\Delta G(T_o, P_o)}{\Delta H_{\text{rxn}}} = \left[ 1 - \frac{T_o}{T_H} \right] \leq 1$$

For example, reaction 3 has  $\Delta G(T_o, P_o) > \Delta H$ , and thus there is no value that satisfies the above relation. Therefore, it is not possible to match the heat and work requirements in terms of a heat pump for this reaction by carrying out this reaction in a single stage.

One way of matching the work and heat requirements is by staging the reaction, i.e., carrying out the process in two stages. The first stage is endothermic and nonspontaneous (reaction 3a) with  $\Delta G_{\text{endo}}(T_o, P_o) < \Delta H_{\text{endo}}$ , whereas the second stage is exothermic and spontaneous (reaction 3b) with  $\Delta G_{\text{exo}}(T_o, P_o) < \Delta H_{\text{exo}}$ . Therefore, it is possible to match the heat and work requirements in the two-stage process. An extension of the analysis performed in sections 3.2.1 and 3.2.2 should be able to reveal information about the operating temperatures when the overall two-stage process is reversible, thereby matching the work and heat requirements.

**3.2.4. Two-Stage Process.** In sections 3.2.1 and 3.2.2, reactions 3a and 3b were considered in isolation. Now consider the two reactions of the system shown in Figure 8 as a black-box system.

Applying the exergy balance (eq 6) to Figure 8 gives

$$I_{\text{overall}} = (nB)_1 - (nB)_3 + Q_H \left( 1 - \frac{T_o}{T_H} \right) + Q_C \left( 1 - \frac{T_o}{T_C} \right)$$

Substituting for the availability (exergy) function using eq 4 gives

$$I_{\text{overall}} = -(\Delta H_{31} - T_o \Delta S_{31}) + Q_H \left( 1 - \frac{T_o}{T_H} \right) + Q_C \left( 1 - \frac{T_o}{T_C} \right) \quad (18)$$

It can be noted that  $\Delta H_{31} = \Delta H_{32} + \Delta H_{21}$ , that  $Q_H = \Delta H_{21}$ , and that  $Q_C = \Delta H_{32}$ . Substituting these relationships into eq 18 gives

$$I_{\text{overall}} = T_o \left[ \Delta S_{31} - \left( \frac{\Delta H_{21}}{T_H} + \frac{\Delta H_{32}}{T_C} \right) \right] \quad (19)$$

It is clear from eq 19 that the irreversibility of the overall process depends on the temperature of both the endothermic and exothermic reactors. Therefore, to

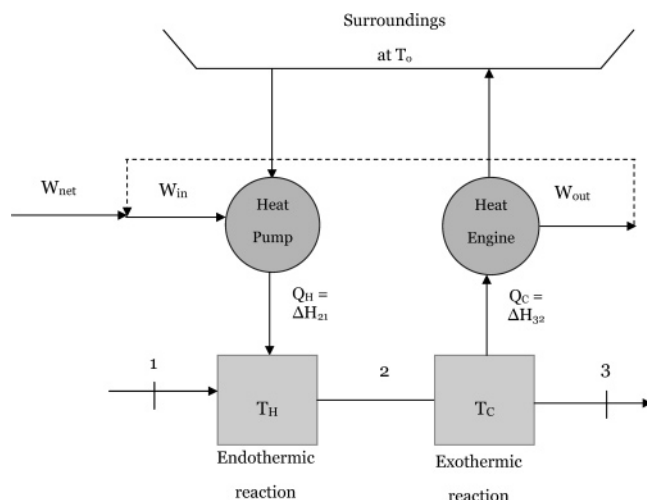


Figure 9. Two-stage process in terms of Carnot engines.

reduce the irreversibility of the entire process, one needs to carefully decide on the temperature of the two reactors simultaneously.

It must be noted that, if no additional work is added to the process,  $I_{\text{overall}}$  must be either equal to or greater than zero because of the second law. A “negative irreversibility” would imply that external work has to be supplied to such a process in order to meet the work requirements.

For the overall process to be reversible, assuming no external work is added to the process, the irreversibility term ( $I_{\text{overall}}$ ) must be equal to zero. Putting  $I_{\text{overall}} = 0$  in eq 19 gives

$$\Delta S_{31} = \frac{\Delta H_{21}}{T_H} + \frac{\Delta H_{32}}{T_C} \quad (20)$$

Equation 20 is an interesting result that reveals that for a reversible overall process there is a specific relationship between the temperatures of the two reactors. The implications of this result will be discussed extensively later.

The above equation could also be attained by considering the process as a combination of Carnot engines: the endothermic reaction as a heat pump and the exothermic reaction as a heat engine. This is depicted in Figure 9.

One is able to integrate the work flows between the endothermic and exothermic reactors. Because the overall process has a positive  $\Delta G$ , the overall balance still requires work to be input into the process, shown in Figure 9 as  $W_{\text{net}}$ .

The net work,  $W_{\text{net}}$ , is given as the sum of  $W_{\text{in}}$  and  $W_{\text{out}}$ , where  $W_{\text{in}}$  and  $W_{\text{out}}$  are given by eqs 8 and 13, respectively. Therefore,  $W_{\text{net}}$  equals

$$W_{\text{net}} = W_{\text{in}} + W_{\text{out}} = \Delta H_{21} \left( 1 - \frac{T_o}{T_H} \right) + \Delta H_{32} \left( 1 - \frac{T_o}{T_C} \right) \quad (21)$$

For a reversible process, the net work,  $W_{\text{net}}$ , must be equal to the change in the exergy change of the overall process, i.e.,  $\Delta B_{31}$  [or  $\Delta G_{31}(T_o, P_o)$ ]. Rearranging leads to eq 20. If the net work,  $W_{\text{net}}$ , is equal to the exergy change [ $\Delta G_{31}(T_o, P_o)$ ], the process is defined as being work integrated.

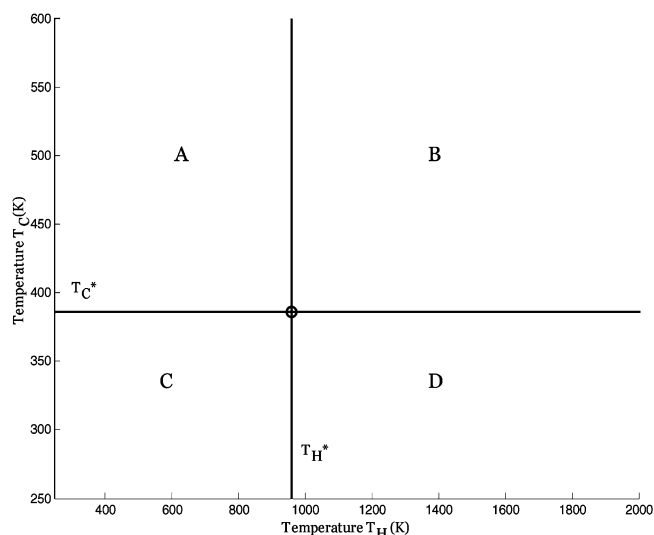


Figure 10. Endothermic and exothermic reversible temperatures.

Consider a plot of the endothermic reactor temperature against the exothermic reactor temperature, as shown in Figure 10. One can plot the reversible temperature of the endothermic and exothermic reactors in order to classify the work flows for the endothermic and exothermic reactors.

Figure 10 shows the point where both reactors are run reversibly in isolation and operate at the reversible temperature,  $T_H^*$  (for the endothermic reaction 3a) defined in section 3.2.1 and  $T_C^*$  (for the exothermic reaction 3b) defined in section 3.2.2. The reversible temperatures of the two reactions ( $T_H^*$  and  $T_C^*$ ) divide the plot into four regions labeled A–D in Figure 10:

(i) In region A, additional work is required for reaction 3a (endothermic reaction) because the temperatures are less than  $T_H^*$ , meaning that the work supplied is less than the exergy change for the process,  $\Delta G_{\text{endo}}(T_o, P_o)$ . Additional work is also required in region A for reaction 3b (exothermic reaction) because the temperatures are greater than the exothermic reversible temperature,  $T_C^*$ . Thus, the work obtained from the reaction is greater than the exergy change for the process,  $\Delta G_{\text{exo}}(T_o, P_o)$ .

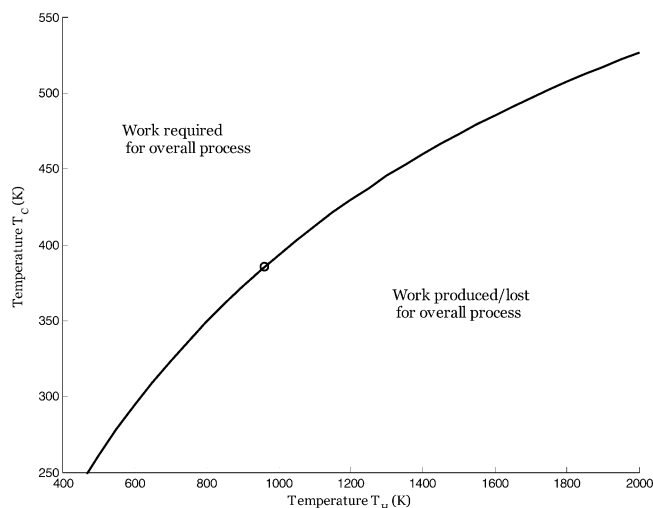
(ii) In region B, work can be potentially produced/lost from reaction 3a (endothermic reaction) because the temperature is greater than  $T_H^*$  because the work put in at these temperatures is less than the exergy change for the process,  $\Delta G_{\text{endo}}(T_o, P_o)$ . Reaction 3b (exothermic reaction) requires extra work in region B because the temperatures are above  $T_C^*$ .

(iii) Region C is the region where reaction 3a requires additional work because the temperature is less than  $T_H^*$  and reaction 3b loses work because the temperature is less than  $T_C^*$ .

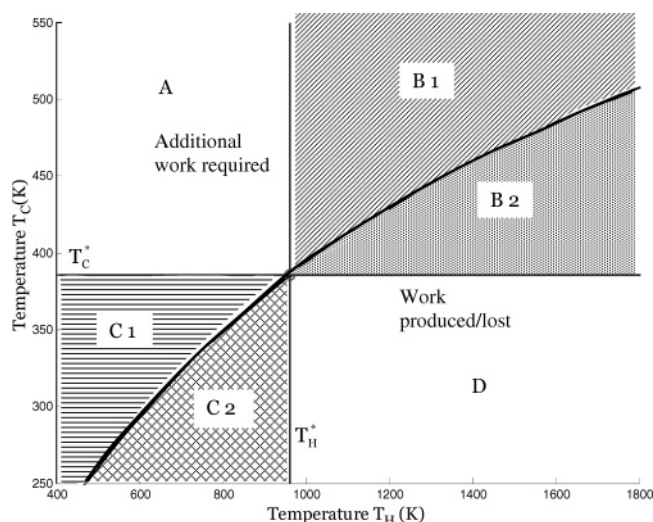
(iv) In region D, work is lost by reaction 3a because the temperature is greater than  $T_H^*$  and reaction 3b also loses work because the temperature is less than  $T_C^*$ .

Regions B and C are the two regions in which there is a possibility of work integrating the process because these are the regions where one reactor/process loses work while the other reactor/process requires work. In region A, both reactors/processes require work input, and in region D, both reactors/processes lose work; thus, there is no opportunity for work integration.

Assuming that the enthalpy and entropy changes of reactions do not vary considerably with temperature,



**Figure 11.** Reversible work-integrated curve as a function of the exothermic and endothermic temperatures.

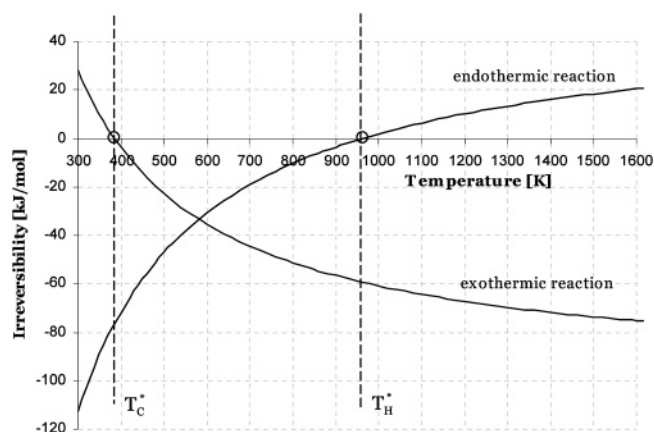


**Figure 12.** Relationship between the temperatures of the reactors in the two-stage reversible process.

the relationship between the temperatures of the two reactors (i.e., reactions 3a and 3b) as given by eq 20 can be plotted and is shown in Figure 11.

Figure 11 shows how the endothermic reactor temperature,  $T_H$ , is related to the exothermic reactor temperature,  $T_C$ , for the overall process to be reversible and thus for a minimum work input. It is clear that considering the two reactors together as a system allows an entire curve of temperatures of the endothermic and exothermic reactors to be defined instead of just a single point where the overall process would be reversible. Above the curve, the irreversibility is “negative”. This means that the net work to the process is less than the exergy change for the process (i.e., the minimum work required for the process), and therefore external work has to be supplied to the process. In the region below the curve, the irreversibility is positive, signifying that the net work to the process is greater than the exergy change for the process. Therefore, there is a loss of exergy to the surroundings, or work can be produced in this region.

Overlapping Figures 10 and 11, as shown in Figure 12, gives more insight into the two stages of the process. It is clear that the work-integrated curve falls in regions B and C. Regions B and C can be divided even further



**Figure 13.** Irreversibility of the endothermic and exothermic reactors.

into regions B1, B2, C1, and C2, as shown in Figure 12. Region B1 corresponds to the region where additional work must be added to reaction 3b (exothermic reaction) because region B1 lies above the reversible curve. Region B2 is the region where reaction 3a (endothermic reaction) will produce/lose work because the region lies below the reversible curve. In region C1, additional work must be added to reaction 3a (endothermic reactions), while in region C2, work can be produced/lost from reaction 3b (exothermic reaction).

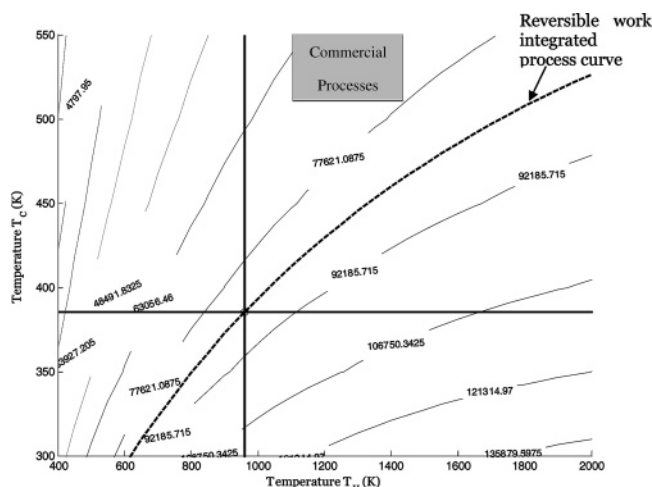
Figure 12 informs one of the work requirements to each stage of the process and is thus useful for analyzing processes. One can determine which stage requires work and which stage loses work and whether the overall process still requires extra work or not. One can also quantify the amount of work to be supplied to each stage as well as the work produced/lost in each stage.

An alternative view is to plot the irreversibility of the two reactors as a function of temperature, as shown in Figure 13.

Figure 13 shows the irreversibility of the two reactors in isolation as a function of the temperature of the reactor. The temperature at which the irreversibility equals zero was defined as the reversible temperature,  $T^*$ . Running the two reactors at these temperatures corresponds to the point shown on the two-stage reversible curve in Figure 11. It can also be seen from Figure 13 that, for the exothermic reactor, the irreversibility is initially positive but becomes “negative” at higher temperatures. The endothermic reactor works in reverse; i.e., at low temperatures the irreversibility of the endothermic reactor is “negative” but becomes positive at higher temperatures. Therefore, by choosing the temperatures of the two reactors in such a way that the irreversibility of the one reactor is positive and the other negative (or vice versa), one can find many sets of temperatures that allow the overall process to be reversible. This allows for the loss of availability in one of the reactors, yet the overall process remains reversible. Figure 13 also allows one to recognize the four regions classified in Figure 10 in terms of the irreversibility.

Commercial processes are limited by the temperature at which the reformers are run (requires high temperatures for a reasonable conversion to be achieved) as well as the catalyst properties of the methanol synthesis step (catalysts usually operate between a temperature range of 500 and 550 K). It can thus be seen from Figure 12 that commercial methanol synthesis processes fall





**Figure 14.** Net work input or output required by the process as a function of the endothermic and exothermic reactor temperatures.

in the region of “negative irreversibility”, thus implying that work needs to be added. Commercial processes operate in region B, i.e., the region in which reaction 3a (similar to steam reforming) loses work whereas reaction 3b (methanol synthesis reaction) requires extra work.

Equation 21 can be used to calculate the work requirement, which can be plotted as contours of iso-work (whether work is input or produced/lost) curves also shown in Figure 14. Figure 14 also shows the reversible curve where the required minimum work input, which is equal to  $\Delta G(T_o, P_o)$  for the overall process, is met by the heat flows. Below the curve, the quantity of work is greater than that of  $\Delta G(T_o, P_o)$ , meaning that work is produced or lost, whereas above the curve, the quantity of work is less than the value of  $\Delta G(T_o, P_o)$ ; therefore, external work is required.

If one regards the extra work input as an increase in the operating costs, one can see that by changing the temperatures of either the endothermic or exothermic reactor one can reduce the operating cost in current plants.

It can also be noticed from Figure 14 that reducing the temperature of the methanol synthesis would result in the reduction of external work required to be supplied and therefore a reduction in the operating costs. An increase in the temperature of the reformer would also reduce the amount of external work required.

It can also be noticed that small changes in the endothermic reactor temperature have a much larger effect on the work required than changes in the temperature of the exothermic reactor, especially at higher temperatures. Therefore, the temperature of the endothermic reactor should be kept as low as possible because the operating costs in terms of work requirements are very sensitive to this.

#### 4. Practical Applications

The technique described allows one to classify existing processes into one of three categories based on their operating temperatures:

**(i) Processes That Lie on the Reversible Work-Integrated Curve.** Processes lying on the reversible curve are work-integrated, do not require further work, and do not reject work. When stages 1 and 2 operate at  $T_H^*$  and  $T_C^*$ , respectively, each individual stage is

reversible. At other temperatures (i.e.,  $T_H^* > T_H > T_H^*$  and  $T_C^* > T_C > T_C^*$ ), each stage would require pumping heat from one stage to the other stage, depending on where the operating temperature lies in relation to  $T_H^*$  and  $T_C^*$ .

**(ii) Processes That Lie above the Reversible Work-Integrated Curve,** i.e., Processes That Require External Work. The external work can be supplied by considering other unit operations such as separation and compression. This will be considered in a following paper.

**(iii) Processes That Lie below the Reversible Work-Integrated Curve,** i.e., Processes That Are Associated with Lost Work.

The authors believe that when designing a process, the designer should aim to operate processes as close to the reversible curve as possible.

Processes of particular interest are those that lie below the reversible curve. These processes equivalently reject work to the surroundings. Because the point of most chemical processes is not to produce work, this is not an effective region to operate in. There is thus a need to determine ways to shift such processes closer to the reversible curve. Possible ways of achieving this are (1) changing the temperature at which the process operates, which is difficult because the temperature range is usually limited by physical constraints, (2) using work pumps, and (3) changing the chemistry (i.e., the reaction involved) of the process such that the  $\Delta G$ ,  $\Delta H$ , and temperature can be matched. These are being investigated by the authors for industrial processes of interest.

#### 5. Conclusions

This paper attempts to understand the implications of a reaction having a positive change in the Gibbs energy of reaction. One of the ways of overcoming this positive change in the Gibbs energy of reaction, staging the reaction, was investigated using the “Solvay technique” as well as a second law analysis. A two-stage reaction process for the production of methanol was considered.

Initially, a exergy law analysis of each reactor was performed separately, allowing one to find the reversible temperature, i.e., the temperature at which thermodynamic efficiency is the greatest. The analysis was then extended to include both reactors. This allows one to define a reversible curve, i.e., a set of temperatures of both reactors that maximizes the efficiency. Regions of positive and “negative” irreversibility were also determined. The reversible curve is useful in deciding on the temperatures of the two reactors. However, because of nonthermodynamic constraints, such as catalyst limitations, the curve is limited in its use. However, by considering other ways of putting in work, one is able to “move” into the regions of negative irreversibility. The two-stage process was also modeled in terms of heat engines, resulting in the same conclusions as the second law analysis.

The tools described in this paper are quite useful during the early stage of the design process. The method allows one to analyze the work flows in the process, thereby giving insight into the work requirements for the process. It also helps identify opportunities and set targets for the process. The method does not require detailed information regarding the process and is based only on thermodynamic properties of the system, there-



fore allowing process integration to be considered at the "black-box" level.

The technique can be applied to various processes, as will be discussed in a following paper.

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