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A Graphical Approach to Process Synthesis and its Application to Steam Reforming

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It is common practice in chemical engineering to design processes sequentially. The type of product desired determines the choice of the feed materials that are introduced into the reactor networks. These in turn lead into the separation networks. The flows of heat and work are the final part of the sequence to be considered, with the application of heat exchanger networks, and any deficiency or excess in these flows is usually compensated for with the use of utilities. Although the ongoing research into reactor, separation, and heat exchanger optimization is of indubitable value, an aspect that is often overlooked in conventional research is the question: How do changes to one of the elements in the sequence affect the others? Most process designers do not address such matters until the next optimization of the sequence begins. The result of this sequential approach to design is that processes may contain a few very efficient units, but may also have others that are highly inefficient. A graphical technique that incorporates the flows of heat and work into the design of the process at a very early stage is proposed. The technique can be used to prepare flow sheets that represent a synthesized version of the elements that make up the complete process, rendering each component highly efficient. This new design tool uses the thermodynamic properties of enthalpy (representative of process heat requirements) and Gibbs free energy (representative of process work requirements) to develop process flow sheets that operate as close to reversibly as possible, and can be used as a foundation for more detailed refinements to achieve the best possible result. A case was described in a previous paper in which the graphical technique was applied to gasification. The application of the technique to the production of syngas by the steam reforming of natural gas is detailed. We show that the steam reforming process can be operated with increased reversibility and can actually consume carbon dioxide, thus representing a process with a carbon efficiency of greater than 100%, if the way in which all the process units interact with one another is used to utmost advantage. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3714–3729, 2013

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Introduction

With the increasing pressure on industries to maximize their productivity and minimize their impact on the environment, the efficient use of work and heat is becoming increasingly important. This raises the question of whether the processes entailed in industry are designed to function at an optimal level.

Traditionally, process design has been sequential: the feed materials enter reactors to form products, which then pass into some kind of separation system that removes impurities and unreacted feed. This type of design creates the very simplest form of flow sheet. At a later stage, attempts are made to improve the functioning of the reactor and separation systems. The sequential approach to process design has been the focus of a great deal of existing research, which has included reactor sequencing,[1–4] heat exchanger network optimization,[5–7] and distillation sequencing.[8–10]

Although there is a great deal of merit in this research, such sequential methods of design can be problematic. For example, reactors are often the first units to be optimized, with the designers placing a strong emphasis on very high overall conversion, which usually requires that the reactors have substantial recycles. However, these recycles put a heavy strain on the separation systems, which will lead to complications when the process designers are working on raising their operational efficiency. Conversely, optimizing the separation systems before the reactor systems can lead to undue strain being placed on the performance of the latter. This leads to processes that may have a few very efficient sections but may be inefficient overall. Again, it is normally the case that the flows of heat and work within a process are considered only after these reactor or separation optimizations are completed and the process flow sheet has been finalized.[11,12]

In this article, we propose an alternative method to sequential design. The concept on which we base this

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graphical technique rests on determining the enthalpy and Gibbs free energy for all unit processes, and representing them as vectors on a plot of enthalpy and Gibbs free energy, called the GH-space. Enthalpy depicts the flows of heat within a process, while Gibbs free energy portrays the flows of work. By manipulating the vectors in the plot, we can determine the overall material, energy, and work balances before any flow sheet exists. These vectors can be used to begin constructing a flow sheet that represents a process that is as thermodynamically as efficient as it can be in its entirety.

In this article, the GH-space is used a synthesis tool that helps to construct the flow sheet. It can also be used as an analytic tool, for example when an existing flow sheet is checked for thermodynamic flaws. However, the latter is the subject of ongoing research, and falls outside the ambit of this article.

In an article published previously, the graphical technique was applied to gasification processes, through which coal was used to produce synthesis gas (syngas), a gaseous mixture of hydrogen and carbon monoxide. It is a highly versatile feedstock that is extensively used in the production of many hydrocarbon products, including a range of alcohols and synthetic fuels. The ratio of hydrogen and carbon monoxide in the syngas varies according to the use for which it is intended. The production of fuels, for instance, usually requires a ratio of 2:1 hydrogen: carbon monoxide.[13]

Although we continue to use the same technique in this article, the subject in this case is the production of syngas via a steam reforming process, through which light hydrocarbons, such as methane and/or propane, are converted into a gaseous mixture of carbon monoxide, carbon dioxide, and hydrogen.

There are three issues that arise in the context of syngas production:

- Typically, reformers emit some carbon dioxide, and release heat by generating high-temperature steam: the model we propose will suggest ways in which this energy can be harnessed without the need to generate steam.[14]
- A great deal of the existing research on steam reforming[15–17] focuses on improving efficiency by examining the catalysts used. This approach focuses almost entirely on the reaction itself, and gives little consideration to the process as a whole.
- An important goal for the designer is improving the thermal efficiency of the process by the recovery of excess heat and work. High-temperature steam can be put to use, and, therefore, it is important to prevent the loss of such energy. If we can find ways to apply this work potential, we can not only use it in other processes but prevent the harm that wastage of heat and work can do to the environment. In the graphical model we are suggesting, recovery is shown by the use of minimizing exergy (the degree of departure from equilibrium with its environment in a system).[18]

The second section of this article provides an explanation of the graphical technique we have developed, and the way in which it can be used to depict the functioning of processes. As the reasoning is complex, we have illustrated the techniques step by step, to prepare the ground for the section on steam reforming that follows.

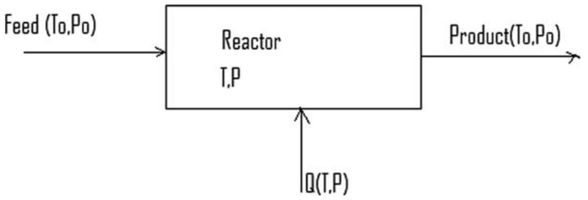

Figure 1. A simple process.

The Graphical Technique

A simple process

The definition of a simple process is one in which the feeds enter and products leave the reactor under ambient conditions.[19] There is also one position in the process operating at temperature T that allows the addition of heat, as is shown in Figure 1. The only irreversibility in a simple process is caused by the temperature at which this heat is added.

The material balance of the simple process is given by

$$0=(\Sigma \upsilon_i N_i)_{\text{products}}-(\Sigma \upsilon_i N_i)_{\text{reactants}} \tag{1}$$

where:

- N_i refers to the amount of component i in either the product or the feed
- υ_i refers to the stoichiometric coefficient of component i

If an energy balance is performed on the simple process, the change in enthalpy across the process can be calculated by

$$\Delta\hat{H}^0_{\text{process}}=Q=\left(\sum_i \upsilon_i \Delta\hat{H}^0_{f,i}\right)_{\text{products}}-\left(\sum_i \upsilon_i \Delta\hat{H}^0_{f,i}\right)_{\text{reactants}} \tag{2}$$

where

- υ_i is the stoichiometric coefficient of the component i.
- The subscript f represents "of formation"
- The superscript 0 represents standard conditions.
- The subscript i represents species i.

This is to say that $\Delta H^0_{\text{process}}$, which is the net heat flow requirement of the process Q, is given by the difference between the enthalpies of formation of the products and the feeds, because both enter and leave at ambient conditions, which removes the enthalpy change attributable to heat capacity.

Similarly, it is possible to calculate $\Delta G^0_{\text{process}}$ (which represents the minimum work requirement W) of the simple process by

$$\Delta\hat{G}^0_{\text{process}}=W=\left(\sum_i \upsilon_i \Delta\hat{G}^0_{f,i}\right)_{\text{products}}-\left(\sum_i \upsilon_i \Delta\hat{G}^0_{f,i}\right)_{\text{reactants}} \tag{3}$$

Where the process requires work and heat (positive values, from Eqs. 2 and 3), these values ($\Delta H^0_{\text{process}}$ and $\Delta G^0_{\text{process}}$) represent the minimum of the amount of heat and work needed to be feasible. If the values were negative, the process would be feasible. The values calculated by Eqs. 2 and 3 would then represent the amount of heat and work that would need to be recovered for the process to be reversible. If the work potential of the heat, or the work itself, from such a process were not recovered, or utilized in some way, the work potential would be lost, and inefficiency would result.

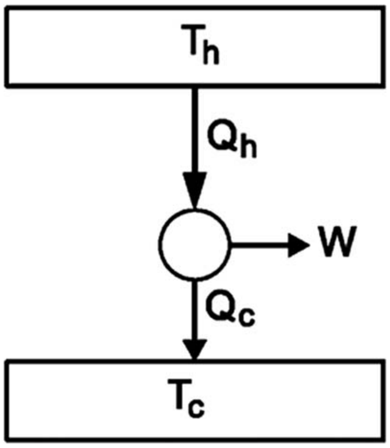

Figure 2. A heat engine depicting the relationship between heat, work, and temperature.

Work addition

Now that the minimum heat and work requirements for a simple process have been defined, the next question is: How are these requirements (heat and work) to be met? Heat addition is self-explanatory: heat is transferred along temperature gradients and is well understood.

But how is work added?

The thermodynamic definition of ΔG, or the work, is given by Eq. 4

$$dG = -SdT + VdP + \sum \mu_i dN_i \tag{4}$$

where μ_i is the chemical potential of species i, dN is the change in the number of moles of species i, dT is the temperature gradient, S is the entropy, V is volume, and dP is the change in pressure.

Equation 4 shows that there are three ways to add work to a process: using heat (TdS term); pressure (VdP term); and change in chemical potential, for example separation (μdN term).

Using heat to add work

In chemical processes, work requirements can be considerable. The bulk of the work is typically transferred via heat, by virtue of the temperature supplied. Processes reject or absorb heat as required by the energy balance, so it is advantageous to use this heat to supply or reject the work from the process simultaneously.

Heat has the potential to carry work by virtue of its temperature, and provides the principle that powers engines, as shown by the diagram of a heat engine in Figure 2.

The maximum amount of work conducted by the heat is given by the well-known Carnot equation for heat engines

$$\hat{W}_c = \hat{Q}\left(1 - \frac{T_c}{T_h}\right) \tag{5}$$

where W_c is the Carnot work, Q is the heat requirements of the process ($Q = \Delta H$ for a process), T_c is the temperature of the cold reservoir, and T_h is the temperature at which the heat is supplied (the hot reservoir).

In an ideal situation, all the work would be carried out by the heat, alternatively expressed as $Q = \Delta H^0_{\text{process}}$ and $W_c = \Delta G^0_{\text{process}}$. This would mean the other two methods of work addition (pressure and chemical potential changes) would not be required. It would also imply that the work from Eq. 5 would be exactly equal to the $\Delta G^0_{\text{process}}$ of the simple process calculated by Eq. 3. It can then be seen that this can happen at only one (Carnot) temperature, which is that at which all the work required/rejected by the process will be conducted by the heat of the process. This would be the ideal operating temperature for the simple process.

However, achieving this temperature often proves unworkable in practice. For example, when the $\Delta H^0_{\text{process}}$ and $\Delta G^0_{\text{process}}$ are very close together, the Carnot temperature will approach infinity; alternatively, when $\Delta G^0_{\text{process}}$ is greater than $\Delta H^0_{\text{process}}$, the Carnot temperature will be below absolute zero. This means that often heat must be added at more reasonable temperatures (resulting in a variation from the Carnot temperature), which results in deficits or excesses in the work requirements of the process. In such cases, the process will have to be designed to accommodate these deficiencies/excesses.

This can be done by turning to the two additional methods for work addition/recovery mentioned previously.

Using pressure to add work

Returning to Eq. 4, we could consider work addition by compression. To solve the integral, we assume an isothermal compression of n moles of an ideal gas

$$\Delta G_{\text{compression}} = nRT \ln\left(\frac{P}{P_0}\right) \tag{6}$$

where n is the moles of gas, R is the universal gas constant, T is the compression temperature, and P and P_0 are the final and initial pressures, respectively.

Equation 6 quantifies the amount of work that must be done on a gas stream to increase its pressure. It is important not to forget the definition of the simple process, in that the products must leave the system at ambient pressure. So, it would be possible to apply Eq. 6 to both the feed and product streams, bearing in mind that the product stream is being decompressed. This makes it possible to calculate the net work requirement for the simple process, which gives rise to

$$\Delta G_{\text{compression,process}} = (n_{\text{in}} - n_{\text{out}})RT \ln\left(\frac{P}{P_0}\right) \tag{7}$$

where n is the moles of gas entering (in) or leaving (out) the system, R is the universal gas constant, T is the compression temperature, and P and P_0 are the final and initial pressures, respectively.

Equation 7 demonstrates an important principle: It is possible to add work to a system using compression only when there are more gas moles entering the system then there are leaving it. If the number of moles does not change, pressure does not add any work to the system; and if there are more moles leaving than entering, work can be recovered from the system.

The useful work that goes into changing the pressure is equal to the isothermal work (see Appendix section Useful Work of Compression is Equal to Isothermal Work for proof), whereas the additional work that is used in an adiabatic compression causes an increase in temperature. Note that the assumption of an ideal gas can be relaxed if so desired.

Using separation to add work

The third method of adding work to a system is via separation. Once again, we assume that the system behaves ideally, although this assumption could be relaxed where desired. The ΔG for mixing will then be given by Eq. 8

$$\Delta G_{\text{mix}} = RT\left(\sum_i x_i \ln x_i\right) \tag{8}$$

where R is the universal gas constant, T is the mixing temperature, and x_i is the mole fraction of component i.

It is worth noting that Eq. 8 contains the appropriate sign to indicate the direction of work flow. In this case, a positive value denotes work addition, which in turn indicates a separation (while a negative sign would refer to a mixing process).

For these ideal systems, the ΔH for separation is zero.

Summary

To reiterate, we have defined a simple process in which both the feed and the products leave the reactor at ambient conditions. In this article, for the purpose of illustrating the graphical technique without getting caught up in the details of more complex calculations, we present all the reaction units as simple processes. However, the assumption of a simple process can be relaxed at any time without affecting the technique; only the final result will change.

The method for calculating the heat and work requirements was defined, and we also showed that there are three ways (heat, pressure, and separation) to add work to the process.

We also showed the useful work added via compression was done isothermally, and defined expressions for work and heat where the components behave ideally. In the interests of clarity (that is, to avoid adding complexity to the calculations), we have used these assumptions throughout this article, although they can be set aside as needed. The overall principles will not change.

Graphical representation of the process work and heat requirements

Having outlined the method of calculating the quantities of heat and work, we can represent them graphically.

The heat and work flows of a process can be drawn onto a ΔH–ΔG plot, hereafter referred to as the GH-space, and we can use the position of the point to describe the nature of the process. We demonstrated this technique in greater detail in our previous paper,[20] in which we divided the plot into various sections and described the nature of the process that belonged to each section.

Other researchers[21] have carried out similar work that also employed a means of plotting ΔH and $T\,\Delta S$. This plot would probably provide a very accurate measure of process efficiency and reversibility.

However, $T\,\Delta S$ is an abstract quantity that is not easily related to an actual, measurable quantity. The plot of ΔH against ΔG provides a simple link between the thermodynamics and the more easily measured quantities of heat and work: ΔH is equal to the heat requirements of a process and ΔG is equal to the work requirements of a process. The next step is to consider a reaction that is carried out as a simple process, as previously defined, to illustrate how it can be plotted in the GH-space.

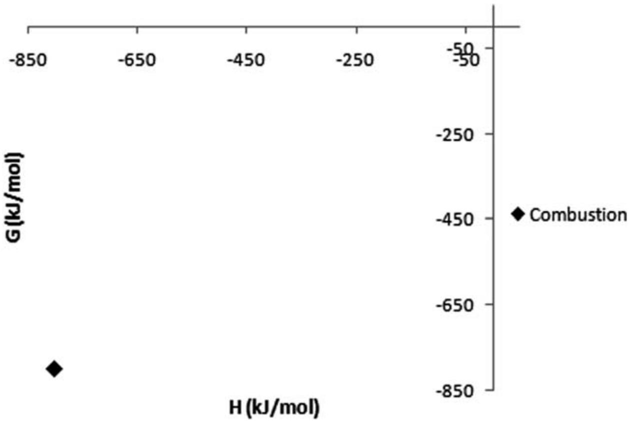

Figure 3. Reaction carried out as a simple process, represented as a point in the GH-space.

Case 1: the combustion of methane in oxygen

The reaction for the combustion of methane in oxygen can be expressed as

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

When Eqs. 2 and 3 are used on this reaction (along with the thermodynamic data provided in Appendix), we find that the reaction is exothermic and work-producing (that is, ΔH and ΔG are both negative values). Having calculated $\Delta H^0_{\text{process}} = -802.35\,\text{kJ/mol}_{CH_4}$ and $\Delta G^0_{\text{process}} = -800.71\text{kJ}\,/\text{mol}_{CH_4}$, we can plot them on Figure 3.

Figure 3 shows the methane combustion reaction drawn onto the GH-space. As can be seen, the point sits in the third quadrant of the axes, as would be expected from an exothermic ($\Delta H^0_{\text{process}}$ is negative) and work-producing reaction ($\Delta G^0_{\text{process}}$ is negative).

This figure also represents the reaction proceeding toward completion, which raises the question: What happens if one or both of the reactants are limited?

If the quantity of both reactants was decreased by half, the reaction (or process) equation would become

$$0.5CH_4(g) + 1O_2(g) \rightarrow 0.5CO_2(g) + H_2O(g).$$

Equations 2 and 3 could then be used again and the ΔH and ΔG recalculated. The alteration in values can be seen drawn onto Figure 4.

Figure 4 shows the values of ΔH and ΔG calculated for differing quantities (1.2, 1, 0.5, and 0.2) of reactants. This is analogous to the "extent of the reaction" (referred to as "extent"), or how much reaction has occurred. It is also clear that limiting how much reaction occurs, decreases the heat and work calculated from Eqs. 2 and 3, and that it does so in a linear fashion on the GH-space.

It should be noted that the "extent of reaction" is not the same as the "conversion". Extent and conversion are related through the process feed, which is not known at the start of the design. The extent is an "amount of reaction", it could also be considered to be a scalar multiplier for the mass, energy, and work balances.

The combustion reaction could thus be represented as a line from the origin to its highest extent, which would represent all the possible extents of reaction. This is illustrated in

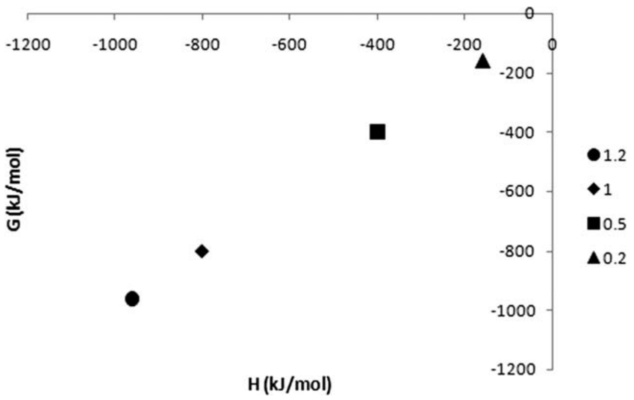

Figure 4. The effect of extent of reaction on the GH-space.

Figure 5. This means that all reactions can be represented as lines on the GH-space. Note that it is possible to have an extent of more than 1 by adding greater amounts of feed rather than less, as represented by the point labeled "1.2" in Figure 4.

The line drawn in Figure 5 represents the combustion reaction occurring at a particular temperature. When ΔH and ΔG are calculated from Eqs. 2 and 3 the temperature of the reaction line is the Carnot temperature as calculated by Eq. 5, where temperature is related to the slope of the process line.

Rearranging Eq. 5

$$T_{\text{Carnot}} = \frac{T_0}{1-\frac{\Delta G}{\Delta H}}$$

The Carnot temperature can be calculated to be 145,000 K. This is an example of a temperature that is unworkable. Clearly, therefore, a modification that allows for more workable temperatures has to be made to assist the calculation of the reaction lines.

Bearing in mind that as long as $C_{\text{p,products}} \approx C_{\text{p,reactants}}$, ΔH is not strongly affected by temperature, we can calculate ΔG for the reaction, at any temperature, from Eq. 5, recalling that $W = \Delta G$. In this way, altering the temperature of a reaction will change the slope of the reaction line on the ΔH–ΔG plot at constant enthalpy, as shown in Figure 6.

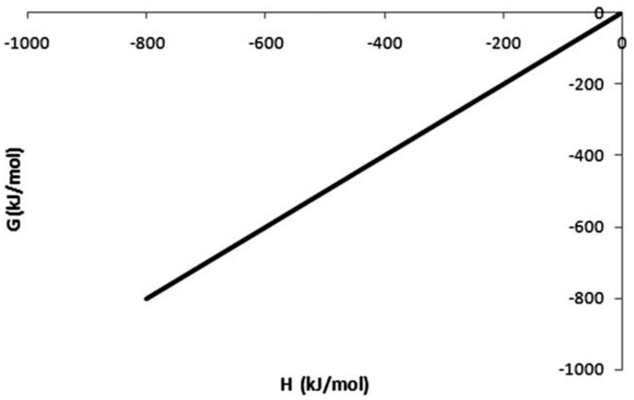

Figure 5. The set of all combustion extents with $0 \leq e \leq 1$ as a simple process.

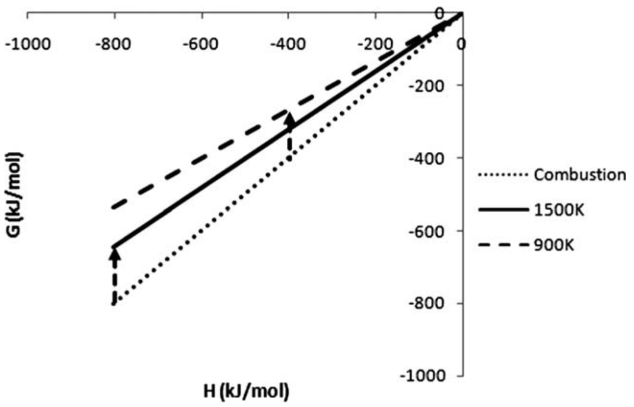

Figure 6. Effect of temperature on a simple process in the GH-space: Combustion

Figure 6 shows the combustion reaction, at its Carnot temperature (150,000 K), as the dotted line; the solid line the combustion reaction at 1500 K; and the dashed line combustion at 900 K. At constant enthalpy, the reaction line has shifted upwards along the dashed arrows as a result of the new ΔG calculated at 1500 K and 900 K, using Eq. 5.

What the graphic in Figure 6 implies is that running an exothermic reaction at a lower temperature decreases the amount of work that can be recovered from the reaction: conversely, running it at a higher temperature increases it. In the case of endothermic processes, using a higher temperature increases the minimum work input required, while a lower decreases the work requirement.

Case 2: combusting methane to form carbon dioxide and water vapor

When methane forms water vapor and carbon dioxide through combustion, the heat and work from combustion is then used to produce additional steam.

The flow sheet of this hypothetical process might look like Figure 7.

The $\Delta H^0_{\text{process}}$ and $\Delta G^0_{\text{process}}$ for the overall complex process shown in this figure can be calculated in two ways. The first of these is to use Eqs. 2 and 3 (or Eqs. 2 and 5, if non-Carnot temperatures are desired) on the "combustion" and "phase change" boxes independently, and add their results.

The second alternative would be to apply the equations to the process as a whole, using the overall feeds and products. In other words

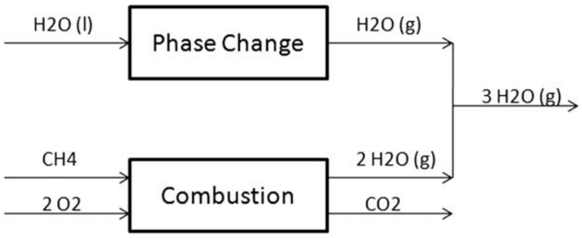

Figure 7. A hypothetical complex process combusting methane to generate steam with mass integration of the steam product.

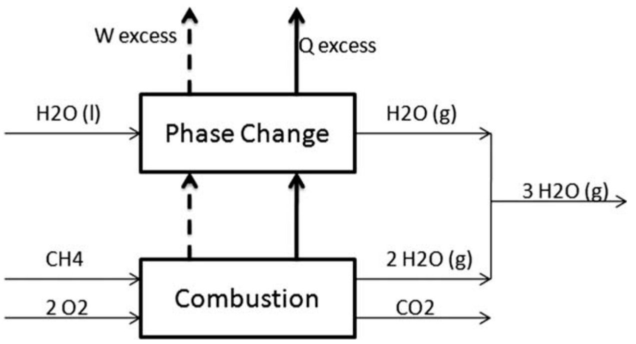

Figure 8. Heat and work flow for the hypothetical complex process.

$$\Delta H_{\text{overallprocess}} = \Delta H_{\text{combustion,process}} + \Delta H_{\text{phase,process}}$$
$$\Delta G_{\text{overallprocess}} = \Delta G_{\text{combustion,process}} + \Delta G_{\text{phase,process}}$$

The heat from the combustion could be used to supply the heat for the phase change. It would also carry work with it by virtue of its temperature. The integration of the heat and work streams can be drawn onto the hypothetical flow sheet shown in Figure 8.

The graphic in Figure 8 shows how the heat from the combustion is used to boil the water. The quantity of heat supplied by combustion is far greater than the amount required by the phase change, so it can be used to carry work (represented by the dashed line). Excess heat could also be represented as an excess work flow. Either way, this excess must be rejected. In general practice, such excesses are simply lost to the environment.

The complex process shown in Figure 8 could also be drawn as an equivalent simple process, as in Figure 9.

In terms of their overall $\Delta H^0_{\text{process}}$ and $\Delta G^0_{\text{process}}$, Figure 7 and Figure 9 are exactly equal. The difference between them rests on the fact that the complex process has two separate units. The advantage of this process is that heat and work can be added or removed at two different temperatures, which increases the number of degrees of freedom in the system. This in turn provides greater opportunity to improve the reversibility of the process, which is not possible in a simple process.

It is clear that the overall ΔH and ΔG for a process is the sum of its individual units. This is not by any means a new result: this principle is already well applied in process energy and work balances. However, it does show that reactions have length (which is defined by the extent of the reaction) and direction (defined by the temperature); and that they can be added together. This means that reactions are not merely lines on the GH-space, they are vectors.

Having established that the heat and work for the overall process is the sum of the heat and work of the units in the process, we can state that not only are reactions vectors on the ΔH–ΔG, but so are the other unit processes of compression and separation. This is to say that any unit process, for which ΔH and ΔG can be calculated, can be represented as a vector on the GH-space.

The next step

In this article, we consider three unit processes: those corresponding to a reactor, a compressor/turbine and a separator. As the compressors are considered as isothermal and the separators ideal, they have no ΔH, and are thus shown as vertical lines on the GH-space. If we were to use adiabatic compressors instead, the compression vector would no longer be vertical, but would have a horizontal component equal to the adiabatic work. This would appear to be similar to that of a reaction vector in that the compressor vector would now have a ΔG and a ΔH value.

Application to Steam Reforming

Defining the system

Having explained the primary idea behind the graphical technique, we can consider how the technique is applied in designing process flow sheets, taking as our example of methane steam reforming to produce syngas. The latter is used to make many products, such as hydrogen, syn-fuels, methanol, ammonia, and waxes. Many of these processes have a reputation for producing and releasing vast quantities of carbon dioxide. By using the GH-space synthesis tool, we can investigate whether (and if so, how) this carbon dioxide production can be avoided; or whether it is simply a thermodynamic limitation of the system.

The steam reforming reaction process is given by

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

Equations 2 and 3 can then be applied to the reforming reaction process, and the heat and work requirements are calculated as

$$\Delta H_{\text{reforming}} = 206.12\,\text{kJ/mol}_{CH_4}$$
$$\Delta G_{\text{reforming}} = 142.16\,\text{kJ/mol}_{CH_4}$$

These are the heat $(206\,\text{kJ/mol}_{CH_4})$ and work addition $(142\,\text{kJ/mol}_{CH_4})$ requirements of a reforming reaction, which also needs gas phase water (steam) as a feed. Because liquid water is the phase that is most readily available, the steam has to be generated. This can be represented as a phase change reaction process (phase)

$$H_2O(l) \rightarrow H_2O(g).$$

Applying Eqs. 2 and 3

$$\Delta H_{\text{phase}} = 44.01\,\text{kJ/mol}_{H_2O}$$
$$\Delta G_{\text{phase}} = 8.56\,\text{kJ/mol}_{H_2O}$$

we find, unsurprisingly, that the phase change reaction also requires an input of heat and work.

The reforming reaction also produces hydrogen and carbon monoxide in a 3:1 ratio. In certain cases, for instance in the production of ammonia or as a first step in high-purity hydrogen production, this may be desirable. However, a ratio of 2:1, which is better suited to downstream processes such

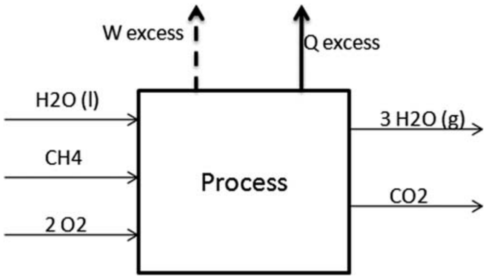

Figure 9. The complex combustion process drawn as a simple process.

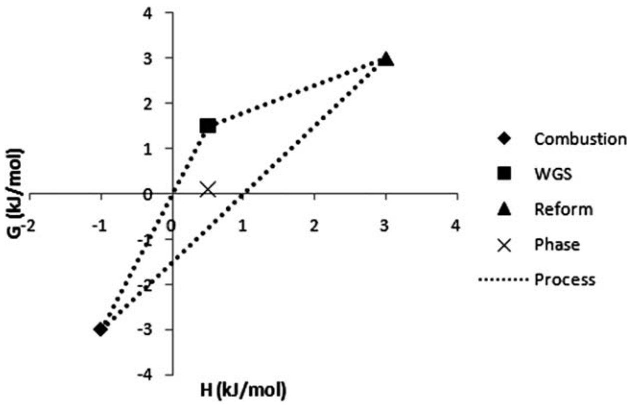

Figure 10. Steam reforming reactions plotted with exaggerated vector angles showing the area of all possible mass, energy, and work balances, and, thus all possible process operating points.

as Fischer–Tropsch synthesis and methanol production, is more commonly used. Changes in the ratio are made possible by the water–gas shift reaction process (WGS)

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g).$$

Again, applying Eqs. 2 and 3

$$\Delta H_{WGS} = 41.19\,\text{kJ/mol}_{CO_2}$$

$$\Delta G_{WGS} = 28.59\,\text{kJ/mol}_{CO_2}$$

The WGS is an equilibrium reaction process. As written, it requires $41\,\text{kJ/mol}_{CO_2}$ of heat and $29\,\text{kJ/mol}_{CO_2}$ of work addition. The WGS equation is written in the opposite direction to what is typical. The direction the material balance equations are written in are, for now, not too important since when the extents of reaction are calculated later, the sign of the extent of reaction will indicate the direction of the material balance.

There are three reactions/processes that require the addition of heat and work. Neither the steam reforming nor the WGS reactions can occur unless the energy requirements are met. These can be supplied through a fourth reaction, combustion

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g).$$

As already shown

$$\Delta H_{combustion} = -800.35\,\text{kJ/mol}_{CH_4}$$

$$\Delta G_{combustion} = -800.71\,\text{kJ/mol}_{CH_4}$$

The combustion reaction process is heat- and work-producing, and thus, can provide all the heat and work required by the other reaction processes.

As we have calculated the enthalpy and Gibbs free energy of all the reactions, we can draw them on the GH-space, as has been done in Figure 10. It is important to note that this figure is not drawn to scale, because in practice the reaction vectors (namely those for the WGS, reforming and phase change) are nearly superimposed, unlike that for the combustion reaction, making it difficult to read the plot clearly.

Figure 10 shows the four reactions for steam reforming drawn onto the GH-space (not to scale). The dotted line joining the three outer reactions depicts the perimeter of an area on the GH-space. The points within this triangular region stand for a portion of the possible material, energy, and work balances that can exist, and represent some of the possible operating points for any steam reforming process. It does not indicate which operating points are best to use, or which processes meet the most desirable specifications for steam reforming.

A quick look at the ΔH and ΔG of the four reactions shows that the combustion reaction provides a great deal more heat and work than is actually needed by the other three reactions put together. As it would be wasteful to provide too much heat and work, we need to control the extent of the combustion reaction so as to provide sufficient heat and work and no more. This can be done by feeding just enough oxygen for the combustion to take place.

There are three constraints on the design of the four reaction process.

1. Because the syngas product will have a hydrogen:carbon monoxide ratio of 2:1, the WGS reaction will have to be adjusted to meet this specification.
2. The extent of the phase change reaction has to be designed to provide just enough steam for the reforming reaction. It is also worth noting that the steam produced by combustion can be used for reforming, allowing the phase change reaction to make up the deficit (if there is one) in the supply of steam.
3. There should be sufficient combustion to provide the correct amount of heat and work (either $\Delta H_{\text{overall process}}$ or $\Delta G_{\text{overall process}}$ should equal zero). This can be achieved through the individual extents of reaction.

The material balance and the ΔH – ΔG plot

We have identified the four reactions that are being considered in the design of the reforming flow sheet as reforming, WGS, phase change and combustion, and defined the design constraints.

With this information, we can perform the material balance on the system

$$N_{CH_4} = N^0_{CH_4} - e_{\text{reform}} - e_{\text{combust}}$$

$$N_{H_2} = N^0_{H_2} + 3e_{\text{reform}} - e_{\text{WGS}}$$

$$N_{CO} = N^0_{CO} + e_{\text{reform}} + e_{\text{WGS}}$$

$$N_{H_2O} = N^0_{H_2O} - e_{\text{reform}} + e_{\text{WGS}} + 2e_{\text{combust}}$$

$$N_{O_2} = N^0_{O_2} - 2e_{\text{combust}}$$

$$N_{CO_2} = N^0_{CO_2} + e_{\text{combust}} - e_{\text{WGS}}$$

where N^0_i is the initial feed of component i, N_i is the remaining component i after reactions have taken place, and e is the extent of reaction.

At this stage, it is useful to set an additional design constraint. There are four unknowns, three constraints are needed. Both the reforming and combustion reactions use methane as their feedstock, so we could take the new design constraint to be that 1 mole of methane in total is fed into the process (although in practice any amount of methane feed could be chosen: it simply becomes a question of scaling). This approach is equivalent to setting the process feed as opposed to the production rate. This means that the reforming and combustion reactions must now share the same 1 mole of methane. This means reforming and combustion "compete" for the same methane feed. To ensure reforming and combustion are able to reach their desired extents the combustion reaction will be controlled by feeding just the right amount of oxygen to limit its extent, the rest of the methane will then be used in reforming. This special constraint is dealt with by the oxygen balance. From the methane balance, assuming the methane reacts to completion with none left unreacted

$$0=1-e_{\text{reform}}-e_{\text{combust}}$$

$$e_{\text{reform}}+e_{\text{combust}}=1$$

From the hydrogen and carbon monoxide material balances, as no hydrogen or carbon monoxide is initially fed to the process, we can calculate

$$\mathrm{N}_{\mathrm{H}_2}=0+3e_{\text{reform}}-e_{\text{WGS}}$$

$$\mathrm{N}_{\mathrm{CO}}=0+e_{\text{reform}}+e_{\text{WGS}}$$

At this point, we must apply Constraint 1 to the material balance in order to obtain the desired H_2:CO ratio. This constraint can be written as

$$\mathrm{N}_{\mathrm{H}_2}=2\mathrm{N}_{\mathrm{CO}}$$

thus substituting the material balance:

$$(3e_{\text{reform}}-e_{\text{WGS}})=2(e_{\text{reform}}+e_{\text{WGS}})$$

$$e_{\text{WGS}}=\frac{1}{3}e_{\text{reform}}$$

What is most significant in this material balance is that for a 2:1 ratio of hydrogen to carbon monoxide the extent of the WGS reaction must always be 1/3 of the extent of the reforming reaction.

Constraint 2 can then be applied to the water material balance. Assume that water will always enter or leave the process in liquid phase only and that the two phases of water are different species. The amount of water initially fed to the process (or the amount of excess water that must be removed from the process afterwards) is equal to the extent of the phase change reaction. Either the initial or final moles of water must be represented as 0. For example, if we consider the final moles of water to be 0, we would be indicating that the process consumes water rather than producing it. From the water material balance, we can derive

$$0=e_{\text{phase}}-e_{\text{reform}}+2e_{\text{combust}}+e_{\text{WGS}}$$

$$e_{\text{phase}}=e_{\text{reform}}-2e_{\text{combust}}-e_{\text{WGS}}$$

In other words, the amount of additional steam that will need to be condensed or recycled is given by the extent of the reforming reaction (which uses steam as a feed) less twice the extent of the combustion and less the extent of WGS, which produce steam (that can be supplied to the reforming reaction). If it turns out that the extent of the phase change reaction is negative, we can infer that the process is actually producing excess water and the phase change reaction needs to proceed in the opposite direction.

An alternative design could take the opposite case and set the initial moles of water to 0, thus assume the production of liquid water, this will make the extent of the phase change reaction positive if the process produces water and negative if it consumes it. In either case, the extent of the phase change will require a simple change of sign.

Finally, we can consider the oxygen balance. If just enough oxygen is supplied to the combustion there will be no excess oxygen remaining. Thus, from the oxygen balance

$$N^0_{\mathrm{O}_2}=2e_{\text{combust}}.$$

It is possible for all the material balances to be written in terms of only one of the reaction extents by substitution. In this article, all the extents have been written in terms of the extent of the reforming reaction. This allows us to choose the extent for the reforming reaction. All the other reaction extents will then have values determined by the material balance, which yields a syngas product of the desired 2:1 specification.

The material balances of all the reforming reactions are given by the following formulations (the extent of the reforming reaction itself is a degree of freedom)

$$e_{\text{combust}}=1-e_{\text{reform}}$$

$$e_{\text{WGS}}=\frac{1}{3}e_{\text{reform}}$$

$$e_{\text{phase}}=\frac{8}{3}e_{\text{reform}}-2$$

At this point, it is possible to select any extent for the reforming reaction. Having done so, we can determine the material balance for the entire process and calculate the ΔH and ΔG for the process as follows

$$\Delta H_{\text{process}}=e_{\text{reform}}\Delta H_{\text{reform}}+(1-e_{\text{reform}})\Delta H_{\text{combust}}+\left(\frac{1}{3}e_{\text{reform}}\right)\Delta H_{\text{WGS}}+\left(\frac{8}{3}e_{\text{reform}}-2\right)\Delta H_{\text{phase}}$$

$$\Delta G_{\text{process}}=e_{\text{reform}}\Delta G_{\text{reform}}+(1-e_{\text{reform}})\Delta G_{\text{combust}}+\left(\frac{1}{3}e_{\text{reform}}\right)\Delta G_{\text{WGS}}+\left(\frac{8}{3}e_{\text{reform}}-2\right)\Delta G_{\text{phase}}.$$

In this equation for $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$, e_{reform} is the degree of freedom. If we vary all the extents of reaction for the reforming reaction between 0 and 1 and calculate $\Delta H_{\text{process}}$ and $\Delta G_{\text{process}}$ at each extent, the design constraints will reduce the area of Figure 10 to a single line, which is shown in Figure 11.

Figure 11 illustrates the operating line for all the possible steam reforming processes that can produce a syngas product that meets the 2:1 H_2:CO product specification, and shows

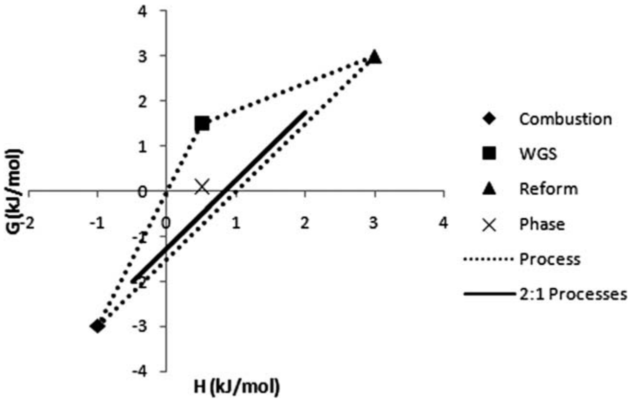

Figure 11. All possible steam reforming processes that produce 2:1 syngas product, shown within the overall mass balance area.

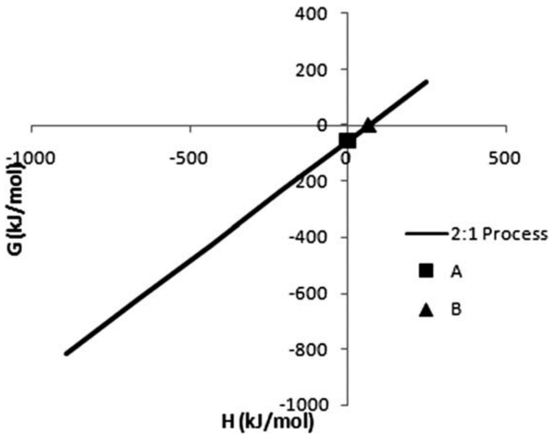

Figure 12. Processes meeting 2:1 specification with the extent of the reforming reaction varying between 0 and 1.

how these 2:1 processes lie within the overall material balance area (It should be noted that Figure 11 is not drawn to scale.).

The area of possible operating points for a steam reforming process has now been reduced to a single straight line by limiting the material balance to a desired product specification. However, before a flow sheet can be developed, we must select a single operating point on the 2:1 operating line. This we can do more conveniently if we draw the 2:1 process line of Figure 11 to correct scale, producing Figure 12.

The line in Figure 12 represents all the possible extents of reaction that could produce a syngas product to the desired specifications. It differs from Figure 11 in that it is drawn to the correct scale, with the actual values of the material and energy balances. In principle, a plant could be designed to operate at any point on the line.

Feasible operating points on the Figure 12 continuum

What if a position in the positive ΔH and ΔG quadrant (to the right of B in Figure 12) was chosen as the operating point? This would represent a process that requires both heat and work. We have already shown that the only available source of heat is the combustion reaction, so choosing to operate in the positive quadrant is not a desirable option because combustion then does not supply sufficient heat.

By the same reasoning, electing to operate between the points A and B is also not advisable. The process in this case produces work, but still needs heat to proceed.

If the process designer chooses to operate at any point to the left of A (in the negative ΔH and ΔG quadrant), the result would be a process that produces both heat and work. In theory, such a process would be functional; but it is not the best option, because it produces too much heat and work. As already noted, the only source of heat and work is the combustion reaction, so that, if too much heat and work is being produced, the extent of that reaction is too great. Operating at such a point is wasteful in terms of energy, and generates excessive amounts of carbon dioxide.

This leads to the conclusion that the best point at which to operate the process at is at A itself. At point A, the process produces work but no heat. Put in other words, by extension of design Constraint 3, the best operating point for the process is an adiabatic process. Therefore, from this point onwards, the operating point of the overall process must always be adiabatic.

It follows that choosing an extent of the reforming reaction ($e_{\text{reform}} = 0.78$) such that the process is overall adiabatic, makes it possible for the designer to determine the process material balance and draw the first postulate flow sheet, as shown in Figure 13.

Figure 13 represents a reformer flow sheet that displays each of the four reactions in its own unit at Carnot reaction temperature (hypothetically, at least), in which the work is carried with the heat, at atmospheric pressure. The operating point represented in Figure 13 is the point marked A on Figure 12.

The split in the methane feed stream is a result of the design constraint introduced with the material balance, in terms of which the reforming and combustion reactions must share a single unit of methane. The water "recycle" stream leaving the WGS unit is necessary because the WGS unit produces some water during its reaction. This water can be added directly to the reformer unit, but if this water is removed from the process instead, the material balance done in the previous section will change. Recycling the water would make the best use of the material flows available.

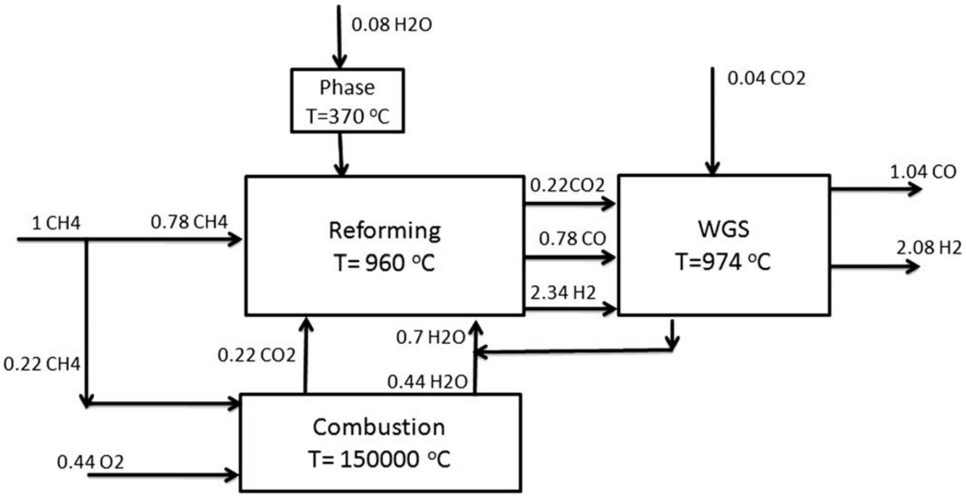

Figure 13. Postulate reformer flow sheet 1.

This process is adiabatic and produces pure components, excess work and a carbon efficiency of 104%. The carbon efficiency is determined by the amount of carbon that leaves the process in the desired product (carbon monoxide, in this case); over the amount of carbon that enters the process with the primary carbon feed (methane, in this case). From Figure 13, it can be seen that there are 1.04 moles of carbon in the carbon monoxide product and 1 mole of carbon in the methane feed. Thus, the carbon efficiency is 104%; the extra "4%" must obviously come from the carbon dioxide feed.

There is a flow of material, heat, and work between the units. Figure 14 represents these different flows with heat as solid lines, work as dashed lines, and mass flows as light solid lines. The circular units in Figure 14 represent heat engines or heat pumps. These "devices" are for illustration purposes. The intention is to show that work is flowing with the heat. Conceptually, this is easiest to show with a heat engine or a heat pump.

Figure 14 shows that all the energy requirements for the process are provided by the combustion unit. As the process is overall adiabatic, the combustion unit provides exactly the right amount of heat for the other process units and the excess work must be rejected from the process in some manner.

A brief examination of Figures 13 and 14 should make it clear that the Carnot temperature for the combustion reaction is neither feasible nor realistic/practical. It is also not a realistic solution to consider the production of pure components, as the products from the reaction units cannot separate themselves. Additionally, the excess work produced by the process should be recovered as real work, to prevent its being lost.

The operating point of the process depicted in Figures 13 and 14 is still the A of Figure 12, which is to say that the process continues to be adiabatic and work-producing.

Note also that the WGS reaction was defined earlier as an equilibrium reaction, but has not been treated as such in Figure 13.

There are still four issues that require resolution before a more complete flow sheet can be designed (or any attempt at simulation made). These issues are set out in the order we propose to address them in the article: WGS equilibrium, operating temperature, pure component production, and work recovery. The ordering is logical. Equilibrium and operating temperatures are parallel considerations, and are, therefore, dealt with simultaneously. Work recovery should be addressed last, as the resolution of all the other issues will have an effect on the amount of work that needs to be recovered, following the maxim that how much work requires recovery needs to be known before it can be recovered. Again, because the full material balance must be known before mixing and separation requirements can be established, this issue is discussed after temperature modification but before work recovery.

Selection of operating temperatures

Figure 13 showed that the Carnot temperature of the combustion reaction would not be practicable operationally. It is, therefore, necessary to modify the temperatures.

The process depicted in Figure 13 produces work at rate of $56\,\mathrm{kJ/mol}_{\mathrm{CH_4}}$. However, Figure 6 demonstrates that changing the operating temperature has an effect only on the ΔG of the process. This means that altering the temperature will affect only the amount of work the overall process will produce/require and not the quantity of heat.

In order to ensure that the reforming reaction proceeds to completion (that is, no methane leaves the reforming reactor), the designer needs to ensure that the reaction occurs at above 800°C. Below this temperature, the equilibrium conversion of methane in the reformer is not 100%, which means that additional separations will be needed to deal with the unreformed methane. The GH-space is capable of dealing with an incomplete methane conversion, but a preferable solution would be to avoid producing any excess methane.

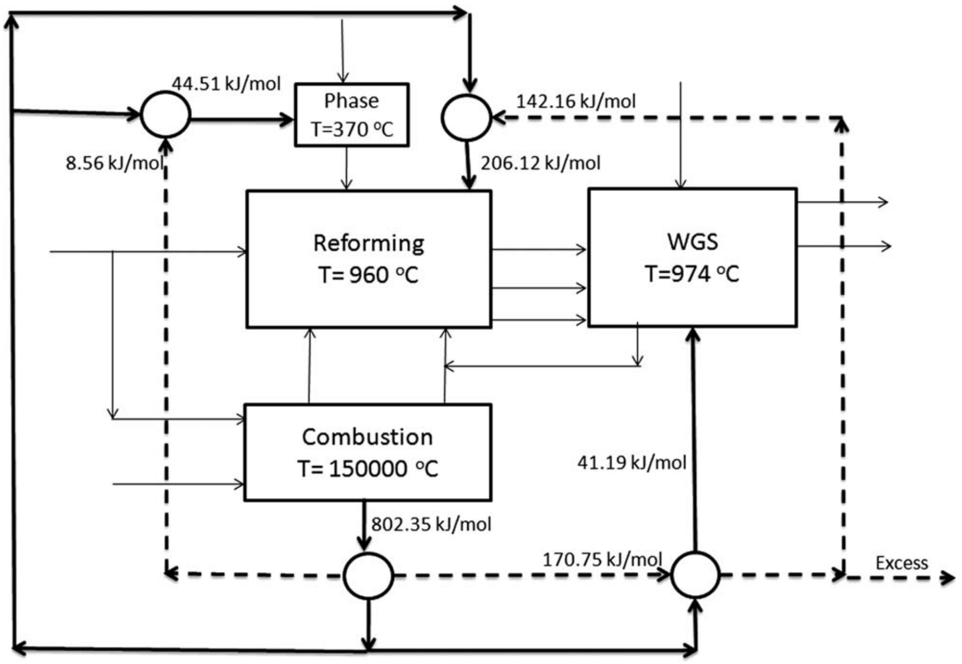

Figure 14. Heat and work flow for the preliminary flow sheet.

As we will show at a later stage, the chosen operating temperature can be treated as a degree of freedom. Any temperature above 800°C could be used: we have selected a reformer temperature of 1000°C to make absolutely sure there is no unreformed methane. This is higher than the thermodynamic complete conversion temperature and below a temperature where the materials of construction will start to become a severe problem and is also in the range of existing methane reforming processes.

As reforming and combustion both use the same mole of methane feed, 1000°C may also be a reasonable temperature at which to perform the combustion reaction. This is analogous to preheating reactor feeds to the reaction temperature.

The temperature change does not affect the material balance shown in Figure 13, so the proportions of the reactions required to produce an overall adiabatic process remain the same. What differs is the amount of excess work produced by the process. This alters the amount of work that could be lost, which in turn would affect how irreversible the process is.

ΔG can now be recalculated for the three reactions, starting with the reaction extents from Figures 13 and 14 and the new operating temperatures, using Eq. 5.

Before the flow sheet can be redrawn, we must select an operating temperature for the WGS reactor. To ensure that the WGS reaction proceeds to a sufficient extent of reaction (as required by the material balance), we have to carry out equilibrium calculations.

From the analysis we carried out prior to plotting Figure 13, we know the desired extent of the WGS reaction. That extent is part of what makes the process adiabatic overall, and produces syngas in the desired ratio. We can use our previous calculations to determine an operating temperature that provides that extent.

Knowing that extent, it is possible to determine an operating temperature that will create an equilibrium that will provide that extent.

The WGS reaction is

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

The equilibrium constant is given by

$$K = \frac{(CO)(H_2O)}{(H_2)(CO_2)} \tag{9}$$

As the ratio of hydrogen to carbon monoxide is 2:1, Eq. 9 reduces to

$$K = \frac{(H_2O)}{2(CO_2)}$$

Equation 9 can easily be written in terms of the material balance around the WGS reaction of Figure 13. A simple alternative would be to write Eq. 9 in terms of the extent of the reforming reaction, using the material balance method shown in section entitled The Material Balance and the ΔH–ΔG Plot.

The equilibrium constant is also given in terms of temperature by the Van't Hoff equation

$$\frac{d\ln K}{dT} = \frac{\Delta H^0_{\mathrm{rxn}}}{RT^2} \tag{10}$$

where $\Delta H^0_{\mathrm{rxn}}$ is the enthalpy of the WGS reaction as calculated by Eq. 2, R is the gas constant, T is temperature, and K is the equilibrium constant.

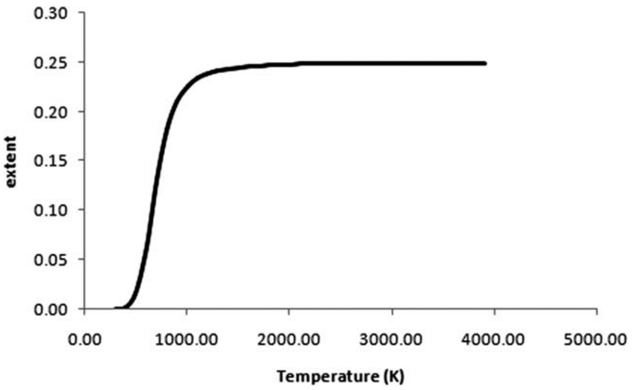

Figure 15. Equilibrium extent and temperature for WGS reaction.By mass balance the required $e_{\mathrm{WGS}} = e_{\mathrm{reform}}/3 = 0.26$.

So, assuming a constant $\Delta H^0_{\mathrm{rxn}}$, the equilibrium is given in terms of the material balance and the temperature. By using Eqs. 9 and 10 appropriately, we can determine the temperature required for a certain extent of reaction, or, conversely, the equilibrium extent for a given temperature.

This can be drawn onto a graph of extent against temperature, as can be seen in Figure 15.

Figure 15 shows that the extent of the WGS reaction asymptotes at 0.25. In other words, no matter how high the temperature, the extent of the WGS equilibrium never exceeds 25%.

However, Figure 13 indicates that the extent of the WGS reaction needs to be 0.26. According to Figure 15, the maximum possible extent is 0.25. This means that the required extent of reaction of 0.26 cannot be accomplished merely by increasing the temperature.

We carried out the equilibrium calculation using only what was already available within the system (which is defined by the mass, energy, and work balance that lead to an adiabatic process overall). Le Chatelier's principle holds that changing the amounts of feed or product can alter the equilibrium. In this case, the latter are set by the product specification, and the hydrogen feed to the WGS reactor is fixed by the reforming reaction. The only other way to increase the extent of the WGS reaction to the desired level is, therefore, to increase the carbon dioxide feed to the WGS reactor.

This means there is an additional degree of freedom. The greater the excess carbon dioxide that is added, the lower the necessary reaction temperature will be.

If the carbon dioxide added is defined as a quantity X, then Eq. 9 will become

$$K = \frac{(H_2O)}{2(X + CO_2)}$$

As mentioned earlier, the Carnot temperature, shown to be 701°C (974 K) in Figure 13, would be the ideal operating temperature, although catalyst operating temperature may affect the choice of temperature. As we know the desired temperature and the required extent, we are able to calculate the amount of carbon dioxide (X) that should be added.

After modifying the reaction temperatures and considering the equilibrium of the WGS reactions, the postulate flowsheet now becomes Figure 16:

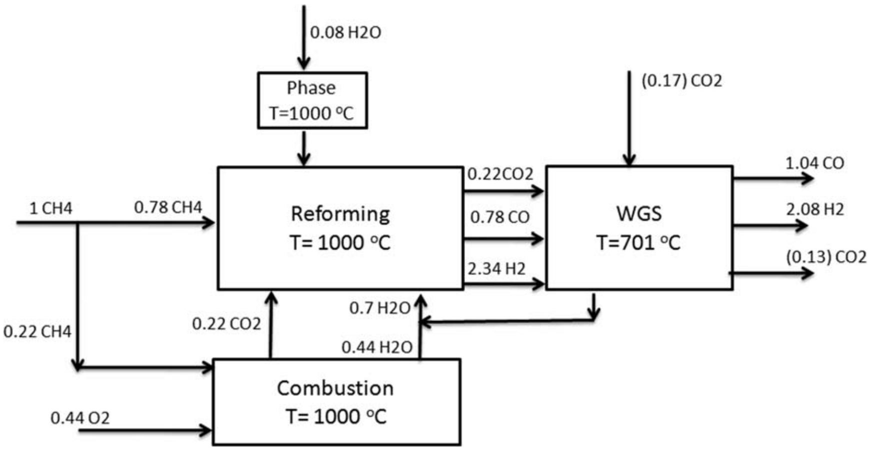

Figure 16. Postulate flow sheet 2 for modified temperature.

Figure 16 shows the flow sheet modified for more reasonable operating temperatures. This process is still adiabatic overall, is a net consumer of carbon dioxide, and produces work at approximately $2\,\mathrm{kJ/mol}_{\mathrm{CH}_4}$. The material and energy balances have not been affected; only the work balance has changed. This means that the flow sheet in Figure 16 is still operating at the point A of Figure 12 but it has now moved vertically along the ΔG axis, changing the amount of work that needs to be recovered.

Figure 16 does not represent the most efficient way to draw the flow sheet. Because the reforming, combustion, and phase change units all operate at the same temperature, we could put these three reactions into a single unit and call it the reformer. Another aspect of this figure worthy of note is that the WGS reactor is emitting less carbon dioxide than it is being fed. It might, therefore, be preferable to reuse the carbon dioxide that is being vented, and make up the carbon dioxide that was consumed in the WGS reaction with a fresh flow of carbon dioxide.

Making these changes results in a new flow sheet, Figure 17.

Figure 17 is a reproduction of Figure 16, but with the carbon dioxide recycle added and the reforming, combustion and phase change reactions combined into a single unit. This process remains adiabatic, work-producing, and carbon dioxide-absorbing, as the overall material balance of the flow sheet has not changed.

In order to be able to recycle water and carbon dioxide, these components must be separated. This forms the subject of the next section.

Pure components: mixing and separation

Having considered the effect of operating temperature on the flow sheet, we turn our attention to the mixing and separation of components.

In Figures 16 and 17, the streams leaving the two reactors will be mixtures and not pure components. We will consider two instances of mixing: that of the products leaving the reformer and that of those leaving the WGS. This mixing can be handled as a vector with a magnitude defined by Eq. 8, as is illustrated in Figure 18.

The direction of the mixing vector will always be vertical, as there is no enthalpy of mixing in the case of ideal mixing. It will also point in a negative direction (downward), as mixing is the opposite of separation (Separation has a positive—upward—direction, because separation always requires work.).

Similarly, we have to separate the mixture leaving the WGS reactor into separate streams of water, carbon monoxide and the product mixture of syngas in order to recover the carbon dioxide and water recycles in Figure 17.

As in the case of temperature modification, the mixing/separation terms have no effect on the proportion of the reactions needed to create an adiabatic process overall, so

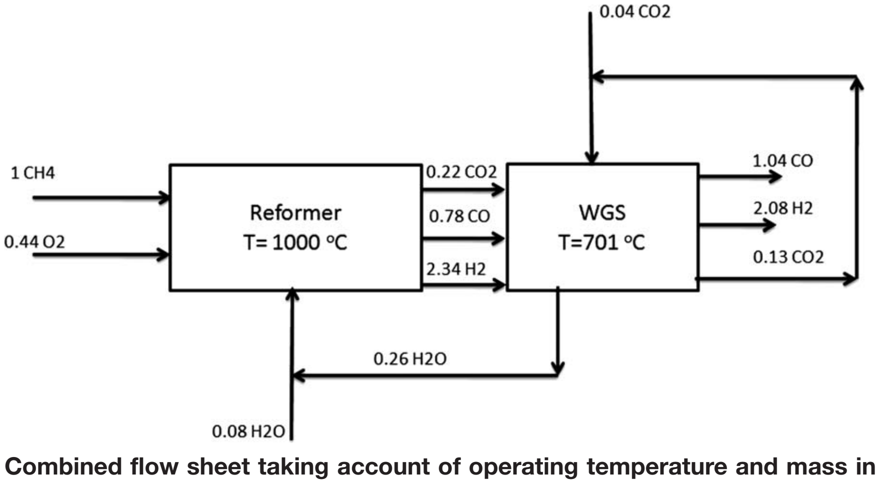

Figure 17. Combined flow sheet taking account of operating temperature and mass integration.

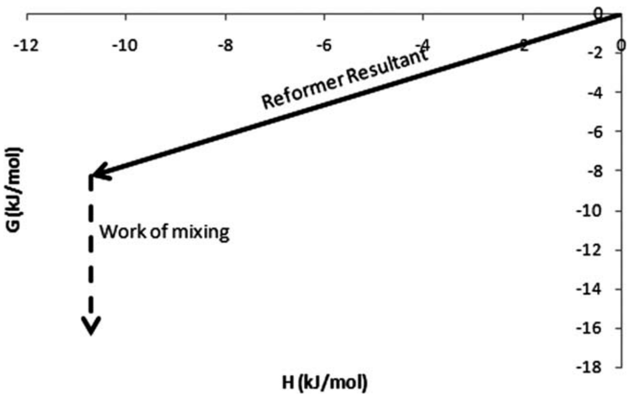

Figure 18. The pure component reformer unit resultant vector being added to the mixing vector.

the material balance remains unchanged. What does alter is the amount of excess work that the process will produce. Mixing will increase it, while separation will decrease it.

After performing the vector additions, we can draw the next postulate flow sheet, Figure 19.

Figure 19 shows a flow sheet in which all the mixing and separation terms have been taken into account. As in all the previous flow sheets, this process remains adiabatic and carbon dioxide-consuming. What is different from Figure 18 is that the amount of work that the process in Figure 19 produces is approximately $14\,\mathrm{kJ/mol}_{\mathrm{CH}_4}$.

Work recovery

Thus far we have shown that all the flow sheets produce amounts of work that vary according to the operating temperatures and whether the effects of mixing and separation are incorporated. The excess work released from the process needs to be recovered in some way. Failing that, the work will simply be lost to the environment. The best way to recover this work would be via shaft work, which, in the case of generators, would take the form of electricity.

However, up to this point we have given no consideration to pressure, which, as previously discussed, provides a means of adding or removing work from a process.

The calculations leading to Figure 18 revealed how much work would need to be recovered from the process. We have also defined the material balance for the process. That means we can use Eq. 7 to determine the only unknown quantity remaining, the pressure.

Equation 7 leads to the finding that a pressure of 8.8 atmospheres would allow the recovery of the excess work generated by the process depicted in Figure 19.

This allows a final flow sheet, Figure 20, to be drawn.

The process shown is adiabatic overall, has a carbon efficiency of 104%, generates electricity and operates at the reasonable pressure of 8.8 atmospheres.

The placement of the final turbine in the process raises an interesting design problem. This turbine can be placed before the separator, as it has been in Figure 20. Alternatively, two separate turbines can be positioned after the separator, one turbine on the syngas product stream and another on the carbon dioxide stream leaving the separator. This choice depends on factors such as the difference in cost of fitting one turbine or two, and whether the separation can be performed more easily at a low or a high pressure. The total quantity of work recovered will remain unchanged, regardless of the turbine placement.

Using the flow sheet in Figure 20, we can now illustrate the heat and work flows within the process. This can be seen in Figure 21.

Figure 21 is identical in mass flow to Figure 20, but also shows the flow of heat and work within the process. Heat is represented by the thick lines, work by the dashed lines, and material by the thin lines.

As can be seen, the first reactor (reformer) is exothermic. By virtue of its temperature, the heat leaving the reformer carries work with it. The heat is transferred to the endothermic WGS reactor, but at a different temperature. This means that the work made available by the reformer heat is greater than the work required by the WGS reactor, creating an excess. Along with the additional work generated by mixing, this excess is recovered, by means of pressure, to generate electricity in a turbine.

The recovery of excess work is accomplished by integrating the feed compressors with the product turbine. Work is required to increase the pressure of the feeds, whereas work is recovered by decreasing the pressure of the products through a turbine. As the amount of gas leaving the process is greater than the amount that enters that process, the amount of work recovered by the turbine is greater than that

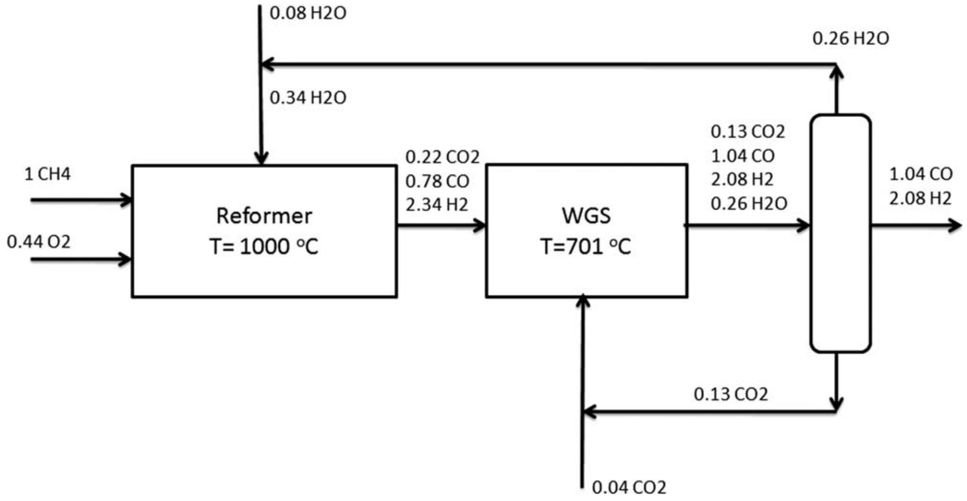

Figure 19. Postulate flow sheet 3 with mixing and separation

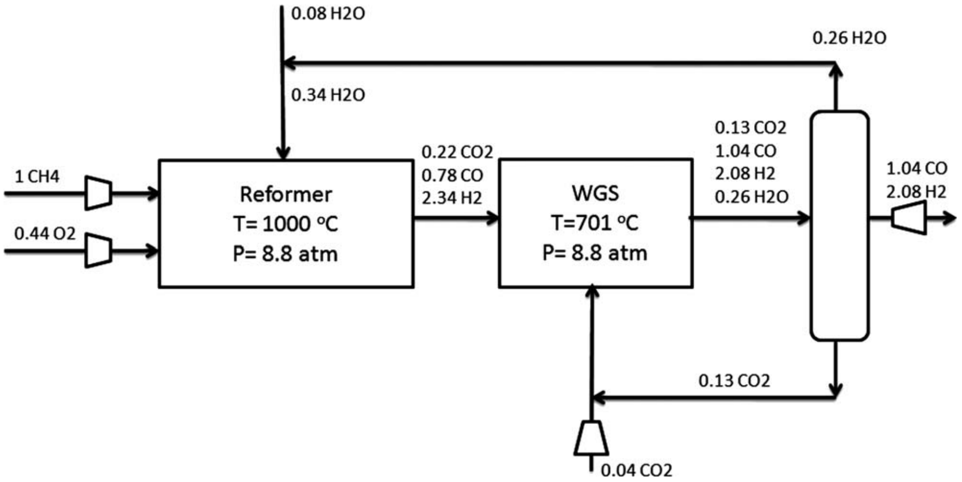

Figure 20. Near reversible steam reforming process with work recovery.

required by the compressors. The turbine can provide the work to operate the compressors, and the excess could then be connected to an electrical generator, or used for some other purpose.

Simulation in ASPEN Plus

Up to this point, we used the graphical technique to create the flow sheets. We can then begin entering these specifications into a simulator to investigate whether there was any agreement between the simulator's calculations and those we used to apply the graphical technique.

Having selected the widely-used chemical process simulator ASPEN Plus, we introduced the process shown in Figure 20 as input.

The model we chose for the reformer reactor was RSTOIC, which is simply a stoichiometric reaction model. It was unnecessary to use a more sophisticated version because in making our original calculations we assumed that the temperature was high enough for the reaction to approach completion. The equilibrium calculations were verified with the simulator and they were both in agreement.

For the WGS reactor, we used an RGIBBS model, which utilizes the technique of finding the equilibrium by locating the minimum Gibbs free energy in the reactor. The equilibrium calculations that were carried out in the development of Figure 20 made use of a slightly different technique, but the results were expected to be similar.

When creating the ASPEN flow sheet, we needed to take special care to make allowance for the assumption that the products and feeds of each reactor should be at the same temperature. We also noted that the treatment of the phases of water at certain temperatures could cause problems.

Having addressed these issues, we ran the simulation.

The result of the simulation was a perfect agreement in the material balance of the simulation and flow sheet. In terms of the energy flows, the simulation flow sheet was very slightly exothermic (about 300 W), whereas the manual flow sheet was adiabatic. The discrepancy is small, however, and could be attributed to issues like differences in the thermodynamic data used.

Conclusion

In this article, we have shown how the flows of heat and work can be used to design a thermodynamically optimal flow sheet for a process. The method described in this article

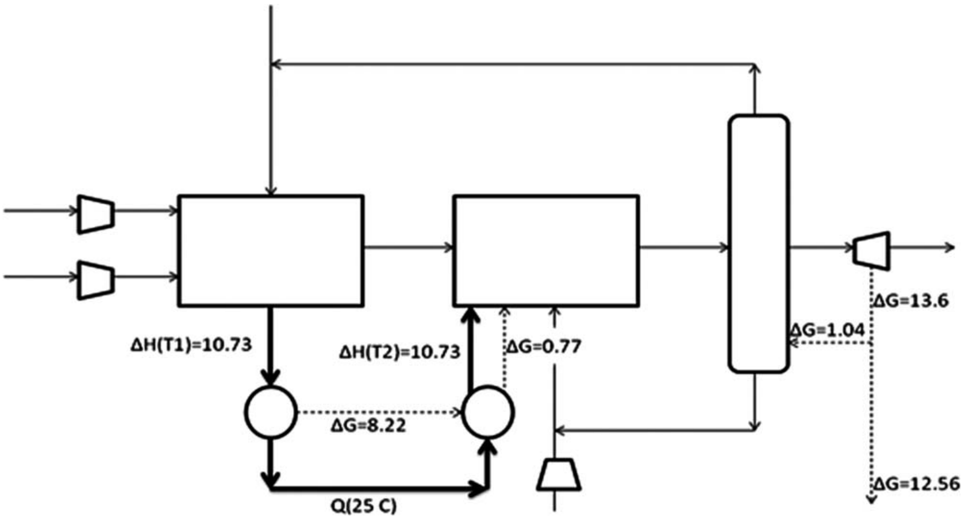

Figure 21. Flow of heat (thick solid lines) and work (dashed lines).

Table 1. Summary of Lost Work with Increasing Process Complexity

Figure Number	Excess Work (kJ/mol)	Comment
13	12.6	Impossible operating temperature
17	2	Ideal case. No mixing or separation considered
20	14	Work recovered with compression/turbine system

can be applied to any process, of any complexity, on a simple two-dimensional set of axes.

This process flow sheet depicts a process that has a carbon efficiency of 104%, is adiabatic (provides its own heat), and produces work as electricity.

By starting with a simplistic case and adding ever-increasing complexity, we improved the flow sheet progressively to the point at which it could be presented in this article.

In Table 1, we show the steps in flow sheet development, along with the potential losses of work if it is not recovered.

Perhaps the greatest advantage of the flow sheet depicted in Figure 20 is that it is a carbon dioxide absorber, as the process uses CO_2 as a feed stock.

Given the design constraint that the process must be adiabatic overall, a carbon efficiency of 104% represents the theoretical thermodynamic limit for this synthesis gas production. However, syngas production is typically only one step within a larger process (syngas being fed into Fischer–Tropsch or methanol synthesis or the hydrogen being used in ammonia synthesis).

It should be noted that supplying too much oxygen to the reformer unit can cause inefficiencies, in that it would allow the combustion reaction to proceed too far, leading to losses in heat and, by extension, work. Additional inefficiencies might arise from practical considerations such as limitations in construction materials.

The flow sheet, Figure 20, represents an ideal situation, what the best possible flow sheet might look like. It provides a basis from which new processes may be developed, and existing processes improved.

The GH-space is a tool that allows the designer to interpret processes and identify major losses. This provides the designer with a valuable indicator of the modifications that should be made to improve the efficiency of the process under scrutiny.

The technique demonstrated in this article is a departure from the traditional method of designing and optimizing a process, one unit at a time. Instead, we have proposed that it may be better to consider a process in terms of the interactions of all the units together, so that it can be designed and optimized as a whole.

Notation

atm = atmospheres
°C = degrees Celsius
e_i = extent of reaction i
g = gas phase
GH-space = the enthalpy-Gibbs free energy plot
ΔG = change in Gibbs free energy
$\Delta G^0_{f,i}$ = gibbs free energy of formation at standard conditions
$\Delta G^0_{\mathrm{rxn}}$ = gibbs free energy of reaction at standard conditions
ΔH = change in enthalpy
$\Delta H^0_{f,i}$ = enthalpy of formation of substance i at standard conditions
$\Delta H^0_{\mathrm{rxn}}$ = enthalpy of reaction at standard conditions
K = degrees Kelvin
K_i = equilibrium constant of reaction i
kJ/mol = kilo-joule per mole
l = liquid phase
N_i = amount of component i
n = moles entering the system
P = pressure
P_0 = ambient pressure (1 atmosphere)
Q = heat
R = gas constant
s = solid phase
T = temperature
T_0 = ambient temperature (298 K)
W = work
WGS = water–gas shift reaction
x_i = mole fraction of component i
v_i = stoichiometric coefficient of component i

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Appendix: Thermodynamic Property Data

Useful work of compression is equal to isothermal work

Table A1. Standard Enthalpies and Gibbs Free Energies of Formation

	H (kJ/mol)	G (kJ/mol)
H_2O(l)	−285.83	−237.13
H_2O(g)	−241.82	−228.57
CO	−110.50	−137.20
CO_2	−393.51	−394.36
CH_4	−74.80	−50.79

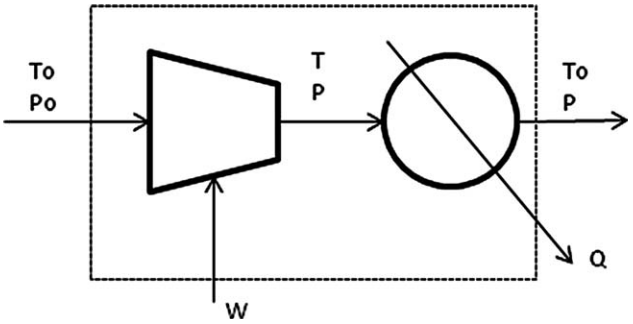

Figure A1. An isothermal compressor.

The diagram, Figure A1, shows a compression system. Material enters the compressor at the initial temperature and pressure, T_0 and P_0.

Work is added adiabatically to the compressor where the temperature and pressure increase to T and P.

The material is then cooled by an amount Q to reduce the temperature back to T_0 and at the pressure P.

An energy balance can be performed over the dashed block

$$H_{\text{in}} + W = H_{\text{out}} + Q$$

Assuming that the enthalpy of the material in the system is not a strong function of pressure, which means the enthalpy of the material entering the system, is nearly equal to the enthalpy of the material leaving the system.

This reduces the energy balance to

$$W = Q$$

An entropy balance can also be performed. Assuming a reversible system this becomes

$$S_{\text{in}} = S_{\text{out}} + \frac{Q}{T_0}$$

And by definition

$$G_{\text{in}} = H_{\text{in}} - T_0 S_{\text{in}}$$
$$G_{\text{out}} = H_{\text{out}} - T_0 S_{\text{out}}$$

Performing the necessary algebra reduces all this to

$$W = G_{\text{out}} - G_{\text{in}}$$

where G_{out} is the Gibbs free energy at pressure P and temperature T_0 and G_{in} is the Gibbs free energy at pressure P_0 and temperature T_0.

This means that the useful work that increases the pressure is equal to the isothermal work. The excess work that is added during an adiabatic compression only increases the temperature not the pressure.

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