# Entropy: Esoteric Concept or Utility Infielder?

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## Introduction

Entropy and the second law of thermodynamics are topics which are generally covered in the undergraduate thermodynamics courses in the chemical engineering curriculum, Heat engines and Carnot cycles are often used as examples and, while beneficial to understanding the overall implications of the second law of thermodynamics, do not serve to connect these important ideas to more realistic problems encountered by chemical engineers in other subject areas. The usefulness of entropy and the second law to aid in understanding chemical engineering unit operations is a topic which is often overlooked in the traditional undergraduate chemical engineering sequence.

The conservation of mass and conservation of energy are analogous to the pitcher and catcher on a baseball team: they each serve a single purpose. The second law, in comparison, is extremely versatile, and can be used for a variety of purposes, much like a utility infielder. One can use the second law to determine whether a process will operate as stated, to evaluate inefficiencies in process operation, and to determine process operating limitations among others. Unfortunately, the second law is often treated as a pinch hitter rather than a utility infielder: brought out of the dugout only when the starters do not yield the desired result. That the second law is sometimes not included as part of the starting team in routine evaluation of thermodynamics problems places students at a disadvantage.

The majority of general thermodynamics textbooks designed for undergraduate use [for example, Moran and Shapiro, 1995; Cengel and Boles, 1994] incorporate a significant amount of material on the second law and present a variety of applications of the second law through examples and chapter problems. In these texts, the examples and problems focus primarily on problems where the second law is utilized to analyze the irreversibility of a process or the performance of a device. The majority of these examples and problems deal with pure components. Mixtures are generally ideal gas mixtures and the examples and problems tend to be very similar in nature - evaluation of the entropy change of mixing or the entropy production when two pure gas species are mixed together.

The application of the second law of thermodynamics to separations problems is of particular interest to chemical engineers. Unfortunately, with currently available textbooks for instruction in undergraduate chemical engineering thermodynamics and mass transfer operations, this topic is often overlooked. There are advanced and/or graduate level texts where this material is discussed [King, 1980; Henley and Seader, 1981], Additionally, the second law is often presented in a manner such as to limit its application to realistic problems involving mixtures. It is in the application to these problems where the second law can provide enlightenment. Particularly

well suited to mixture problems is the use of the combined first/second law of thermodynamics. Many important features of separations can be readily explained through examination of the combined first/second law of thermodynamics. This paper focuses on two such examples.

**Background**

The classic approach to thermodynamics involves the use of the conservation of mass and energy principles along with the second law. Focusing on open systems, the general conservation of mass principle is written [Moran and Shapiro, 1995; Sandler, 1989]:

$$\frac{dm_{cv}}{dt} = \sum_{in}\dot{m}_i - \sum_{out}\dot{m}_i \tag{1}$$

The conservation of energy principle written for this open system is:

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum_m \dot{m}\left[ Hi + \frac{V_i^2}{2g_c} + \frac{gZ_i}{g_c} \right] - \sum_{out}\dot{m}_i\left[ H_i + \frac{V_i^2}{2g_c} + \frac{gZ_i}{g_c} \right] \tag{2}$$

The use of these conservation principles is instilled in the undergraduate student. Written in this general form for multiple inlet/ multiple outlet systems, the undergraduate student becomes conversant with the relative importance of the various terms in these expressions and often utilizes keywords to simplify the general form to the specific form valid for a particular problem.

The second law formulated into a balance equation is written:

$$\frac{dS_{cv}}{dt} + \sum_{in}\dot{m}_i S_i - \sum_{out}\dot{m}_i S_i = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{\sigma}_{cv} \tag{3}$$

The last term in this expression, $\dot{\sigma}_{cv}$, is the rate of entropy production. In Smith and van Ness [1987], this term is denoted $\Delta S_{univ}$. For irreversible processes, this term must be positive; for reversible processes, it is zero; and for processes which are impossible, it is negative. The difficulty with this formulation is that students do not necessarily connect this quantity to the lost work for the system. If one assumes that heat is transferred to or from a single reservoir maintained at a temperature of $T_{surr}$, then this balance can be written:

$$\frac{dS_{cv}}{dt} + \sum_{in}\dot{m}_i S_i - \sum_{out}\dot{m}_i S_i = \frac{Q_{cv}}{T_{surr}} + \dot{\sigma}_{cv} \tag{4}$$

If one considers only steady state problems (which encompasses the vast majority of separations problems that one might encounter), then the accumulation terms in equations (1) through (4) are zero, and the combined first/second law of thermodynamics can be obtained through combination of equations (2) and (4) to eliminate the rate of heat transfer, $\dot{Q}_{cv}$. Retaining the term involving the entropy production rate, this yields:

$$\dot{W}_{cv} + T_{surr}\dot{\sigma}_{cv} = \sum_{in}\dot{m}_i\left[ H_i + \frac{V_i^2}{2g_c} + \frac{gZ_i}{g_c} - T_{surr}S_i \right] - \sum_{out}\dot{m}_i\left[ H_i + \frac{V_i^2}{2g_c} + \frac{gZ_i}{g_c} - T_{surr}S_i \right] \tag{5}$$

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The term, $T_{surr}\dot{\sigma}_{cv}$, is the irreversibility or lost work, $\dot{W}_{lost}$. The use of this form is particularly informative in a large number of the commonly examined problems in undergraduate thermodynamics. For example, the performance of a turbine (pump) compared to the performance of an isentropic turbine (pump) is readily undertaken with this form. For a single inlet/single outlet turbine (or pump) with negligible kinetic and potential energy change, equation (5) reduces to:

$$\dot{W}_{cv} + T_{surr}\dot{\sigma}_{cv} = \dot{W}_{cv} + \dot{W}_{lost} = \dot{m}\left[H_{in} - T_{surr}S_{in}\right] - \dot{m}\left[H_{out} - T_{surr}S_{out}\right] \tag{6}$$

To evaluate the power output for the isentropic turbine (pump), one sets $S_{in}$ equal to $S_{out}$, the lost work to zero, evaluates the outlet enthalpy given the outlet pressure and inlet entropy, and uses the simplified equation (6) to compute the power output (input). For the performance of the turbine (pump), one evaluates the state properties, enthalpy and entropy, for the given inlet and outlet streams, and substitutes to obtain the power output (input) for the actual device. The lost work is always positive and in the case of adiabatic operation for a turbine (pump) is equal to the entropy contribution on the right side of equation (6). The concept of lost work is perhaps more meaningful to students compared to $\Delta S_{univ}$ utilized by Smith and van Ness [1987], This formulation immediately reveals to the student that one cannot obtain the isentropic work from a turbine and that one must supply more than the isentropic work to a pump. The isentropic efficiency, defined as actual work divided by isentropic work for a turbine and isentropic work divided by actual work for a pump, is sometimes confusing to undergraduate students. Utilizing the combined first/second law can provide this information in a more recognizable form, The combined first/second law can also provide substantial insight into mixing and separation problems.

**Application to Mixtures and Separation Problems**

A very common example used to demonstrate the irreversibility of mixing processes is the mixing of pure gaseous components to forma mixture, with equilibration of the mixture at a specified temperature and pressure. For example, consider the general problem when Tank A contains gas A at $T_A$ and PA, while tank B contains gas B at $T_B$ and $P_B$. Initially isolated from each other, a valve between the rigid, insulated tanks is opened and the gases allowed to equilibrate. One additional item of information must be given for each tank: either the initial number of moles of gas in the tank, $n_{i,0}$ or the volume of the tank, Vi. Assuming that the pressure is sufficiently low that the ideal gas equation of state adequately describes the behavior and that heat capacities are independent of temperature, one can use the first law to determine the final temperature of the equilibrated system:

$$T_{final} = \frac{n_{A,0}C_{v,A}T_A + n_{B,0}C_{v,B}T_B}{n_{A,0}C_{v,A} + n_{B,0}C_{v,B}} \tag{7}$$

The final pressure is found using the ideal gas law for the combined system:

$$P_{final} = \frac{(n_{A,0} + n_{B,0})RT_{final}}{(V_A + V_B)} \tag{8}$$

The entropy change for the process is given by:

$$n_{TOTAL}\Delta S = (n_{A,0} + n_{B,0})S^{IG}(T_{final}, P_{final}, y_i) - (n_{A,0})S^{IG}(T_A, P_A, y_i) - (n_{B,0})S^{IG}(T_B, P_B, y_i) \tag{9}$$

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For an ideal gas mixture, the entropy is given by [Sandler, 1989]:

$$S^{IG}(T,P,y_i) = \left(\sum_{i=1}^{N} y_i C_{p,i}\right) \ln\left(\frac{T}{T_{ref}}\right) - R \ln\left(\frac{P}{P_{ref}}\right) - R \sum_{i=1}^{N} y_i \ln(y_i) \tag{1o}$$

For a pure gas (N=1), only one term from each summation contributes with $y_1 = 1$. Thus, equation (1 O) can be used for either a pure gas or a mixture.

Consider the case where oxygen is contained in both tanks A and B. The heat capacities, C, and $C_p$, are assumed to be constant and equal to 5R/2 and 7R/2, respectively. Tank A contains 1 gmol of oxygen at a temperature of 293 K and a pressure of 1.5 bar. Tank B contains 2 gmol of oxygen at a temperature of 373 K and a pressure of 3 bar. The valve is opened and the system is allowed to equilibrate. The final temperature and pressure are determined using equations (7) and (8) and found to be 346.3 K and 2.34 bar, respectively. The entropy change for this equilibration process can now be determined. For the final state and for the two initial states, $y_1 = 1$. Substitution of the final temperature and pressure along with the initial conditions in each tank yields:

$$n_{TOTAL} \Delta S = (n_{A,0} + n_{B,0}) S^{IG}(T_{final}, P_{final}, y_i) - (n_{A,0}) S^{IG}(T_A, P_A \, y_i) - (n_{B,0}) S^{IG}(T_B, P_B, y_i)$$

$$= (3 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{346.3K}{T_{ref}}\right) - R \ln\left(\frac{2.34 \text{bar}}{P_{ref}}\right) - R(1) \, \ln(1) \right]$$

$$-(1 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{293K}{T_{ref}}\right) - R \ln\left(\frac{1.5 \text{bar}}{P_{ref}}\right) - R(1) \ln(1 \right] \tag{11}$$

$$-(2 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{373K}{T_{ref}}\right) - R \ln\left(\frac{3.0 \text{bar}}{P_{ref}}\right) - R(1) \ln(1) \right]$$

All of the terms involving $T_{ref}$ and $P_{ref}$ sum to zero. Evaluation gives an total entropy change for the process of + 0.12 J/K.

If one now replaces the oxygen in tank B with nitrogen and carries out the same evaluation, the irreversibility of the mixing process becomes quite apparent. Replacement with nitrogen (2 gmoles at 373 K, 3 bar; the same conditions as before) yields no change in the calculated final temperature and pressure - these remain 346.3 K and 2.34 bar, However, in the evaluation of the entropy change for the process, the final state is now a mixture with $y_1 = 0.33$ and $y_2 = 0.67$. Thus, the entropy change is given by:

$$n_{TOTAL} \Delta S = (3 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{346.3K}{T_{ref}}\right) - R \ln\left(\frac{2.34 \text{bar}}{P_{ref}}\right) - R(.33) \ln(.33) - R(.67) \ln(.67) \right]$$

$$-(1 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{293K}{T_{ref}}\right) - R \ln\left(\frac{1.5 \text{bar}}{P_{ref}}\right) - R(1) \ln(1) \right] \tag{12}$$

$$-(2 \text{gmol}) \left[ \left(\frac{7R}{2}\right) \ln\left(\frac{373K}{T_{ref}}\right) - R \ln\left(\frac{3.0 \text{bar}}{P_{ref}}\right) - R(1) \ln(1) \right]$$

Evaluation gives an entropy change for the process of+ 2.021 J/K, 17 times larger than when the equilibration involved the same gas in each tank. The magnitude of this change compared to that for the equilibration of a pure gas can help to reinforce the irreversible nature of the mixing process.

While this example helps students to recognize the implications of mixing two different gases together, a further analysis involving the combined first/second law can provide even more meaningful information with regards to separations. As a followup example to the mixing problem, one considers the work required to restore each system to its original state. Thus, beginning with 3 gmol/min of oxygen at 346,3 K and 2.34 bar, what is the minimum work requirement to produce a stream of oxygen at 293 K and 1.5 bar at 1 gmol/min flow and a stream at 373 K and 3 bar at 2 gmol/min flow? One can have the students design a process train which could be used to accomplish the separation - a flow splitter following by a heat exchanger and compressor to produce the high pressure stream and a throttling valve following by a chiller to produce the low pressure stream and then carry out a thermodynamic evaluation of these processes including inefficiencies that arise in their operation, A minimum work requirement would be obtained by utilizing the combined first/second law for each device in the process train.

In the case of the nitrogen/oxygen mixture, restoring it to the original state of the system is a bit more challenging. To distill the nitrogen/oxygen mixture would require a reduction in the system temperature to below the critical points of the given components. The cryogenic distillation of air to produce liquefied gases is performed on an industrial scale and thus, students could consult the literature or an appropriate chemical technology handbook to analyze the unmixing process, An alternative separation process for this mixture would be gas permeation where a gas stream at elevated pressure is introduced on one side of a semi-permeable membrane and the partial pressure serves as the driving force for separation of components through the membrane. The minimum work requirement for membrane processes such as permeation has been examined by Humphrey and Siebert [1992],

One important feature of separations that becomes immediately apparent when one examines the combined first/second law for such a process is that as one approaches high purity for either product stream, the minimum work requirement for separation increases quite rapidly. When one examines the combined first/second law for a separation process where two pure product streams are produced from a single binary feed mixture, the minimum work requirement is found by setting the lost work to zero in equation (5), Additionally, kinetic and potential energy effects are assumed negligible.

$$\dot{W}_{min} = \sum_{in} \dot{m}_i \left[ H_i - T_{surr} S_i \right] - \sum_{out} \dot{m}_i \left[ H_i - T_{surr} S_i \right] \qquad (13)$$

The separation of a binary mixture can be examined through use of equation (1 3). In the junior level thermodynamics class at Mississippi State University, a significant number of lectures concern vapor liquid equilibria, predominantly focused on binary mixtures. One of the easiest methods that can be used to explain non-ideal behavior in liquid solutions is a graphical illustration of the effect of these non-idealities on the equilibrium pressure over a solution. The equilibrium pressure is predicted given the system temperature and the overall composition of the liquid phase through:

$$P = \sum_{i=1}^{N} x_i \gamma_i P_i^{sat} = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \qquad (14)$$

Thus, the effect of positive deviations from ideal behavior (y, > 1) is to increase the equilibrium pressure over that an ideal solution would produce and the effect of negative deviations from ideal behavior ($\gamma_i$ < 1) is to decrease the equilibrium pressure below that of an ideal solution (y, =1). Often, these results are depicted graphically in a P-x-y diagram. In this diagram, one can also see that the effect of positive deviations is to push the bubble point (P-x) and dew point (P-y) curves apart from one another. Thus, the separation of the binary mixture is easier (i.e., requires less energy) than if the mixture behaved ideally. Positive deviations that are large enough to lead to the formation of an azeotrope still demonstrate this same feature in a restricted portion of the P-x-y diagram - over a range in composition from one pure component to the azeotrope, the separation will require less energy than if the system behaved ideally over this limited composition range. The effect of negative deviations from ideal behavior is to push the bubble point and dew point curves closer to one another, thereby making the separation more difficult. The impact of non-ideal liquid phase behavior on the energy requirements for separation can be presented utilizing the combined first/second law as simplified in equation (13) through which these same conclusions can be reached more readily,

If the analysis is restricted to isothermal processes following Henley and Seader [1981], then the heat transfer occurs at the system temperature and $T = T_{surr}$. This allows the combination of terms appearing in equation (13) to be replaced by the Gibbs free energy, G. This gives:

$$\dot{W}_{min} = \sum_m \dot{n}_i [G_i] - \sum_{out} \dot{n}_i [G_i] \tag{15}$$

If one considers the separation of a feed mixture into two product streams, then incorporation of the definition of the Gibbs free energy for the mixture yields [Henley and Seader, 1981]:

$$\dot{W}_{min} = \dot{n}_1 G_1 - \dot{n}_2 G_2 - \dot{n}_3 G_3 = T\left[ n_1 \left(\sum_{i=1}^{N} y_i \ln \right)_1 - \dot{n}_2 \left(\sum_{i=1}^{N} y_i \ln \hat{f}_i \right)_2 - \dot{n}_3 \left(\sum_{i=1}^{N} y_i \ln \hat{f}_i \right)_3 \right] \tag{16}$$

where $\hat{f}_i = x_i \gamma_i P_i^{sat}$ is the fugacity of species i in the liquid solution. Upon substitution of this expression into equation (16), one can immediately evaluate the various contributions to the minimum work requirement for a given separation.

$$\dot{W}_{min} = RT\left[ \dot{n}_1 \left(\sum_{i=1}^{N} x_i \ln(x_i \gamma_i P_i^{sat}) \right)_1 - \dot{n}_2 \left(\sum_{i=1}^{N} x_i \ln(x_i \gamma_i P_i^{sat}) \right)_2 - \dot{n}_3 \left(\sum_{i=1}^{N} x_i \; n(x_i \gamma_i P_i^{sat}) \right)_3 \right]$$

$$= RT\left[ \begin{array}{l} \dot{n}_1 \left(\sum_{i=1}^{N} x_i \ln(x_i) \right)_1 - \dot{n}_2 \left(\sum_{i=1}^{N} x_i \ln(x_i) \right)_2 - \dot{n}_3 \left(\sum_{i=1}^{N} x_i \ln(x_i) \right)_3 \\ -\dot{n}_1 \left(\sum_{i=1}^{N} x_i \ln(\gamma_i) \right)_1 + \dot{n}_2 \left(\sum_{i=1}^{N} x_i \ln(\gamma_i) \right)_2 + \dot{n}_3 \left(\sum_{i=1}^{N} x_i \ln(\gamma_i) \right) \end{array} \right] \tag{17}$$

All of the terms involving $P_i^{sat}$ cancel by virtue of the mass balance relationships. For a binary mixture that can be modeled as an ideal solution, the last three terms involving the activity coefficient(s), $\gamma_i$, will equal zero since y, is unity for the entire composition range for each species, The effect of deviations from ideal behavior on the minimum work requirement are readily apparent. A system with positive deviations from ideal behavior (y, > 1)

will require less work to separate while a system with negative deviations will require more work than the ideal solution.

In this formulation, one can also analyze the case where two pure product streams are produced from a binary mixture. Only the terms involving the feed stream would survive ($\dot{n}_1$) since for the two product streams, both the mole fraction and the activity coefficient would be unity. Again, the effect of liquid phase non-ideality on the work requirement is readily apparent:

$$\dot{W}_{min} = RT\left[\dot{n}_1\left(\sum_{i=1}^{N}x_i\ln(x_i)\right)_1 - \dot{n}_1\left(\sum_{i=1}^{N}x_i\ln(\gamma_i)\right)_1\right] \tag{18}$$

Comparison of equations (17) and (18) also reveals that the minimum work of separation for the separation of the binary mixture into its pure components represents an upper limit to the minimum work requirement where the product streams are mixtures (i.e., the separation is not complete), The influence of product purity on the separation can be examined through use of equation (17). If one requires one product stream to have a purity of greater than 99 %, one can easily compare the work requirement for producing 99 % versus 99.9% product through equation (17). The rapid escalation in the minimum work requirement as the purity specification is increased is obvious when the combined first/second law is utilized in the analysis due to the appearance of the logarithmic relationship.

## Conclusion

Separation processes are unique to the chemical engineering curriculum and form the foundation for the chemical process industries. The second law has not been utilized extensively to analyze separations processes at the undergraduate level, Incorporation of this type of analysis provides students with additional tools through which they can better understand the irreversibilities present in mixing processes and more readily observe the effect of purity requirements and non-ideal solution behavior on the energy requirements for a given separation.

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