On the Principles/Importance of Thermodynamics

Dr. A. Özer Arnas
Professor of Mechanical Engineering
United States Military Academy at West Point
West Point, NY 10996

Introduction

Precise thermodynamics education is a requirement to discuss issues that one faces in thermodynamics and resulting studies in global warming, energy conversion and other energy related topics that affect sustainability of the environment in the global sense. For this reason, learning, understanding and meaningful and relevant application of topics in thermodynamics are required. To accomplish this, educating students at the undergraduate and graduate levels in classical, statistical and non-equilibrium thermodynamics becomes important. Here a short synopsis of fundamentals of classical thermodynamics are discussed with the intent of bringing clarity to the laws of thermodynamics and their application in design of experiments, applications in other fields such as heat transfer, and physical interpretation of the mathematical relations that are so useful in explaining why certain things happen in thermodynamics and nature. Nature is the ultimate customer.

For all scientist and engineers, the courses that end in –ics must be studied and understood well with their correct and precise application, such as mathematics, physics, chemical kinetics, mechanics as well as ethics and economics. Of course, thermodynamics is one portion of mechanics that is very important in the education of all engineers. It relates natural phenomena to some order and disorder. From a thermal energy point of view therefore, thermodynamics is the science that dictates what happens in nature and what not and why. Thus to better understand nature, the implications of energy usage on the environment and sustainability of what we enjoy today, we need to study precise thermodynamics.

Definitions

Definitions in thermodynamics must be precise to make everything that follows correct. Thus, in nature, there are only three types of systems. The closed system is one for which the mass within the boundaries remain a constant, such as a tank or a piston-cylinder arrangement. The filling/emptying system is the one that a tank with a valve characterizes where mass can either enter or leave the tank. Both cannot occur simultaneously. If a system has mass entering and leaving the boundaries, then it is called open.

There are only eight thermodynamic properties. The measurable ones are pressure, p, volume, V, and temperature, T. As a consequence of the first law of thermodynamics, internal energy, U, is introduced followed by the second law of thermodynamics and the introduction of entropy, S. Then three convenience properties are defined in terms of the five above: enthalpy H = U+pV, the Gibbs’ function G = H-TS, and the Helmholtz potential F = U-TS. The rest should be called physical properties of a system, such as the mass m.

In thermodynamics equilibrium is required to solve a problem. By definition, when two systems reach the same temperature T, they are called to be in thermal equilibrium. When they reach the same pressure p, they have mechanical equilibrium, and when they have the same electrochemical potential μi, they have chemical equilibrium. When all three happen simultaneously, then thermodynamic equilibrium exists.

One of the more important statements in thermodynamics is the state principle. This principle is important not only in thermodynamic analyses but in applied areas like heat transfer. This principle states that any two independent and intensive thermodynamic properties would define any of the others and fix a thermodynamic state and the situation is unique no matter which choice is made. A lack of understanding of this principle may lead into published work which has no meaning at all, Chawla (1978). Thus once a thermodynamic state is defined then a characteristic line that connects any two such states is called a thermodynamic process. A sequence of thermodynamic processes ending up at the initial thermodynamic state is called a thermodynamic cycle.
Conservation equations

These equations that apply may be obtained using the Reynolds’ Transport Theorem. Its use is common to all of these conservation laws and will be done systematically for each one of them. Considering at time \( t \), \( B_{system}(t) = B_{CV}(t) \) and at time \( t + \Delta t \), \( B_{system}(t + \Delta t) = [B_{CV}(t + \Delta t) + B_{out} - B_{in}] \) where the amount of \( B \) that exited the control volume is given as \( B_{out} = b(m_{out}) = b(\rho)(V_{\rho out})(A_{out})(\Delta t) \) and \( B_{in} = b(m_{in}) = b(\rho)(V_{\rho in})(A_{in})(\Delta t) \) is the amount of \( B \) that entered the control volume. Subtracting the first term from the second and dividing by \( \Delta t \) results in

\[
\frac{B_{system}(t + \Delta t) - B_{system}(t)}{\Delta t} = \frac{B_{CV}(t + \Delta t) - B_{CV}(t)}{\Delta t} + \frac{b[(\rho)V_{\rho out}](A_{out})(\Delta t) - b[(\rho)V_{\rho in}](A_{in})(\Delta t)]}{\Delta t}.
\]

Taking the limit of this equation as \( \Delta t \) approaches 0 yields the simplified equation

\[
\frac{dB_{CV}}{dt} = \frac{dB_{system}}{dt} + \int_{CS} \rho b \vec{V} \cdot \vec{n} dA
\]

where the outflow and inflow terms for the entire control surface in this equation gives

\[
\frac{dB_{system}}{dt} = \frac{dB_{CV}}{dt} + \int_{CS} \rho b \vec{V} \cdot \vec{n} dA
\]

where the dot product, \( (\vec{V} \cdot \vec{n}) \), is defined as \( (V \cos \theta) \) where \( \theta \) is the angle between \( \vec{V} \) to \( \vec{n} \). The total amount of extensive property \( B \), \( (B = m \, b) \), in the control volume is determined by integrating over the entire control volume as \( B_{CV} = \int_{CV} \rho b dV \). Upon substitution and combination, the Reynolds Transport Theorem is obtained as

\[
\int_{CV} dB_{CV} = \int_{CS} \rho b \vec{V} \cdot \vec{n} dA
\]

where the left hand term is the time rate of change of extensive property \( B \) in the system, the first term on the right hand side of the equation is the time rate of change of intensive property \( b \) in the control volume, and the second term on the right hand side of the equation is the net flow of intensive property \( b \) across the control surface. A positive value indicates net flow across the control surface is out of the control volume while a negative value indicates net flow across the control surface is into the control volume.

There are two conservation equations, that of mass and energy – the first law of thermodynamics. For the case of conservation of mass,

- **Closed system**: \( \sum m = \text{constant} \).
- **Open system**: \( \sum_{in} m = \sum_{out} m \).
- **Filling system**: \( m_{initial} + \sum_{in} m = m_{final} \).
- **Emptying system**: \( m_{initial} - \sum_{out} m = m_{final} \).

Applying the Reynolds’ Transport Theorem to the first law of thermodynamics, the result becomes

\[
\frac{dE_{system}}{dt} = \int_{CV} \rho c dV + \int_{CS} \rho c (\vec{V} \cdot \vec{n}) dA.
\]

This statement is very similar to money and banking; the difference is that nature does not permit overdraw of funds, namely one cannot use what is not there, whereas the bank just charges us money for overdraft. At steady state, therefore, \( \delta Q - \delta W = dU \). For a cycle, \( \oint \delta Q = \oint \delta W \) resulting in the fact that \( \oint dU = \oint (\text{property}) = 0 \). This is a very important result which will be used later. Application of the above theorem to various systems in nature results in the first law of thermodynamics as

- **Closed system**: \( Q_{in} - W_{in} = U_{f} - U_{i} \).
- **Open system**: \( Q_{i} - W_{i} = \sum_{i} m(h + V^2/2 + gz) - \sum_{i} m(h + V^2/2 + gz) \).
- **Filling system**: \( Q_{in} - W_{in} = m_{i} u_{2} - \sum_{i} m(h + V^2/2 + gz) - m_{i} u_{1} \).
- **Emptying system**: \( Q_{in} - W_{in} = \sum_{i} m(h + V^2/2 + gz) + m_{i} u_{2} - m_{i} u_{1} \).
Sign convention in thermodynamics

We cannot overemphasize the importance of this since most, if not all, textbooks do not strictly follow the convention. What convention is followed is not important, the consistent use of it is. For example, Callen (1960) says that all energy in is positive and all energy out is negative, and in that text this is followed consistently whereas most commonly used undergraduate and graduate textbooks do not, as is shown in the Bibliography and References of Arnas, et al (2003). Precision is very important, as is mentioned in Obert (1960) In most textbooks, all energy transfer due to a difference of temperature only called heat, in is positive and heat out is negative, and all energy transfers due to a potential difference other than temperature called work, in is negative and work out is positive giving us HIP to WIN. In all that we will do, this convention will be followed due to its universal and more common usage. For the equivalence of heat to absolute temperature, consider a Carnot cycle, Fig.1. It is made of two reversible adiabatic lines and two constant temperature heat reservoirs. If the working fluid is considered to be an ideal gas, for simplicity of algebra, then the energy added at T_H is given by, for an ideal gas,

\[ Q_{hc} = \frac{mR}{M} T_H \ln \frac{V_c}{V_b} \].

Similarly for the process (d-a), \( Q_{dc} = \frac{mR}{M} T_L \ln \frac{V_d}{V_a} \); thus the ratio becomes \( \frac{Q_{dc}}{Q_{hc}} = \frac{T_L}{T_H} \left( \frac{\ln \frac{V_d}{V_a}}{\ln \frac{V_c}{V_b}} \right) \). Since the process (a-b) is reversible and adiabatic, then \([- m c_v dT = p \, dV] = \left[ \frac{mR}{M} T \frac{dV}{V} \right] \). This integrates to give for process (a-b) the result of \( \left[ \frac{mR}{M} T \int c_v \frac{dT}{T} = \ln \frac{V_c}{V_a} \right] \). For the process (c-d), a similar results is obtained as \( \left[ \frac{mR}{M} T \int c_v \frac{dT}{T} = \ln \frac{V_c}{V_a} \right] \). Therefore, since the limits of integration are reversed, the equivalence gives \( \left[ \ln \frac{V_a}{V_b} = \ln \frac{V_c}{V_d} \right] \) or \([-[\ln V_c - \ln V_b] = [\ln V_a - \ln V_d] \) resulting in \( \left( \ln \frac{V_c}{V_b} \right)\left( \ln \frac{V_a}{V_d} \right) = -1 \). This upon substitution yields the expected result of \( \frac{-Q_L}{Q_{hc}} = \frac{T_L}{T_H} \). This relation permits one to substitute temperatures for heat quantities in the determination of Carnot performance criteria which quickly give extremum values for the actual efficiencies for engines, \( \eta \), as well as coefficient of performances for refrigerators, \( \beta \), and heat pumps, \( \gamma \). It must be remembered that one of the heat quantities is negative, out of a system, as it should be since the ratio of absolute temperatures is always positive. With reference to Arnas, et al (2003), we can examine the various
Performance characteristics of devices

Consider a heat engine that receives energy \( Q_H \) from a reservoir at \( T_H \) and produces work \( -W_{\text{net}} \) while rejecting energy \( -Q_L \) to a reservoir at \( T_L \). Since the performance of any device is measured by the ratio of the net useful effect to the total cost to obtain that effect, then

\[
\eta = \frac{-W_{\text{net}}}{Q_H}.
\]

Also we have \( \sum E_{\text{in}} = \sum E_{\text{out}} \) giving

\[
\left( Q_H - W_{\text{net}} - Q_L \right) = 0.
\]

Solving for \( W_{\text{net}} \) and substituting into the efficiency equation, the result becomes

\[
\eta = \left( 1 - \frac{T_L}{T_H} \right).
\]

For a refrigerator, the net effect is the cooling that we get, \( Q_L \), from a cold reservoir at \( T_L \). The work required to pump this energy is \( W_{\text{net}} \), and the energy given off to the environment at a temperature \( T_H \) is \( -Q_H \). Therefore, the performance parameter, coefficient of performance for a refrigerator becomes

\[
\beta = \left( \frac{Q_L}{W_{\text{net}}} \right) = \left( \frac{-Q_H}{-Q_H + (-Q_L)} \right) = 1 \left( \frac{-Q_H}{Q_L} \right) \left( \frac{1}{1 - \frac{Q_L}{Q_H}} \right) \]

which reduces to

\[
\beta = \left( \frac{T_L}{T_H - T_L} \right)
\]

for a Carnot refrigerator.

For a heat pump, the net effect is the heating that we get, \( -Q_H \), into a reservoir at a temperature of \( T_H \). The work required to pump this energy is \( W_{\text{net}} \), and the energy that is taken out of the environment at a temperature \( T_L \) is \( Q_L \). Therefore, the coefficient of performance for a heat pump becomes

\[
\gamma = \left( \frac{-Q_H}{W_{\text{net}}} \right) = \left( \frac{-Q_H}{-Q_H + (-Q_L)} \right) = 1 \left( \frac{-Q_H}{Q_L} \right) \left( \frac{1}{1 + \frac{Q_L}{Q_H}} \right)
\]

which reduces to

\[
\gamma = \left( \frac{T_H}{T_H - T_L} \right)
\]

for a Carnot heat pump. It is also easy to prove that \( \gamma = (1 + \beta) \) using the results obtained above.

Second law of thermodynamics

The second law of thermodynamics denies a system the possibility of utilizing energy in a particular or arbitrary way. There are two basic definitions of the second law which were stated at different times by different people, historically speaking.

**Kelvin-Planck statement**

It is impossible to construct an engine which is operating in a cycle that will produce no effect other than the extraction of energy from a reservoir and the performance of an equivalent amount of work. Thus an efficiency of 100% is not a possibility.

**Clausius statement**

It is impossible to construct a device which while operating in a cycle will produce no effect other than the transfer of energy from a colder to a hotter body. Thus a refrigeration unit requires energy input as work; otherwise it cannot function.

These two statements are equivalent and the assumption of the validity of one leads to the situation given by the other. Consider that the Kelvin-Planck statement is valid. If now one constructs a refrigerator running with the work of the engine and extracting energy \(-Q_L\) from the cold reservoir, then the engine-refrigerator system is one which absorbs energy from a cold reservoir and transfers it to the hot reservoir without any external work, a situation which the Clausius statement refutes. If this were possible, the energy in the oceans at a low and cold temperature could be utilized to run all kinds of equipment without any external work; an impossible situation known to all.

If now the Clausius statement is considered to be valid, then the refrigerator functions without any external work. At the same time, an engine placed between the same two reservoirs produces work. The refrigerator-
engine system leads to a situation where an amount of energy is absorbed from a hot reservoir and an equivalent amount of work is performed, a situation that the Kelvin-Planck statement refutes. If this were valid, all the fuel consumed in the engine of a car would be used in the form of work without any losses whatsoever; another impossible situation that is well known to all. All physical systems must function in such a way as not to violate either one of these statements. Otherwise a perpetual motion machine of the second kind will result.

The CARNOT Principle

This is one of the fundamental principles of thermodynamics. It says that there is no heat engine operating between two given reservoirs that can be more efficient than a Carnot heat engine operating between the same two reservoirs. To prove this statement, assume that the reverse is true. Then since the Carnot engine is reversible, it can be reversed to operate as a refrigerator. Therefore, if the engine E is more efficient than the Carnot engine CE, the result becomes \( \eta_E > \eta_{CE} \).

![Figure 2. The graphical explanation of the Kelvin-Planck and Clausius statements of the second law.](image)

This can also be written as \( \frac{W}{Q_H} > \frac{W}{Q_C} \) giving as the final result \( Q_C > Q_H \). If this is the case, then there is a net flow of energy in the form of heat from the cold to the hot reservoir without any consumption of work or other external effects. Such a result is impossible since it leads to the contradiction of the Clausius statement of the second law of thermodynamics. Thus the original assumption was wrong which says that the efficiency of an engine cannot be larger than that of a Carnot engine operating between the same two reservoirs. A corollary to the Carnot principle is that all Carnot engines operating between the same two temperature reservoirs \( T_H \) and \( T_L \) have the same efficiency. The proof of this statement follows from the above. Assume that the first one is more efficient than the other. A contradiction will be observed. Then assume the other way around. The same contradiction will be obtained. The only possibility remaining, therefore, is naturally the equivalence of the two efficiencies.

Entropy

Entropy is a thermodynamic property which comes about as a result of the second law of thermodynamics. To demonstrate its existence, following Zemansky (1943) and Mooney (1953), consider a reversible process from an initial state \( i \) to a final state \( f \) and use the first law to give \( Q_f - W_f = (U_f - U_i) \). From \( i \) and \( f \) draw two reversible adiabatic lines. Then construct a reversible isotherm (a-b) so that the area above and below the isotherm and between the original process (i-f) and the adiabatic lines are equal. Thus we obtain that \( W_f = W_{iabf} \). Therefore, now the heat terms give \( Q_f = Q_{iabf} \) since \( (U_f - U_i) \) does not change because of the general character of a thermodynamic property. Also \( Q_{in} \) and \( Q_{if} \) are equal to zero since they are adiabatic.
processes resulting in \( (W_{f}) = (W_{ab}) = (W_{ai} + W_{ab} + W_{if}) \). Therefore, the result becomes \( Q_{ab} - W_{if} = (U_{f} - U_{i}) \) giving the final result that \( Q_{ab} = Q_{if} \). In general, therefore, an arbitrary reversible process can always be replaced by a zigzag path between the same state points consisting of a reversible adiabatic line, a reversible isotherm, and another reversible adiabatic line, such that \( Q_{\text{original process}} = Q_{\text{isotherm}} \).

![Figure 3. Development of the Carnot cycle.](image)

now the heat terms give \( Q_{if} = Q_{ab} \) since \((U_{f} - U_{i})\) does not change because of the general character of a thermodynamic property. Also \( Q_{ia} \) and \( Q_{bf} \) are equal to zero since they are adiabatic processes resulting in \( (W_{f}) = (W_{ab}) = (W_{ai} + W_{ab} + W_{if}) \). Therefore, the result becomes \( Q_{ab} - W_{if} = (U_{f} - U_{i}) \) giving the final result that \( Q_{ab} = Q_{if} \). In general, therefore, an arbitrary reversible process can always be replaced by a zigzag path between the same state points consisting of a reversible adiabatic line, a reversible isotherm, and another reversible adiabatic line, such that \( Q_{\text{original process}} = Q_{\text{isotherm}} \).

![Figure 4. Development of Clausius’ statement and entropy.](image)

Now, to reach the definition of thermodynamic quantity entropy, consider a smooth reversible cycle as shown in Fig. 4. On it inscribe reversible adiabatic lines of thickness \( \Delta \). For each slice or arc, which is a reversible process, inscribe an isotherm so that the condition given above is satisfied. The cycles thus formed are all Carnot cycles with the characteristic relationship obtained between heat transfer and absolute temperature ratios. Thus for the first cycle drawn, \( \left\{ \frac{Q_{H_{i}}}{T_{H_{i}}} = \frac{T_{H_{i}}}{T_{i_{1}}} \right\} \) or \( \left\{ \frac{Q_{H_{i}}}{T_{H_{i}}} + \frac{Q_{L_{i}}}{T_{L_{i}}} = 0 \right\} \). In a similar fashion, for the second cycle we have \( \left\{ \frac{Q_{H_{2}}}{T_{H_{2}}} + \frac{Q_{L_{2}}}{T_{L_{2}}} = 0 \right\} \). Adding these two results and generalizing for the sum of all such cycles,
then \( \sum_{i} \frac{Q_i}{T_i} = 0 \). In the limit as \( \Delta \to 0 \), the adiabatic lines come closer thus making the heat quantities infinitesimal resulting in \( \int_{rev} \frac{\partial Q}{T} = 0 \) which is the important Clausius theorem.

\[
\int_{rev} \frac{\partial Q}{T} = 0
\]

Figure 5. A reversible cycle.

Now consider two reversible processes \( R_1 \) and \( R_2 \) starting from the initial state \( i \) and ending at the final state \( f \), Fig. 5. Since they are reversible, it is possible to change the sense of \( R_2 \). Since \( R_1 \) and \( R_2 \) now form a reversible cycle, then

\[
\int_{R_1 R_2} \frac{\partial Q}{T} = 0 \quad \text{and} \quad \int_{i s_2 j} \frac{\partial Q}{T} = 0
\]

This results in the most general relation for the integral in a reversible process

\[
\int_{i R} \frac{\partial Q}{T} = 0 \quad \text{and} \quad \int_{i}^{f} \frac{\partial Q}{T} = 0
\]

which says that if a reversible path is chosen, the path itself is not important so long as the process starts at \( i \) and ends at \( f \). The quantity is, therefore, given by the end states and not the path. As is the case in the first law of thermodynamics, \( \int \partial Q - \int \partial W = \int dU \) and \( \int dU = 0 \) since internal energy is a thermodynamic property, then

\[
\int_{rev} \frac{\partial Q}{T} = 0
\]

is a thermodynamic property and is called entropy, \( S \). Therefore, \( \int_{rev} dS = (S_f - S_i) \) or for an infinitesimal process, \( \int_{rev} \frac{\partial Q}{T} = dS \) that forms the mathematical formulation of the second law of thermodynamics. It is, therefore, seen that there is a similarity between the two laws of thermodynamics and their definition of internal energy and entropy. To further extend this discussion to the inequality of Clausius, consider the fact that all heat engines operating between a given high temperature source, \( T_H \), and a lower temperature sink of \( T_L \), none can have a higher efficiency than the Carnot engine. Thus using the figure above, but this time having the process at \( T_H \) to be irreversible, then the result obtained is

\[
\left( 1 + \frac{Q_{rev}}{Q_{H,rev}} \right) \leq \left( 1 + \frac{Q_L}{Q_{REV}} \right)
\]

Using the fact that \( \frac{-Q_L}{Q_H} = \frac{T_L}{T_H} \) is for reversible energy transfers, then

\[
\frac{Q_{rev}}{Q_{H,rev}} \leq \left( 1 - \frac{T_L}{T_H} \right)
\]

Transposing and keeping in mind that there is a negative sign, the result becomes

\[
\frac{\partial Q_{rev}}{T_L} \geq \frac{\partial Q_{H,rev}}{T_H}
\]

Using the definition of entropy as given above, \( dS \geq \left( \frac{\partial Q_{H,rev}}{T_H} \right) \) or
\[ \int dS \geq \left( \frac{\delta Q}{T} \right)_{\text{IRREV}} \]

which states that in all real processes entropy increases and the equality is only for the reversible process. This further reduces the result to what is expected, the inequality of Clausius, the fact that \[ \int \left( \frac{\delta Q}{T} \right)_{\text{IRREV}} \leq 0. \]

If the entropy changes of the system are added to the entropy changes occurring in the surroundings as a result of the changes in the system, the sum represents the total changes of the system and the surroundings and is called the entropy change of the universe or entropy generation, \( \sigma \). For a reversible process, let \( \delta Q_{\text{rev}} \) amount of energy be absorbed by the system. Then \( \left( dS_{\text{system}} = \frac{\delta Q_{\text{rev}}}{T} \right) > 0 \) since it has been put into the system. Since this energy has to be given up by the surroundings, then \( \left( dS_{\text{surroundings}} = \frac{\delta Q_{\text{rev}}}{T} \right) < 0. \) As a result, the entropy generation is \( dS_{\text{universe}} = d\sigma = 0 \). Thus, when a reversible process is performed, the entropy of the universe remains unchanged.

The second law representation of the systems that we are interested in is as follows:

Closed system: \[ \Delta \sigma = m(s_2 - s_1) - \sum_j \left( \frac{Q_j}{T_j} \right) \]

Open system: \[ \Delta \sigma = \sum_i \left( m_i s_i \right) - \sum_i \left( m_i s_i \right) - \sum_j \left( \frac{Q_j}{T_j} \right)_{\text{ie}} \]

Filling system: \[ \Delta \sigma = m_2 s_2 - \sum_i \left( m_i s_i \right) - m_1 s_1 - \sum_j \left( \frac{Q_j}{T_j} \right)_{\text{ie}} \]

Emptying system: \[ \Delta \sigma = \sum_i \left( m_i s_i \right) + m_2 s_2 - m_1 s_1 - \sum_j \left( \frac{Q_j}{T_j} \right)_{\text{ie}} \]

The product of the environment temperature \( T_e \) with \( \Delta \sigma \) is called the irreversibility, \( I_{ie} \) of the process. Therefore, either entropy generation or irreversibility can be used to discuss the given situation. It is not important which choice is made. It is this irreversibility that gives rise to pollution and degradation of the environment leading to unsustainability of the present quality of life in nature.

**Exergy**

Exergy or available energy is the capacity to perform useful work with a given amount of energy. This can also be considered as the taxation of energy by nature. What nature is saying that although we may have an amount of energy that we should be able to use, the portion of that energy between the lowest available temperature \( T_d[K] \) and \( 0[K] \) is the amount that is taken out by nature before any useful work can be obtained, \( (T_d \Delta S) \). Unlike the government’s share of our income as taxes, this amount is not negotiable. Therefore, this amount goes back to nature, unfortunately in the form of pollution. This result also states that if we want to produce useful products, such as electricity or transportation, we agree to pollute the environment. Thus to be conscious of our responsibilities to our and future generations, better conversion technologies and conservation seem to be the only immediate solutions since any power generation MUST produce pollution of some sort that we may not be able to accept. Intelligent use of resources, therefore, must happen; otherwise the consequences are not very desirable.

The exergy formulation for the systems that we are interested in are given below without a detailed derivation. However, the principles presented above suffice to obtain them.
Closed system:
\[ A_{12} = \sum_j Q_j (1 - \frac{T_0}{T_j}) + (U_1 - U_2) + p_0(V_1 - V_2) - T_0(S_1 - S_2) - T_0\Delta\sigma \]

Open system:
\[ A_{2\sigma} = \sum_j Q_j (1 - \frac{T_0}{T_j}) + \sum \dot{m}[h - T_0s] + \frac{V^2}{2} + g\varepsilon - \sum \dot{m}[h - T_0s] + \frac{V^2}{2} + g\varepsilon - T_0\Delta\sigma \]

Filling system:
\[ A_{\sigma} = \sum_j Q_j (1 - \frac{T_0}{T_j}) + \sum \dot{m}[h - T_0s] + \frac{V^2}{2} + g\varepsilon + m_1(u_1 + p_0v_1 - T_0s_1) - m_2(u_2 + p_0v_2 - T_0s_2) - T_0\Delta\sigma \]

Emptying system:
\[ A_{\sigma} = \sum_j Q_j (1 - \frac{T_0}{T_j}) - \sum \dot{m}[h - T_0s] + \frac{V^2}{2} + g\varepsilon + m_1(u_1 + p_0v_1 - T_0s_1) - m_2(u_2 + p_0v_2 - T_0s_2) - T_0\Delta\sigma \]

Use of these equations will give us the availability of energy, or exergy, for maximum obtainable work in any given system.

**Nonmeasurable thermodynamic properties**

The classical method of eliminating non-measurable thermodynamic properties is successive use of the Maxwell relations. However, this method is very time consuming at times since one does not know exactly in which direction the elimination must take place. Sometimes, due to this uncertainty, it does not work. There is a method, however, called the method of Jacobians which accomplish the same result in a very systematic way without any guess work, Somerton and Arnas (1985). Although the method was first introduced fifty years prior to this, the only text known that discuss these is that of Callen (1960).

This methodology has been used extensively to explain certain thermodynamic phenomena, to design experiments, and to eliminate the non-measurable thermodynamic properties, Arnas (2000). The measurable thermodynamic properties are \( p, T, V \). Also the specific heats at constant pressure and volume, respectively, \( c_p = \frac{\partial U}{\partial T} \), \( c_v = \frac{\partial U}{\partial T} \), the coefficient of thermal expansion, \( \alpha = \frac{1}{v} \frac{\partial V}{\partial T} \), and the isothermal compressibility, \( \kappa = -\frac{1}{v} \frac{\partial V}{\partial p} \) of substances can be measured. Using these parameters and since thermodynamic properties are mathematically well behaved functions, namely the order of differentiation does not make any difference, i.e. \( \frac{\partial}{\partial X} \left( \frac{\partial Z}{\partial Y} \right) = \frac{\partial}{\partial Y} \left( \frac{\partial Z}{\partial X} \right) \), the elimination of the non-measurable properties becomes simple.

In general, the Maxwell relations are obtained from \( \{dZ=MdX+NdY\} \) as \( \left( \frac{\partial M}{\partial Y} \right)_X = \left( \frac{\partial N}{\partial X} \right)_Y \). Since \( U = U(S,V) \) then \( dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \). Comparing this equation to the Gibbs’ equation, \( dU=TdS-pdV \), it is seen that \( \left( \frac{\partial U}{\partial S} \right)_V = T \) and \( \left( \frac{\partial U}{\partial V} \right)_S = -p \). Additionally, using the above property, we can get the equality \( \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial p}{\partial S} \right)_V \).

Similar equalities can be obtained using the other Gibbs equations that relate other properties, i.e. enthalpy, \( H = H(S,p) \) and \( \{dh = TdS + Vdp\} \), the Gibbs function \( G = G(T,p) \) and \( \{dG = -SdT + Vdp\} \), and the Helmholtz potential \( F = F(T,V) \) and \( \{dF = -SdT - pdV\} \). These are also useful in elimination of some of the non-measurable terms and thermodynamic properties.
In Somerton and Arnas (1985), the theory as well as the use of the method is given. For the general equation of \( \{dZ = M \, dY + N \, dX\} \), the Jacobian formulation can be written as \([\{Z,\xi\} = M[\{Y,\xi\} + N[\{X,\xi\}] \) where \( \xi \) is any other thermodynamic property. Also, the equalities \([\{Z,\xi\}] = 0, [\{Z,\xi\}] = [\{\xi,\xi\}] \), and \( \frac{\partial(X,Y)}{\partial(X,Y)} = 1 \) are very useful.

From fundamentals of mathematics we have \( \frac{\partial Y}{\partial X} = \left( \begin{array}{c} \frac{\partial Y}{\partial \xi} \\ \frac{\partial Y}{\partial \xi} \end{array} \right) \). Using the first law of thermodynamics for a cycle, we get \( \int \delta Q = \int \delta W \) since \( \int \delta dU = 0 \). In Gibbs form, \( \{dU = T dS - p dV\} \) giving for a cycle \([T \, ds = p \, dV] \) which in Jacobian form becomes \([T, S] = [p, V] \). The systematic use of these will permit one to convert nonmeasurable terms into measurable ones including \( p, v, T, c_p, c_v, \) and \( \kappa_T \).

The general methodology, therefore, is:

1. Write down the given in terms of Jacobians.
2. Reduce by Maxwell equations using the various Gibbs equations.
3. Use the definition of \( c_p, c_v, \alpha, \) and \( \kappa_T \) to further reduce the given equation.
4. If everything is done correctly, the result should only contain \( p, v, T, c_p, c_v, \alpha, \) and \( \kappa_T \). If not, an error has been made; you need to go back and redo everything.

If this methodology is not used, then one goes around and around until a solution is obtained and one does not know if the route taken is the correct one. The advantage of the method of Jacobians is that the result shows if a mistake has been made.

The examples given in Somerton and Arnas (1985) are for learning the methodology. We will also look at other relations and get the physical significance of some other important thermodynamic phenomena, for example throttling, \( \mu = \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{c_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right] \) and the speed of sound in any medium, \( c^2 = \left( \frac{\partial p}{\partial \rho} \right)_s = \frac{\partial p}{\partial \left( \frac{1}{v} \right)} \).

As an example, start with \( c_v = T \left( \frac{\partial s}{\partial T} \right)_p \). Therefore, following the methodology given,

**STEP 1.**

\[
\left( \frac{\partial s}{\partial T} \right)_p = \left( \frac{\partial (s, v)}{\partial (p, T)} \right) - \left( \frac{\partial (s, v)}{\partial (p, p)} \right) \left( \frac{\partial (p, T)}{\partial (p, p)} \right) \]

**STEP 2:** However, the denominator is by definition \( \{-v \, \kappa_T\} \). Therefore,

\[
\left( \frac{\partial s}{\partial T} \right)_p = \frac{1}{v \, \kappa_T} \left( \frac{\partial s}{\partial p} \right)_p - \frac{1}{v \, \kappa_T} \left( \frac{\partial s}{\partial T} \right)_p \left( \frac{\partial s}{\partial T} \right)_p
\]

Using the Maxwell relation, \( \left( \frac{\partial s}{\partial p} \right)_T = -\left( \frac{\partial v}{\partial T} \right)_p \) which comes from the Gibbs form of the Gibbs’ function equation, and the definitions of \( c_p, \alpha, \) and \( \kappa_T, \frac{c_v}{T} = \frac{1}{v \, \kappa_T} \left[ \frac{\partial s}{\partial p} \right] \). Rearranging, \( \left( \frac{c_p - c_v}{T} \right) = \frac{\alpha \, v^2}{\kappa_T} \).

For an ideal gas, this general result reduces to \( \left( \frac{c_p - c_v}{T} \right) = \frac{\mathcal{R}}{M} \), where \( \mathcal{R} \) is the Universal gas constant and \( M \) is the molecular mass of the ideal gas, a well known relationship. It is also possible to show that for an incompressible substance, i.e. liquid water, \( (c_p - c_v) = 0 \) which says that for those we must just use \( c \) as the specific
heat without any subscripts. For those substances for which we have tables, enthalpies must be used and not
\( \Delta h = c \Delta T \), another common mistake in literature, Çengel and Boles (2008). In analyzing other derivatives
of interest, these methodologies become very useful as well when we go through those quantities, for example
\( \frac{\partial U}{\partial V} \) and \( \frac{\partial H}{\partial p} \), and their values for an ideal gas. In Armas (2000), these along with other characteristics
are further studied. The slope of various functions on the Mollier chart, an (h-s) diagram,
\[ \left( \frac{\partial h}{\partial s} \right)_T = \left( T - \frac{\partial T}{\partial v} \right)_p, \quad \left( \frac{\partial h}{\partial s} \right)_p, \quad \left( \frac{\partial h}{\partial s} \right)_T, \] and other thermodynamic diagrams, such as the (p-h) for refrigerants, i.e.,
\[ \left( \frac{\partial p}{\partial h} \right)_s = -\frac{c_v}{c_p} \left( \frac{\partial p}{\partial v} \right)_T, \]
is also explained to clarify the physics involved; for an ideal gas, this reduces to
\[ \left( \frac{\partial p}{\partial h} \right)_s = -\frac{c_v}{c_p} = \frac{k}{v}, \] where \( k \) is the ratio of the specific heats, \( \left( k = \frac{c_p}{c_v} \right) \).

To obtain pressure-temperature relation for an ideal gas under reversible adiabatic conditions, we start with
\[ \left( \frac{\partial p}{\partial T} \right)_s \quad \frac{p_s}{T_s} = \frac{s}{T_s}. \] Substituting for the numerator and the denominator from Jacobian properties, then
we get
\[ \left( \frac{\partial p}{\partial T} \right)_s = \frac{-c_v}{T_v} \left( [T, p] \right)_s = \frac{c_p}{T} \left( \frac{\partial T}{\partial v} \right)_p, \] which is a general result. Using the ideal gas equation, the partial derivative on the right can be evaluated. Using the difference between the two specific heats for an ideal gas, as was shown above, the result becomes
\[ \left( \frac{\partial p}{\partial T} \right)_s = \frac{p c_p}{T} \frac{1}{k-1}. \] Therefore,
\[ \frac{dp}{dT} = \frac{k}{k-1}, \] which upon integration gives the well known result
\[ T = p^{\frac{k-1}{k}}. \] This result is only valid if we have an ideal gas which undergoes a reversible and adiabatic, constant entropy, process. Again, this fact is not trivial and must be kept in mind before this result can be used. Similar results can be obtained for \( \left( \frac{\partial v}{\partial T} \right)_s = \frac{-c_v}{T} \left( \frac{\partial T}{\partial v} \right)_p, \) applied to an ideal gas would give,
\[ \frac{dv}{v} = \frac{1}{1-k}. \] For \( \left( \frac{\partial p}{\partial v} \right)_s \) we get the result, in general,
\[ \left( \frac{\partial p}{\partial v} \right)_s = k \left( \frac{\partial p}{\partial T} \right)_s. \] This equals for an ideal gas
\[ \frac{dp}{dv} = -k \] giving \[ p = v^{1-k}. \]

The total intent in all this was to verify the physics of the situation using mathematics. Mathematics is just a
tool to totally explain these physical phenomena that characterize nature. Nature is what physics is; mathematics
is the explanation mechanism and nothing more.

**Design of Experiments**

In engineering, experimental verification of analysis or computational results is extremely important. For that, it
is necessary to design experiments. Experiments can only be designed for those parameters for which we can
make measurements. As was discussed before, the measurable parameters in thermodynamics are \( p, T, v, c_p, c_v, \alpha, \) and \( \kappa T \). Therefore, the designed experiment can only involve these parameters.
As an example of this important issue, consider the Clausius’ equation which is
\[
\frac{dp}{dT}_{\text{saturation}} = \frac{Q_{12}}{Tv_f - v_l}.
\]
By considering the T-s diagram, it is obvious that the heat transferred is equal to \(Q_{12} = T(s_f - s_l)\). From the Gibbs’ equation for enthalpy, \(\{dh = Tds + \nu dp\}\), and since at saturation the pressure and temperature are constants, then \(\{dh = Tds\}\) giving \([(h_2 - h_1) = T(s_2 - s_1)]\). Upon substitution, \(\frac{dp}{dT}_{\text{saturation}} = \left\{ \frac{(v_2 - v_1)}{Tv_f - v_l} \right\}\), where 2 refers to the saturated vapor state, \(g\), and 1 to the saturated liquid state, \(f\). Therefore, the Clausius equation becomes,
\[
\frac{dp}{dT}_{\text{saturation}} = \frac{h_g}{Tv_f}.
\]
Clapeyron modified this equation by making certain assumptions. The first assumption is that \(v_g \gg v_f\) which is an acceptable one since the vapor specific volume is much greater numerically than the liquid specific volume, as can be seen in the Steam Tables, Çengel and Boles (2008). The second assumption is that of an ideal gas for the vapor, i.e. \(v_g \equiv v = \left(\frac{\gamma R}{M}\right)\frac{T}{p}\) which, upon substitution, makes the Clausius’ equation
\[
\frac{dp}{dT}_{\text{saturation}} = \frac{h_g}{\gamma R}\left(\frac{p}{T^2}\right).
\]
Collecting like terms, this equation reduces to
\[
\frac{dp}{dT} = \frac{h_g}{\gamma R}.
\]
and simplifying, the Clausius-Clapeyron equation is obtained as
\[
\frac{d(ln p)}{d\left(\frac{1}{T}\right)} = \frac{h_g}{\gamma R}\text{ which is only valid if } v_g \gg v_f\text{ and we have an ideal gas for constant } h_g.\text{ All of these three assumptions must be satisfied before the results of the experiment can have any significance. Therefore in the design of the experiment we must consider these facts very carefully.}

In designing an experiment, the first assumption for the Clausius-Clapeyron equation is satisfied when one looks in the Steam Tables, Çengel and Boles (2008), to compare the numerical values of the specific volume as a vapor and a liquid. The second assumption, an ideal gas, requires some more discussion. When we look at the compressibility diagram for substances, we see that the compressibility for all substances approach unity, meaning they approach the characteristics of an ideal gas, as the reduced pressure of the substance approaches zero, i.e. \(Z \to 1\) as \(P_{\text{Reduced}} = \frac{P}{P_{\text{Critical}}} \to 0\). This result signifies that the experiment must take place at low real pressures, i.e. below atmospheric, since the critical pressure for steam is 22.09[MPa] to make sure that we are approaching zero for the reduced pressure to guarantee ideal gas situation. Finally, constant \(h_g\) assumption requires that the measurements must take place at a pressure an increment above and an increment below the saturation pressure under investigation. By taking this increment small and splitting it up for as many precise measurements as possible, all that is needed to do is to plot \((\ln p)\) versus \(\frac{1}{T}\) using the absolute temperature.

The slope of the line is negative, as the Clausius-Clapeyron equation requires, and will give the value \(h_g\) once the molecular mass of water is used. Other fluids can also be used in this experiment; the only requirement is to make sure that \(Z \to 1\) and \(P_{\text{Reduced}} = \frac{P}{P_{\text{Critical}}} \to 0\) for the liquid that is used.

For the speed of sound or the Joule-Thomson coefficient similar experiments can be designed, constructed, and experimental results can be obtained once their measurable forms are derived, as was done above. This methodology is good for any quantity for which an experiment is to be designed; the important thing to keep in mind
is the assumptions under which the result is obtained. If any one of the assumptions is not met, then the experiment will not give the expected results.

This, of course, is not different from any scientific/engineering analysis or experiment. The results obtained are only as good as the assumptions made and that the results are only valid under those assumptions. This may sound trivial but we will show that it is a mistake made quiet commonly by researchers and/or authors of textbooks.

**Errors made in literature**

When one studies the literature carefully, one does find fundamental errors made due to the fact that simple understanding of thermodynamics is lacking. As we have already discussed very early on the state principle and the fact that any two independent intensive thermodynamic properties are sufficient to define a thermodynamic state, it is really of no consequence which two are selected since the final result has to be unique.

Chawla (1978) selects three different combinations of properties to determine the speed of sound. In the first case, the variables selected are the velocity, the pressure, and the enthalpy. The result for the speed of sound turns out to be

\[
c^2 = \frac{1}{\left(\frac{\partial \rho}{\partial p}\right)_h + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial h}\right)_p}
\]

where \(\rho\) is the density, inverse of \(v\). The second case is for the velocity, the density, and the pressure. This time the result obtained becomes

\[
c^2 = \left[ -\frac{\rho \left(\frac{\partial h}{\partial \rho}\right)_p}{\rho \left(\frac{\partial h}{\partial \rho}\right)_p - 1} \right]
\]

The third case is for the velocity, the pressure and the temperature. The result obtained is,

\[
c^2 = \frac{1}{\left[ -\left(\frac{\partial \rho}{\partial T}\right)_p \right] + \left(\frac{\partial \rho}{\partial p}\right)_T \left(\frac{\partial h}{\partial p}\right)_T - 1}.
\]

However, from the definition of the speed of sound, \(c^2 = \left(\frac{\partial \rho}{\partial \rho}\right)_s\) and using the methodology given above, it is indeed very simple to show that the analytical result is \(c^2 = -v^2 \left(\frac{\partial p}{\partial v}\right)_s = -v^2 \left[ \frac{ps}{v,s} \right] = -v^2 \left(\frac{c_s}{c_v}\right) \left(\frac{\partial p}{\partial v}\right)_T\).

No matter which two properties along with the velocity is chosen, this is the result that must be obtained. Results are obtained in terms of nonmeasurable properties which are consequently solved numerically, Chawla (1978). Since the series variation of these properties do not have the same character, numerical truncation errors result in different forms for the answers. The author then tries to justify why they are different. However, we have seen that the result has got to be unique, the state principle, and it is demonstrated once again by Arnas (2000). All three results above analytically are the same, as it should be. Numerically, they are not! Therefore, a fundamental understanding of thermodynamics is very important to explain physical phenomena.
Shortcomings of textbooks

Apart from the shortcomings of books on Thermodynamics, and there are many, similar shortcomings that exist in other textbooks because of lack of being precise that discuss, for example, Heat Transfer which is an applied course heavily dependent on thermodynamic principles. The student is learning from the textbooks; therefore, they trust the contents as they must. However, if the topics are not precisely covered, then they learn the wrong material.

As an example, we will consider condensation phenomena since it is an important process in thermodynamics, as we have discussed above in the case of the Clausius-Clapeyron equation and the steam experiment, and since we must design condensers for technological purposes, using heat transfer. When one considers the condensation phenomenon as discussed in textbooks, also as was done by Arnas et. al (2004), there are many assumptions that are made to be able to analyze the physical situation. Unfortunately in all of these, the assumptions that are made are not justified for the final result. The final result is the same in all of the references, the only thing different are the symbols used. However, the student does not know if a given situation actually satisfies all the assumptions made. Therefore, for all situations, the only design equation is the one found in the texts and that one is used blindly. It is indeed possible to find situations where anyone of these conditions is not met which would make the equation useless. In Arnas et.al (2004) not only is the result obtained very rigorously and in a very clear and analytical fashion, the conditions under which the result is valid are also very clearly given so that the user, the student, researcher or the design engineer is able to ascertain if the problem actually fits the final design equation for convection in condensation.

In another study by Arnas et. al (1980), it was shown that the two-phase flow design equations are not usable under all conditions since they tend to decrease the entropy generation for certain combinations of flow rates and geometries; a condition that violates the second law of thermodynamics. Naturally, under those conditions the equations cannot be used for design purposes and other correlations must be searched.

What has been attempted here is to show the importance of correct use of precise thermodynamics in teaching of thermodynamics as well as in all other fields of science and technology. If it is not used precisely, errors are made that could affect the designed equipment or lead to disastrous situations in extreme cases. In engineering we cannot make mistakes since, unlike the doctor, we do not kill one person at a time! Our failures are watched and seen by the whole world, for example the Space Shuttle disaster. We must teach well, in a correct way, and precisely and demand of our students at all levels the same precision in their work, Arnas (2005). Only in that fashion can be sure that the next generation of engineers/scientists understands the critical ramifications of what is at stake. This is more important than anything else that we can teach our students; their understanding and appreciation of the importance of their precise work.

Conclusions

In this paper, the precise teaching of thermodynamics has been emphasized since these topics are used in other fields of science and technology. The textbooks must be correct giving the precise description of systems, equations and conclusions. Otherwise the students learn the wrong information and apply it in the same fashion. It has also been shown that methodologies exist for physical interpretation of mathematical expressions in thermodynamics by eliminating nonmeasurable quantities such as entropy, designing thermodynamic experiments and investigating various applications in other fields of science and technology that use thermodynamic principles. The emphasis has been in correct and precise work, a quality that we must impose on our students. This type of instruction would ultimately affect students who are aware of the nature, the effect of everyday usage of energy on the environment, and what needs to be done within the restrictions of nature to be sustainable at least at the levels that we enjoy today. Of course, these must be done in all aspects of education not only in the education of engineers, in general, and thermodynamics education, in particular. Success in this will make life better now and forever.

The previous pages have emphasized undergraduate work. It is indeed very important to extend this into statistical and nonequilibrium thermodynamics for graduate students. The challenges of energy use, pollution and sustainability all depend on clear, precise and correct study of these and appropriate applications. It can and should be pursued very aggressively throughout.
Acknowledgement

The view expressed herein are those of the author and do not purport to reflect the position of the United States Military Academy, the Department of the Army, or the Department of Defense.

Nomenclature

A  Area [m²]
B  Any extensive thermodynamic property
b  Any intensive thermodynamic property, b=B/m
c  Specific heat [kJ/(kg-K)]; also speed of sound [m/s]
E  Energy [kJ]
e  Specific energy [kJ/kg]
F  Helmholtz potential [kJ]
G  Gibbs free energy [kJ]
H  Enthalpy [kJ]
h  Specific enthalpy [kJ/kg]
k  Ratio of specific heats, k=(c_p/c_v)
M  Molecular mass [kmol]; also arbitrary function
m  Mass [kg]

m  Mass flow rate [kg/s]
N  Arbitrary function
n  Unit vector
p  Pressure [kPa]
Q  Heat [kJ]
\mathcal{R}  Universal gas constant [kJ/(kmol-K)]
S  Entropy [kJ/K]
s  Specific entropy [kJ/(kg-K)]
T  Temperature [K]
t  Time [s]
U  Internal energy [kJ]
u  Specific internal energy [kJ/kg]
V  Volume [m³]
v  Specific volume [m³/kg]
\( \vec{V} \) Velocity [m/s]
\( W \) Work [kJ]
\( X \) Arbitrary function
\( Y \) Arbitrary function
\( Z \) Arbitrary function; also compressibility factor [-]
\( z \) Elevation [m]

Greek symbols
\( \alpha \) Coefficient of thermal expansion [1/K]
\( \beta \) Coefficient of performance for a refrigerator
\( \gamma \) Coefficient of performance for a heat pump
\( \Delta \) Difference
\( \delta \) Increment
\( \eta \) Efficiency for an engine
\( \Theta \) Angle [°]
\( \kappa_T \) Isothermal compressibility [1/kPa]
\( \mu \) Joule-Thomson coefficient [K/kPa]
\( \xi \) Arbitrary thermodynamics property
\( \rho \) Density [kg/m³]
\( \sigma \) Entropy generation [kJ/K]

Subscripts
\( E \) Engine
\( CE \) Carnot engine
\( CV \) Control volume
\( f \) Liquid phase
\( fg \) Phase change from liquid to vapor
\( g \) Vapor phase
\( H \) High
\( L \) Low
\( v \) Volume
p Pressure

References

On the physical interpretation of the mathematics of thermodynamics

A. Özer Arnas *
Mechanical Engineering Department, Bogaziçi University, Bebek 80815 Istanbul, Turkey
(Received 26 October 1999, accepted 3 November 1999)

Abstract—The use of mathematical relations is discussed with the idea of enhancing the teaching–learning process in thermodynamics. It is emphasized that the physical interpretation of mathematical relations is of importance in explaining thermodynamic phenomena, showing how thermodynamic tables are made, the physical interpretation of thermodynamic diagrams, the design of experiments, and research in fields that require thermodynamics, particularly for quantities that involve nonmeasurable thermodynamic properties. It is believed that the appropriate use of these relationships contributes to the clear understanding of thermodynamic concepts, processes and systems.

Nomenclature

- $c$: speed of sound $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldot
pendent [1–3]. It is indeed easy, but interesting, to show that the end result is the same, as it should be, and a simple analysis does prove it very elegantly [7]. In one of the examples given below, this is proven. As a matter of fact, similar concepts were used to clarify the numerical difficulties of two-phase flow situations that commonly arise in nuclear thermal hydraulics as well as two-phase correlations that are used for design [8].

There are different ways to solve for or discuss these useful relations. Here the method of Jacobians [4] is used. This is a personal preference and other methods may be used equally successfully depending on one’s choice. The method is not discussed here; rather it is used to show the results of some thermodynamic situations of interest.

1.1. Example 1

In this example, the slope of a constant volume line in the superheated region of the Mollier diagram will be investigated. The result will be applied to an ideal gas, since steam at elevated temperatures acts as one, and its functional form, in general, will be determined.

The quantity that is to be investigated is \( \frac{\partial h}{\partial s} \) since the \( h-s \) diagram is the Mollier diagram. As a first step, this relation is written in terms of Jacobians as

\[
\left( \frac{\partial h}{\partial s} \right)_v = \frac{[h, v]}{[s, v]} \tag{1}
\]

Then, the terms that involve \( u, h, g \) and \( f \), specific internal energy, enthalpy, the Gibbs and Helmholtz potentials, respectively, are eliminated by using equations of the form

\[
\frac{dh}{dT} = T \, ds + v \, dp \tag{2}
\]

written in the form of Jacobians as

\[
[h, X] = T[s, X] + v[p, X] \tag{3}
\]

where \( X \) is any other thermodynamic property. Thus in this case,

\[
[h, v] = T[s, v] + v[p, v] \tag{4}
\]

Since in a cycle, from the first law,

\[
[T, s] = [p, v] \tag{5}
\]

and since the definition of the specific heat at constant volume is

\[
\frac{c_v}{T} = \frac{[s, v]}{[T, v]} \tag{6}
\]

then the combination of equations (1), (4), (5) and (6) gives

\[
\left( \frac{\partial h}{\partial s} \right)_v = T \left[ 1 + v \frac{\left( \frac{\partial p}{\partial T} \right)_v}{c_v} \right] \tag{7}
\]

This result shows that the constant volume line on the Mollier diagram is that of temperature along with a correction term. For an ideal gas,

\[
\frac{\partial p}{\partial T} = \frac{c_p - c_v}{v} \tag{8}
\]

which upon substitution into (7) gives

\[
\left( \frac{\partial h}{\partial s} \right)_v = kT \tag{9}
\]

This, therefore, shows that the slope of the constant volume line of an ideal gas on the Mollier diagram follows that of the temperature increased by the factor of the ratio of specific heats. For a given situation, the validity of the ideal gas assumption must be investigated before equation (9) can be used. Equation (7), however, is the generalized result and is applicable to steam at any state.

Other slopes on the Mollier diagram can also be investigated to better explain and clarify the physical interpretation of the diagram. Similarly, other diagrams can be investigated. The undergraduate and graduate students find this approach very useful and learn on their own the mathematics of the Jacobians in its mathematical context since the physical significance can be better understood.

1.2. Example 2

The relation between the pressure, \( p \), and temperature, \( T \), in a reversible adiabatic process is useful in solving many important and interesting problems. The application of the result to a special case of an ideal gas with constant specific heats is also very useful in solving many problems of significance. Therefore, the relation that is to be investigated can be written as \( \frac{\partial p}{\partial T} \), which becomes in terms of Jacobians

\[
\left( \frac{\partial p}{\partial T} \right)_s = \frac{[p, s]}{[T, s]} \tag{10}
\]

With the use of equation (5) and the definition of specific heat at constant pressure,

\[
\frac{c_p}{T} = \frac{[s, p]}{[T, p]} \tag{11}
\]
equation (10) reduces to

\[ \frac{\partial p}{\partial T} = \frac{c_p}{T} \frac{\partial T}{\partial v} \]  

\[ \text{(12)} \]

For the case of an ideal gas,

\[ \frac{\partial T}{\partial v} = \frac{p}{c_p - c_v} \]  

\[ \text{(13)} \]

Upon substitution into equation (12),

\[ \frac{\partial p}{\partial T} = \frac{p}{T} \frac{k}{k - 1} \]  

\[ \text{(14)} \]

For the case of an isentropic process, which is the case of interest, then

\[ \frac{dp}{p} \frac{p}{dT/T} = \frac{k}{k - 1} \]  

\[ \text{(15)} \]

results in a relation given as

\[ T = p^{(k-1)/k} \]  

\[ \text{(16)} \]

which is valid for an isentropic process of an ideal gas with constant specific heats. Equation (16) is not only well known but also used extensively. Similar results between \( p \) and \( v \), and \( T \) and \( v \) can also be obtained following through a similar procedure.

### 1.3. Example 3

Maxwell relations can be found from the Jacobians themselves and need not be introduced separately. Indeed, the relations are only yet another way of expressing the integrability condition of a property. Thus for a cyclic process in a simple system, the area in a \( p-v \) diagram, representing reversible net work out, will transform to the same area in a \( T-s \) diagram, representing reversible net heat in, as in equation (5). In mathematical representation,

\[ \frac{\partial (p,v)}{\partial (T,s)} = 1 \]  

\[ \text{(17)} \]

For example,

\[ \left( \frac{\partial s}{\partial p} \right)_T = \left( \frac{\partial (s,T)}{\partial (p,T)} \right) \]  

\[ \text{(18)} \]

It seems to be desirable to introduce Maxwell relations this way since it refers to the fundamental law by which energy and its Legendre transformations are indeed properties or potential functions subject to Maxwell relations [5].

### 1.4. Example 4

As an example of design of experiments, consider the measurement of the speed of sound, which is defined as

\[ c^2 = \left( \frac{\partial p}{\partial p} \right)_T \]  

\[ \text{(19)} \]

where \( \rho \) is the density of the medium and is equal to the inverse of the specific volume. In view of the fact that the entropy is a nonmeasurable quantity, it must be eliminated in favor of those that are measurable. Using equations (6) and (11), the speed of sound becomes

\[ c^2 = -k \left( \frac{\partial p}{\partial \rho} \right)_T \]  

\[ \text{(20)} \]

which now is totally measurable. Therefore, an isothermal experiment must be designed in which the variation in pressure with respect to density must be measured.

Although it is a well known fact that the choice of thermodynamic properties that characterize a physical situation is arbitrary as long as those properties are independent, one finds in the literature situations where this fact is overlooked in some thermal hydraulics research [6–8].

Assuming that the variables are \( V, p, \) and \( h \), where \( V \) is the flow velocity, the speed of sound reduces to [6]

\[ c^2 = \frac{1}{(\partial \rho/\partial p)_h + (1/\rho)(\partial \rho/\partial h)_p} \]  

\[ \text{(21)} \]

The first term is obtained as

\[ \left( \frac{\partial \rho}{\partial \rho} \right)_h = -\rho^{-2} \left( \frac{\partial v}{\partial \rho} \right)_h = -\rho^{-2} \left[ h, v \right] \]  

\[ \text{(22)} \]
With the use of equations (4), (6) and (11), it can be shown that equation (22) reduces to
\[
\frac{\partial \rho}{\partial p} = - \rho^2 \left\{ \frac{1}{k} \left( \frac{\partial v}{\partial p} T - \frac{1}{\rho c_p} \left( \frac{\partial u}{\partial T} \right)_p \right) \right\} \tag{23}
\]

From equations (4) and (11), it follows that the second term of equation (23) can be expressed as
\[
\frac{1}{\rho} \left( \frac{\partial \rho}{\partial h} \right)_T = - \frac{\rho}{c_p} \left( \frac{\partial v}{\partial T} \right)_p \tag{24}
\]

When equations (21), (23) and (24) are combined, equation (20) is obtained.

Assuming the variables are \( V, \rho, \) and \( p, \) the speed of sound reduces to [6]
\[
c^2 = \frac{-\rho(\partial h/\partial p)_p}{\rho(\partial h/\partial p)_p - 1} \tag{25}
\]

The numerator is the inverse of equation (24). Since
\[
\frac{\partial T}{\partial p} \rho \frac{\partial \rho}{\partial p} \left( \frac{\partial h}{\partial p} \right)_T = -1 \tag{26}
\]
the denominator of equation (25) can be written as
\[
\rho \left( \frac{\partial h}{\partial p} \right)_T - 1 = \rho \left[ \frac{h, \rho}{p, \rho} \right] - 1 = c_v \rho \left( \frac{\partial T}{\partial p} \right)_T \tag{27}
\]
where equations (4) and (6) are used. When equations (24), (25) and (27) are combined, equation (20) is obtained.

Assuming the variables as \( V, \rho, \) and \( T, \) the speed of sound reduces to [6]
\[
c^2 = \left\{ \left[ -\frac{(\partial h/\partial T)p}{\rho c_p} \right] \left[ \rho \left( \frac{\partial h}{\partial p} \right)_T - 1 \right] + \left( \frac{\partial p}{\partial T} \right)_T \right\}^{-1} \tag{28}
\]

The only term to analyze is \( \rho(\partial h/\partial T) - 1 \) which simplifies to
\[
\rho \left( \frac{\partial h}{\partial p} \right)_T - 1 = -(T \rho) \left( \frac{\partial v}{\partial T} \right)_p \tag{29}
\]
where equations (4) and (17) are used. From the identity [3]
\[
(c_p - c_v) = T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial p}{\partial T} \right)_v \tag{30}
\]
and the equations (28) and (29), equation (20) follows.

It is, therefore, obvious that no matter what properties are chosen, the final result is unique because of the fundamental concepts of thermodynamics [7]. However, if the results in [6] were not reduced in this fashion, they would have to be evaluated numerically. Since the series representation of enthalpy, entropy and other nonmeasurable terms are not similar, the numerical solutions of equations (21), (25) and (28) will give different results. The justification for it was attempted [6]. It is now proven that that attempt is really a communication that has absolutely no thermodynamic basis [7].

It is, therefore, seen that the method of Jacobians is indeed a very powerful one to simplify the various mathematical relations encountered in the study of thermodynamics and gives them physical significance. It is this physical significance that further increases the appreciation that the students have for thermodynamic reasoning and, as a result, they can better relate, understand and learn thermodynamics [10–12] and makes the teaching of the subject more pleasurable.

Other experiments can also be designed using the techniques and methodologies developed above and in the literature. In the past, along with the speed of sound, experiments have been designed for the Joule–Thomson coefficient and the Clausius–Clapeyron equation with great success and enthusiasm.

2. CONCLUDING REMARKS

It is indeed obvious that the applications of these techniques are very meaningful and give even further insight to why and how things happen. When the student is taught these methodologies, the learning should improve. If the mathematical topics are approached in this fashion, the thermodynamic concepts and equations make more sense [9].

These concepts and methodologies have been used for undergraduates, and graduate students, with extreme success in the United States, Belgium, the Netherlands, Italy and Turkey. The students have been able to relate to thermodynamics better once they see and understand the reasons behind the natural happenings.

REFERENCES


EUROPEAN TWO-PHASE FLOW GROUP MEETING

University of Strathclyde - Glasgow

June 3-6, 1980

THERMODYNAMIC EXPLANATION OF SOME NUMERICAL DIFFICULTIES IN MULTIPHASE FLOW ANALYSES

by

O.A. ARNAS, H.A.M. HENDRIKSEN, C.W.J. van KOPPEN

Laboratory of Heat Technology
Eindhoven University of Technology
The Netherlands
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>i</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>ii</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Formulation - Partial Derivatives</td>
<td>2</td>
</tr>
<tr>
<td>Formulation - Second Law of Thermodynamic Explanation of Slip Conditions</td>
<td>5</td>
</tr>
<tr>
<td>Steady - State Entropy Variation</td>
<td>8</td>
</tr>
<tr>
<td>Discussion</td>
<td>9</td>
</tr>
<tr>
<td>Conclusions</td>
<td>10</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>10</td>
</tr>
<tr>
<td>References</td>
<td>11</td>
</tr>
</tbody>
</table>
SUMMARY

In numerical differentiation of various partial derivatives of thermodynamic variables, noise is introduced and the accuracy of the results are reduced. These partial derivatives come about due to the dependence of the system on thermo-hydraulic parameters. In early years, researchers attempted to circumvent this situation by trying to manipulate the equations, LEVY (1965) and MOODY (1965). Later certain other derivatives were substituted, PORTER (1975), or new methods were suggested, BRYCE (1976, 1977). Recently, an attempt has been made to determine the speed of wave propagation for compressible liquid flows with heat transfer, CHAWLA (1978).

In this paper, a general analysis is carried out to eliminate nonmeasurable thermodynamic quantities, which have to be present in a thermo-hydraulic analysis of multiphase flows, in terms of measurable ones using the method of JACOBIANS, CALLEN (1960). As a result, it is seen that for critical flow studies, the ISOTHERMAL COMPRESSIBILITY of the steam-water mixture is needed. The present analysis completely defines all partial derivatives in terms of the p-V-T data and other physical properties, i.e., heat capacities, coefficient of volume expansion, isothermal compressibility - all measurable quantities.

Also, starting with the hyperbolic regime of the hydrodynamic equations, BRYCE (1976, 1977), an entropy production equation is derived using as the characteristic parameters pressure, quality and mass flow rate per unit area. It is shown that no entropy production case is approached when the rates of momentum and energy additions per unit length are zero with small rate of mass flow per unit area. The effect of area variation in the flow direction is included in the analysis. This result also restricts the choice of slip correlations eliminating those that tend to decrease the entropy production in the physically acceptable set of characteristic parameters. The paper is concluded with a discussion on the appropriate choice of these characteristic parameters.
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>(L^2)</td>
</tr>
<tr>
<td>a</td>
<td>coefficients of equation (26)</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>heat capacity</td>
<td>(ML^2/Tt^2)</td>
</tr>
<tr>
<td>D</td>
<td>defined by equation (42)</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>energy per unit length</td>
<td>(ML/t^2)</td>
</tr>
<tr>
<td>F</td>
<td>Helmholtz free energy</td>
<td>(ML^2/t^2)</td>
</tr>
<tr>
<td>G</td>
<td>mass flow rate, (M/L^2t); also Gibbs free energy</td>
<td>(ML^2/t^2)</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
<td>(ML^2/t^2)</td>
</tr>
<tr>
<td>h</td>
<td>specific enthalpy</td>
<td>(L^2/t^2)</td>
</tr>
<tr>
<td>M</td>
<td>momentum per unit length</td>
<td>(M/t)</td>
</tr>
<tr>
<td>m</td>
<td>mass, (M); also in equation (20)</td>
<td>(M/L)</td>
</tr>
<tr>
<td>N</td>
<td>number of moles</td>
<td>mole</td>
</tr>
<tr>
<td>n</td>
<td>a positive integer</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>(M/Lt^2)</td>
</tr>
<tr>
<td>S</td>
<td>entropy</td>
<td>(ML^2/Tt^2)</td>
</tr>
<tr>
<td>s</td>
<td>slip ratio</td>
<td>-</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature</td>
<td>(T)</td>
</tr>
<tr>
<td>U</td>
<td>internal energy</td>
<td>(ML^2/t^2)</td>
</tr>
<tr>
<td>u</td>
<td>specific internal energy</td>
<td>(L^2/t^2)</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>(L^3)</td>
</tr>
<tr>
<td>x</td>
<td>flow quality, (\dot{m}_G/\dot{u})</td>
<td>-</td>
</tr>
<tr>
<td>(\bar{x})</td>
<td>freeze quality, (m_G/Vp)</td>
<td>-</td>
</tr>
<tr>
<td>x</td>
<td>variable thermodynamic property in equation (5)</td>
<td>-</td>
</tr>
<tr>
<td>z</td>
<td>flow direction coordinate</td>
<td>(L)</td>
</tr>
</tbody>
</table>

**Subscripts**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td>component</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>constant pressure</td>
<td>(M/Lt^2)</td>
</tr>
<tr>
<td>S</td>
<td>reversible adiabatic - isentropic</td>
<td>(ML^2/Tt^2)</td>
</tr>
<tr>
<td>T</td>
<td>isothermal</td>
<td>(T)</td>
</tr>
<tr>
<td>V</td>
<td>constant volume</td>
<td>(L^3)</td>
</tr>
</tbody>
</table>
Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>void fraction</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>coefficient of volume expansion</td>
<td>$1/T$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>ratio of heat capacities at constant pressure to volume</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>roots of equation (26)</td>
<td></td>
</tr>
<tr>
<td>$\kappa$</td>
<td>compressibility</td>
<td>$Lt^2/M$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>chemical potential</td>
<td>$ML^2/t^2\text{mole}$</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>defined by equation (23)</td>
<td>$L^3/M$</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>defined by equation (24)</td>
<td>$L^3/M$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>$M/L^3$</td>
</tr>
</tbody>
</table>
INTRODUCTION

Multiphase flow analyses, due to their thermo-hydraulic character, invariably have various partial derivatives relating thermodynamic variables. These have caused difficulties in explaining the physics of the problems and the results obtained in the analyses.

Levy(1965) and later Moody(1965), in their discussion of two-phase critical flow, use the equation

\[
G^2_S = - \frac{\partial p}{\partial V} S
\]  

(1)

neglecting the friction and head losses. In attempting to evaluate this partial derivative between \( p \), \( V \) and \( S \), Levy(1965) uses the results he obtained (1960) for quality-void fraction relationship, equation (12) of (1965). Unfortunately, this relation based on a momentum model (1960) is wrong leading him into difficulties not only in evaluating nonmeasurable thermodynamic quantities, such as entropy, but also in trying to explain the results obtained. Moody(1965) tries to manipulate equation (1) so as to obtain an equivalence in the form of

\[
G^2_S = - \frac{1}{V} \frac{\partial H}{\partial V} S
\]  

(2)

However, instead of one nonmeasurable quantity, this equation has two, \( H \) and \( S \). Thus, his further analysis becomes more suspect in his attempts to find equivalences for the terms. As a matter of fact, he states that, "... there may be criticism regarding the manipulation of equations (52) and (53) ...", (1965). Extending and generalizing the work of Moody(1965), Porter(1975) introduces partial derivatives among the thermodynamic variables \( H \), \( p \) and \( T \). Since all his work is numerical, the differentiation of these relationships introduce difficulties as well as loss in accuracy owing to noise introduced, Chawla(1978). Bryce(1976) selected \( u \), \( p \) and \( C \) as the basic thermo-hydraulic variables, ended with various relationships between \( h \), \( u \), \( p \) and \( o \). For these, RELAP-JK steam tables and numerical evaluation were used which once again introduce numerical difficulties. Later Bryce(1977) selected \( p \), \( X \) and \( G \) as the basic variables; however, this didn't change the fundamental difficulties. It is also to be noted that this choice of basic variables is by no means arbitrary but must be based on thermo-hydraulic fundamentals of two-phase flow situations. – In this paper, we shall discuss the works of Bryce (1976, 1977) not only to clarify the partial derivatives, but also to discuss the second law of thermodynamic explanation of the slip conditions. Recently, Chawla(1978) made an attempt to explain the equivalency of different expressions obtained for speed of wave propagation depending on the choice of basic variables. However, the methodology used is not only cumbersome but also the results leave certain fundamental concepts unanswered.
FORMULATION - PARTIAL DERIVATIVES

In the practical applications of thermodynamic theory, the experimental situation to be analyzed often requires a certain partial derivative among thermodynamic variables to be evaluated. As an example, we may be concerned with the analysis of the temperature change which is required to maintain the volume of a single component system constant if the pressure is increased slightly. This temperature change is,

\[
dT = \left( \frac{3T}{3p} \right)_{V,N} \, dp
\]

and consequently we are interested in an evaluation of the partial derivative given above. More difficulties are caused if the partial derivatives include nonmeasurable basic quantities, \( U \) and \( S \), or non-measurable derived quantities, \( H \), \( G \) and \( F \). A general feature of the derivatives that arise in this way is that they generally involve both intensive and extensive parameters at constant mole numbers. "... of all such parameters, only three can be independent, and any given derivative can be expressed by an identity in terms of an arbitrarily chosen set of three basic derivatives. This set is conventionally chosen as \( c_p \), \( \beta \) and \( \kappa_T \).", Callen(1960).

To circumvent the nonmeasurable quantities that invariably appear in multiphase flow problems, we propose a procedure which makes free use of the Maxwell relations of thermodynamics and which reduces the formal manipulation of derivatives to a simple recipe, the JACOBIAN TRANSFORMATIONS. This method can be outlined as:

**STEP 1.** Express the given partial derivative in terms of Jacobians.

**STEP 2.** If any nonmeasurable thermodynamic property other than entropy appears in the Jacobians, eliminate it by using equations similar to,

\[
dU = T \, dS - p \, dV + \sum_j \mu_j \, dN_j
\]

\[
|U,x| = T \, |S,x| - p \, |V,x| + \sum_j \mu_j \, |N_j,x|
\]

and others for \( N \), \( G \) and \( F \) from their defining equations. At this time, entropy should be the only property left to be eliminated.

**STEP 3.** To eliminate the entropy, use the definitions of the heat capacities,

\[
\kappa_p = T \left( \frac{3S}{3T} \right)_p
\]

\[
c_V = T \left( \frac{3S}{3T} \right)_V
\]

\[
\]
the equality,

\[ c_V = c_p - \frac{T V S^2}{m \kappa_T} \]  \hspace{1cm} (7)

or, since Jacobians are cyclic integrals, from the first law of thermodynamics,

\[ |T, S| = |p, V| \] \hspace{1cm} (8)

**STEP 4.** The derivatives between \( p, V \) and \( T \) can be eliminated by the definition of the coefficient of volume expansion,

\[ \beta = \frac{1}{V} \frac{\partial V}{\partial T} \] \hspace{1cm} (9)

and the isothermal compressibility,

\[ \kappa_T = -\frac{1}{V} \frac{\partial T}{\partial p} \] \hspace{1cm} (10)

or, by the cyclic thermodynamic property relation,

\[ \frac{\partial V}{\partial T}_p \frac{\partial T}{\partial p}_V \frac{\partial p}{\partial V}_T = -1 \] \hspace{1cm} (11)

**STEP 5.** The resulting expression should now be in terms of the three properties, \( p, V \) and \( T \), and \( c_p, \beta \) and \( \kappa_T \). If not, a mistake has been made.

Levy (1965) had used the partial derivative \( \frac{\partial p}{\partial V} \), equation (1). Thus,

\[ \frac{\partial p}{\partial V}_S = \frac{|p, S|_V S}{|V, S|_V} = \frac{|S, p|_V}{|S, V|_V} \]

Using equations (6) and (10), simultaneously,

\[ \frac{\partial p}{\partial V}_S = \frac{c_p}{c_V} \frac{|T, p|_V}{|T, V|_V} \]

\[ = -\frac{\gamma}{V \kappa_T} \]

which makes the critical flow rate, equation (1),

\[ Q^2 = \frac{\gamma}{V \kappa_T} \] \hspace{1cm} (12)

Moody (1965) manipulates equation (1) to obtain equation (2). Thus, the value of the partial derivative
\[ \frac{\partial H}{\partial V} \] 

is needed. Using the method outlined above and the definition of enthalpy with equations (4) and (5) for constant number of moles,

\[ |H, x| = T \left| S, x \right| + V \left| p, x \right| \]

or

\[ |H, S| = T \left| S, S \right| + V \left| p, S \right| \]

\[ = V \left| p, S \right| \]

Thus,

\[ \frac{\partial H}{\partial V} \bigg|_S = \frac{T_p S}{V, S} \]

\[ = \frac{V \left| p, S \right|}{|V, S|} = V \frac{S_p}{S, V} \]

Using equations (6) and (10), respectively,

\[ \frac{\partial H}{\partial V} \bigg|_S = V \frac{c_p}{c_v} \frac{T_p}{T, V} \]

\[ = - \frac{\gamma}{\kappa_T} \]

Substituting into equation (2)

\[ G^2_S = \frac{\gamma}{V^2 \kappa_T} \]

which is the same as equation (12).

Porter(1975) has relations between H, p and T. Thus, using equation (13) and substituting from equation (8) and (9), the final result is

\[ \frac{\partial H}{\partial p} \bigg|_T = V (1 - TB) \]

Bryce(1976) had the need for derivatives between the variables U, p and V. Therefore, using equations (5), (6), (10) and (11), the final result for one such partial relationship becomes,

\[ \frac{\partial p}{\partial V} \bigg|_U = \frac{1}{\kappa_T} \left( \frac{p^2}{c_v} - \frac{\gamma}{V} \right) \]

Bryce(1977), due to the choice of a different set of characteristic parameters, had derivatives amongst H, V and p. The value for one such derivative, using equations (13), (6) and (9), is

\[ \frac{\partial H}{\partial V} \bigg|_p = \frac{c_p}{\beta V} \]

(17)
Chawla (1978), apart from the ones dealt with above, used the partial derivatives,
\[
\frac{\partial V}{\partial P}_H, \quad \frac{\partial H}{\partial P}_V
\]
Thus, using the above methodology, their values become, respectively,
\[
\frac{\partial V}{\partial P}_H = \frac{V}{c_p}\left(c_v\kappa_T - V\beta\right) \tag{18}
\]
\[
\frac{\partial H}{\partial P}_V = \frac{c_v\kappa_T}{\beta} + V \tag{19}
\]
As a result of the formulation presented above, it is seen that all partial derivatives of thermodynamic properties can be defined in terms of the heat capacities, the coefficient of volume expansion, the isothermal compressibility along with the pressure, volume and temperature. These are all directly measurable or can be determined from measurable data, Rowlinson (1969). It is also to be noted that more fundamental data needs to be obtained on these quantities for various steam-water mixture combinations so that design criteria can be established in a more meaningful fashion.

FORMULATION - SECOND LAW OF THERMODYNAMIC EXPLANATION OF SLIP CONDITIONS

The methodology originally suggested by Bryce (1976, 1977) prompted this second law of thermodynamics based investigation of slip correlations of multiphase flow analyses. A minimum entropy production based analysis was first carried out by Zivi (1964) and caused a lot of discussion, most of it well founded, among various researchers, i.e., Levy, Wallis, Zuber, among others. Later, Moody (1965) arrived at a similar slip correlation; however, the results obtained did not satisfy those who were arguing about the proposed approach. Above we have referred to this problem. Bryce (1976, 1977) presented a mathematical approach to obtain characteristic roots of the equation systems describing one-dimensional transient two-phase flow approximations to the combined mass, momentum and energy equations. For some flow situations, the equations are found to possess complex valued characteristic roots causing the equations to be non-hyperbolic. This situation was also noticed and discussed by Simpson and Rooney (1975). This, in turn, results in the violation of the second law under these flow situations, Bryce (1977). To circumvent this difficulty, Bryce proposes a flow-dependent slip correlation which expands the range of applicability but not resolve the real problem.

To give continuity to the discussion, we choose the same terms and nomenclature as Bryce (1977). Thus, for the situation described by him under the assumptions made, the conservation equations are,
\[
\dot{m} = \frac{\partial \rho A}{\partial t} + \frac{\partial \rho A}{\partial z} \tag{M/Lt} \tag{20}
\]
MOMENTUM: \[ \dot{\phi} = \frac{3}{\delta t} \frac{\partial \phi}{\partial \phi} + \frac{\partial \phi}{\partial \phi} + \frac{\partial G^2 A\phi}{\partial t} \] 

ENERGY: \[ \dot{\phi} = \frac{3}{\delta t} \frac{\partial \phi}{\partial \phi} + \frac{\partial hG}{\partial \phi} + \frac{\partial G^2 A\phi}{\partial t} + \frac{\partial G^3 A\phi^2}{\partial \phi} \] 

where the following definitions are used:

\[ v_1 = \frac{1}{\phi} \left[ \frac{(1-X)^2}{(1-\phi)} + \frac{X^2}{\phi} \right] \]

\[ v_2 = \frac{1}{\rho^2} \left[ \frac{(1-X)^3}{(1-\phi)^2} + \frac{X^3}{\phi^2} \right] \]

and where \( X \), the flow quality, and \( \bar{X} \), the freeze quality, are related by the slip ratio, \( s \), as

\[ s = \left[ \frac{X}{1-\bar{X}} \right] \left[ \frac{1-\bar{X}}{\bar{X}} \right] \]

In his study, Bryce (1976) selected \( u, \rho \) and \( G \) as the characteristic functions but changed them to \( p, X \) and \( G \) in (1977). Of course, the choice is not arbitrary and we shall discuss this further later. Using \( p, X \) and \( G \) as the thermodynamic and hydraulic characteristic functions, respectively, and following the mathematical method presented by Bryce (1976, 1977), the coefficients of the equation,

\[ a_1\phi^3 + a_2\phi^2 + a_3\phi + a_4 = 0 \]

are given as,

\[ a_1 = \rho \left[ \rho, u \right]_{p,X} + G^2 \left( \frac{1}{\rho} \left[ \rho, \phi \right]_{p,X} \right) \]

\[ a_2 = -\left( \rho \left[ \rho, u \right]_{X,G} + G \left( 2\rho \phi \left[ \rho, u \right]_{p,X} + \rho, h \left[ p,X + \phi \left[ \rho, \phi \right]_{X,G} \right) \right) \right. \]

\[ + G^2 \left( \frac{1}{\rho} \left[ \rho, \phi \right]_{X,G} \right) \]

\[ a_3 = \frac{P}{\rho} \left[ \rho, h \right]_{X,G} + G \left( \left[ \rho, h \right]_{X,G} \right) \]

\[ + G^2 \left( 2\phi \left[ \rho, h \right]_{p,X} + \rho \left[ u, \phi \right]_{p,X} - \frac{P}{\rho} \left[ \rho, \phi \right]_{p,X} \right) \]

\[ - \frac{1}{2} \frac{\phi \left[ \rho, \phi \right]_{p,X} + \frac{3}{2} \phi^2 \left[ \rho, \phi \right]_{p,X} }{\phi} \]
\[ + G^{3} \left( \frac{\partial \rho, \nu^{2}}{\partial x} \right)_{x,G} - \left( \frac{\partial \rho}{\partial x} \nu_{1} \right) \]

\[ + G^{4} \left( \nu_{1} \frac{\partial \rho, \nu^{2}}{\partial p} - \frac{3}{2} \nu^{2} \frac{\partial \rho}{\partial p} \nu_{1} \right)_{p,x} \]

\[ + G^{5} \left( \frac{\partial \nu_{2}}{\partial \nu_{1}} \right) \]

(29)

\[ a_{u} = G \frac{\partial h}{\partial x} + G^{3} \left( \frac{\partial \nu^{2}}{\partial x} + \left( \frac{\partial \nu_{1}}{\partial x} \right) \right)_{p,x} \]

\[ + G^{5} \left( \frac{\partial \nu_{2}}{\partial \nu_{1}} \right)_{p,x} \]

(30)

where

\[ \left| \rho, \nu_{1} \right|_{p,x} = \frac{\partial \rho}{\partial x} \frac{\partial \nu_{1}}{\partial x} - \frac{\partial \rho}{\partial \rho} \frac{\partial \nu_{1}}{\partial \rho} \]

\[ \left( \frac{\partial \rho}{\partial \rho} \frac{\partial \nu_{1}}{\partial \rho} \frac{\partial \nu_{1}}{\partial \rho} \right) \]

(31)

\[ \frac{\partial \nu_{1}}{\partial \rho} \frac{\partial \nu_{2}}{\partial \rho} \frac{\partial \nu_{2}}{\partial \rho} \]

\[ \frac{\partial \nu_{1}}{\partial \rho} \frac{\partial \nu_{2}}{\partial \rho} \frac{\partial \nu_{2}}{\partial \rho} \]

et cetera. The values of \( a_{2} \) and \( a_{3} \) differ considerably from those of Bryce (1977).

The roots of equation (26) are real and the conservation equations are hyperbolic if

\[ \left( \frac{\frac{a_{2}}{a_{1}} - \frac{1}{3} \frac{a_{2}}{a_{1}}^{2}}{a_{1}} \right)^{3} + \frac{27}{4} \left( \frac{2}{27} \left( \frac{a_{2}}{a_{1}} \right)^{3} - \frac{a_{2}}{3a_{1}^{2}} \frac{a_{3}}{a_{1}} + \frac{a_{4}}{a_{1}} \right) \leq 0 \]  

(32)

Equation (32) has been investigated thoroughly. To eliminate the possibility of any singularity,

\[ a_{1}^{5} \geq 0 \]  

(33)

This is always satisfied, for the system of the characteristic variables selected, since

\[ \left| \rho, u \right|_{p,x} > 0 \]

\[ \left| \rho, \nu_{1} \right|_{p,x} > 0 \]  

(34)

for any value of \( G \), the mass flow rate. Therefore, the numerator of equation (32) when a common denominator is found, must be less than or equal to zero. To assure this criterion, it was found that for terms of order of \( G^{2+n} \) negligible, with a positive, equal to zero or an integer, i.e., low mass flow rates,

\[ -\left| \rho, p \right|_{x,G} \leq 0 \]  

(35)
The reason why we cannot make any prediction for higher flow rates is the fact that algebraically, the numerator of equation (32) with the equations (27), (28), (29) and (30) becomes unmanageable. Equation (35) is again much different than the results obtained by Bryce (1977). Therefore, those relationships between \( p, \rho, \gamma \) and \( G \) that satisfy the condition of equation (35) will guarantee hyperbolicity of the governing equations for low mass flow rates.

STEADY-STATE ENTROPY VARIATION

For the case of no mass addition and under steady-state conditions, equations (20), (21) and (22) reduce, respectively, to give:

**MASS.** \[ 0 = \frac{\partial G A}{\partial z} \] (36)

**MOMENTUM.** \[ \dot{m} = A \frac{\partial p}{\partial z} + \frac{\partial G^2 A u_1}{\partial z} \] (37)

**ENERGY.** \[ \dot{e} = \frac{\partial h G A}{\partial z} + \frac{1}{2} \frac{\partial G^3 A u_1^2}{\partial z} \] (38)

Also, since the characteristic dependence has been taken to be on \( p, \gamma \) and \( G \), then

\[ S = S(p, \gamma, G) \] (39)

This results in the relation, upon differentiation,

\[ \frac{dS}{dz} = \frac{3S}{3p} \frac{dp}{dz} + \frac{3S}{3\gamma} \frac{d\gamma}{dz} + \frac{3S}{3G} \frac{dG}{dz} \]

which simplifies, using the definition of enthalpy, into

\[ \frac{dS}{dz} = \frac{3h}{\partial \gamma} \frac{dp}{dz} + \frac{3h}{\partial \gamma} \frac{d\gamma}{dz} + \frac{3h}{\partial \gamma} \frac{dG}{dz} \]

\[ T \frac{dS}{dz} = \frac{3h}{\partial \gamma} \frac{dp}{dz} + \frac{3h}{\partial \gamma} \frac{d\gamma}{dz} + \frac{3h}{\partial \gamma} \frac{dG}{dz} \]

\[ \frac{dA}{dz} \]

for constant mole numbers. Obtaining the derivatives (\( dX/dz \)) and (\( dp/dz \)) from the set of equations (36)-(38), equation (40) finally becomes,

\[ T \frac{dS}{dz} = \frac{M}{D A} \left[ G^2 \left\{ \left| h, u_1^2 \right|_{p, \gamma} - \frac{1}{\rho} \left( \frac{\partial h}{\partial \gamma} + \frac{G^2}{2} \frac{\partial u_1}{\partial \gamma} \right) \right\} \right] \]

\[ + \frac{5G}{DA} \left[ \left| u_1, h \right|_{p, \gamma} + \frac{1}{\rho} \frac{\partial u_1}{\partial \gamma} + \frac{1}{G^2} \frac{\partial h}{\partial \gamma} \right] \]
\[ + \frac{G^2}{DA} \frac{dA}{dz} \left[ \rho \frac{\partial h}{\partial x} \frac{\partial \rho}{\partial p} \left( v_h + \frac{1}{\rho} \right) \right] \]

\[ + G \left[ h, v_2 \right]_{x, G} + \frac{1}{\rho} \left[ v_1, h \right]_{x, G} \]

\[ + G^2 \left( \rho \frac{\partial h}{\partial p} \left( v_2 \frac{\partial v_1}{\partial x} + \frac{v_1}{2} \frac{\partial v_2}{\partial x} \right) \right) \]

\[ + \frac{3 \rho}{\rho} \frac{\partial v_2}{\partial p} + \frac{v_1}{2} \frac{\partial v_2}{\partial p} \right) \]

\[ + \frac{G^3}{\rho} \left[ v_1, v_2 \right]_{x, G} - \left[ h, v_1, v_2 \right] \right) \] (41)

where

\[ D = \frac{\partial h}{\partial x} + G^2 \left[ \frac{\partial v_2}{\partial x} + \left[ v_1, h \right]_{p, x} + \frac{G^2}{2} \left[ v_1, v_2 \right]_{p, x} \right] \] (42)

The entropy generated as a result of friction, heat addition or variation of the flow area is depicted in equation (41). However, it is rather easy to show that for any choice of \( p \) and \( x \), there is a characteristic mass flow rate \( G \) for which equation (42) equals zero or becomes negative. It is, nevertheless, very difficult to deduce from equation (41) whether or not this particular mass flow rate would violate the second law, because of partial derivatives between thermodynamic and hydraulic terms. Similar difficulties are faced if the characteristic variables of \( u, \rho, G \) were to be used as was done by Bryce(1976).

**DISCUSSION**

It is seen that the choice of the thermo-hydraulic characteristic variables for a multiphase flow problem is very critical for a meaningful analysis to be performed. One thing is for sure that these variables are not to be arbitrarily selected but rather be based on fundamental criteria. The intent of a thermodynamic analysis of multiphase flow is to determine which slip correlations result in the violation of the second capital law. Therefore, the characteristic variables to be selected must be such that the entropy generation can be determined in terms of generally accepted slip correlations. To do this, the works of Butterworth(1975) and Isbin and Biddle(1979) are investigated. It is seen that the slip correlations depend on the pressure, \( p \), the flow quality, \( x \), and the void fraction, \( c \). From a thermodynamic point view, it may be more advantageous to select the density, \( \rho \), in place of the flow quality, \( x \), since the to be obtained partial derivatives may be evaluated with ease utilizing the methodology outlined in the first part of this paper. In any case, however, the sets \( u, \rho, G \) or \( p, X, G \) donot permit one to make a detailed study of the effect of the choice of slip correlation on the entropy production.
CONCLUSIONS

It is shown that the partial derivative relations obtained amongst various thermodynamic properties in multiphase flow analyses can be reduced to measurable quantities of heat capacities, coefficient of thermal expansion, isothermal compressibility and pressure-volume-temperature data. This permits one to reduce the loss in accuracy owing to noise introduced in the direct numerical differentiation of these derivatives.

It is also shown that the choice of the thermo-hydraulic characteristic parameters in multiphase flow problems are not arbitrary but must be related to available slip correlations so that the effect of slip on entropy production can be studied. It is proposed that this choice may most logically be the pressure, density and the void fraction. In this fashion, it is hoped that the effects of the mass flow rate, friction, energy addition and flow conduit area variation can be better incorporated into an entropy production equation which in turn may give bounds on the validity of most experimental data and/or theoretical work.

ACKNOWLEDGEMENTS

The second part of the work presented owes much to previous studies made, in particular, by Bryce(1976, 1977). We thank him for his response to our inquiry concerning this. Also, the first author thanks Louisiana State University for the sabbatical leave of absence, and the Eindhoven University of Technology for giving him the latitude to work at his convenience with no special demands on his time. For creating this fruitful atmosphere, special thanks are due to Prof. ir. C.W.J. van Koppen.
REFERENCES


ON THE SIGN CONVENTION IN THERMODYNAMICS – AN ASSET OR AN EVIL

A. Özer Armas, PhD., P.E.  
Daisie D. Boettner, PhD.¹  
Margaret B. Bailey, PhD., P.E.

Department of Civil and Mechanical Engineering  
United States Military Academy  
West Point, NY 10996

Kate Gleason College of Engineering  
Rochester Institute of Technology  
Rochester, NY 14623

ABSTRACT

In thermodynamics the sign convention normally used is energy added to a system in the form of heat is taken as positive and that added in the form of work is taken as negative – HIP to WIN (heat in positive – work in negative). This is a common sign convention although some texts specify that all forms of energy added to a system as heat or work are positive. However, regardless of the sign convention adopted for heat and work interactions, later in the same text the specified convention is abandoned in favor of magnitudes or absolute values. This occurs particularly in relation to cycle analyses in which the absolute value is used for energy transfers. Generally for reversible cycles there is no proof as to why the ratio of energy added/rejected via heat transfer equals the ratio of the absolute temperatures of the thermal reservoirs. To promote sign convention consistency, this paper develops the appropriate relationship between energy transfers and thermal reservoir temperatures for reversible cycles and applies the result to power producing and power consuming engineering devices.

INTRODUCTION

Many students consider thermodynamics to be a difficult course. At the United States Military Academy (USMA) at West Point, teaching thermodynamics becomes even more challenging since the students who take this course are truly heterogeneous. According to Albert et al. (2001), students enrolled in the course may major in diverse fields of study such as foreign languages, history, and political science as well as ABET accredited majors in engineering and computer science. During each semester thermodynamics is taught within forty-seven lecture periods with each period being fifty-five minutes long. As described by Albert and Armas (2002) and Klauwender et al. (2002), the course includes four laboratory experiments to solidify topics that are discussed in class. Several instructors teach thermodynamics at USMA. They meet weekly to discuss the material in upcoming lessons and all other necessary topics. During these meetings, the issue of energy transfer in the form of heat and work is discussed at length to include what sign convention to use. As in most undergraduate thermodynamics books, the sign convention used in this course is energy added to a system in the form of heat is taken as positive and that added in the form of work is taken as negative – HIP to WIN. Of course, as discussed by Callen (1960), other sign conventions may be used. A reasonable approach is to adhere to the sign convention initially presented when solving any given problem.

This paper is presented for two reasons. The first reason is to promote sign convention consistency. As indicated by Lewins (1998) many individuals find sign convention use perplexing. Most engineering textbooks listed in the BIBLIOGRAPHY section of this paper describe a sign convention when introducing heat transfer and work. However, in lieu of maintaining the sign convention, the authors adopt the use of magnitudes or absolute values later in the text. Changing the sign convention for varying applications requires

¹ Corresponding author; e-mail address: id7792@usma.edu
some justification and typically confuses the novice student. The situation can become very confusing when the altered sign convention is used in the discussion of heat engine efficiency and refrigeration cycle and heat pump cycle coefficients of performance.

The second reason for this paper is to promote correct and precise thermodynamics. Oberst (1960) says that Keenan "...aroused interest of the author in thermodynamics (and in preciseness)". It is this preciseness that the paper attempts to illustrate.

**DISCUSSION**

Once a text initially establishes a sign convention for energy transfers, it should consistently follow that convention to alleviate any confusion. One example of sign convention application is in the analysis of the Carnot and reverse Carnot (refrigeration and heat pump) cycles to determine the limiting performance of ideal devices. Reversible processes do not exist in nature; however, according to Hutchinson (1957) "Reversible processes form an asymptote to REALITY." By using the established sign convention in analysis of the Carnot cycle, the equivalence of heat transfer ratio to absolute temperature ratio results. Although Van Ness (1969) in his most elegant monograph suggests that "This is proved in virtually every thermodynamics textbook ever written, and the proof will not be repeated here," the extensive bibliography of English-language publications included at the end of this article does not support this statement.

This paper offers two analyses of the Carnot cycle and an analysis of the reverse Carnot cycle. The aim is to show that the negative ratio of heat transfer associated with a high temperature reservoir to heat transfer associated with a low temperature reservoir is equivalent to the ratio of the absolute temperatures of the high and low temperature reservoirs. This result is expressed in Eq. 1.

$$\frac{-Q_H}{Q_L} = \frac{T_H}{T_L}$$  \hspace{1cm} (1)

In these analyses, an ideal gas is used as the working substance since the performance of devices does not depend on the choice of the working substance. Equation 1 is also written in textbooks without the minus sign, which signifies that the absolute values are used since the absolute temperature ratio is always positive.

**CARNOT CYCLE ANALYSIS #1**

Following Zemansky (1937), consider a Carnot cycle operating between a high temperature reservoir (source), $T_H$, and a low temperature reservoir (sink), $T_L$, as shown in Fig. 1:

![Figure 1. Pressure-Volume and Temperature-Entropy Graphs for the Carnot Cycle](image)

This analysis examines the four processes that comprise the cycle starting from the very fundamental equations of thermodynamics that students have learned by the time this topic appears. Using a closed system with no shaft work, consider Process 1 → 2 (Isentropic Compression). The first law of thermodynamics states that

$$\delta Q - \delta W = dU$$  \hspace{1cm} (2)

$$\delta Q = 0$$ for an isentropic process (since it is adiabatic and reversible) and $\delta W = pdV$ due to system boundary work. For an ideal gas, $dU = mc_v dT$. Upon substitution of these relationships into Eq. 1 and simplification, one obtains from the first law

$$-pdV = mc_v dT$$ \hspace{1cm} (3)

The ideal gas equation in its most general format is

$$pV = \frac{mRT}{M}$$ \hspace{1cm} (4)

with the Universal gas constant, $R = 8.314$ [kJ/(mol-K)], and molecular mass of any ideal gas taken as $M$ [kg/kmol]. Substitution for $p$ from Eq. 4 into Eq. 3 results in

$$-\left(\frac{mRT}{M}\right)\frac{dV}{V} = mc_v dT$$

$$\frac{dV}{V} = c_v dT$$  \hspace{1cm} (5)

Integrating over process 1 → 2 and using the source and sink temperatures, $T_H$ and $T_L$, respectively, the resulting equation becomes,

$$\left(\frac{R}{M}\right)\ln\frac{V_2}{V_1} = \frac{T_H}{T_L} c_v dT$$ \hspace{1cm} (6)

Now consider Process 3 → 4 (Isentropic Expansion). Equation 5 applies to this process since the same substitutions and assumptions used for Process 1 → 2 apply in this case. Integrating over process 3 → 4 and using the source and sink temperatures, $T_H$ and $T_L$, respectively, Eq. 5 becomes

$$\left(\frac{R}{M}\right)\ln\frac{V_4}{V_3} = \frac{T_H}{T_L} c_v dT$$ \hspace{1cm} (7)

Equating Eqs. 6 and 7 and manipulating algebraically yields

$$\left(\frac{R}{M}\right)\ln\frac{V_4}{V_3} = \left(\frac{R}{M}\right)\ln\frac{V_2}{V_1}$$
\[
\ln \frac{V_4}{V_3} = -\ln \frac{V_2}{V_1}
\]
\[(\ln V_4 - \ln V_3) = -(\ln V_2 - \ln V_1)\]
\[(\ln V_4 - \ln V_1) = (\ln V_3 - \ln V_2)\]
\[-(\ln V_1 - \ln V_2) = \ln \frac{V_2}{V_1}\]
\[-\ln \frac{V_1}{V_4} = \ln \frac{V_3}{V_2}\]
\[
\frac{V_3}{V_4} = \frac{V_1}{V_2} = -1
\]
\[
\frac{Q_H}{Q_L} = \frac{\left(\frac{mR}{M} T_R \ln \frac{V_3}{V_2}\right)_{T_R}}{\left(\frac{mR}{M} T_L \ln \frac{V_1}{V_4}\right)_{T_L}}
\]
and simplifies to
\[
\frac{Q_H}{Q_L} = \frac{T_R}{T_L} \frac{\ln \frac{V_3}{V_2}}{-\ln \frac{V_1}{V_4}}
\]
Substituting Eq. 8 into Eq. 13 yields
\[
\frac{Q_H}{Q_L} = \frac{T_R}{T_L} (-1)
\]
which is equivalent to Eq. 1.

Next consider Process 2 \(\rightarrow\) 3 (Isothermal Expansion at \(T_R\)). Starting with Eq. 1, \(\delta Q = 0\) since this process is not adiabatic. \(\delta W = pdV\) due to system boundary work and \(dU = mc_v dT\) for an ideal gas. Substitution of these relationships into Eq. 1 results in
\[
\delta Q - pdV = 0
\]
\[
\frac{\delta Q}{2} = \frac{3}{2} pdV
\]
Substitution for \(p\) from Eq. 4 into Eq. 9 and integrating between states 2 and 3 result in
\[
Q_{23} = \left(\frac{mR}{M} T_R\right) \frac{3}{2} \frac{dV}{V}
\]
Letting \(Q_H = Q_{23}\) results in
\[
Q_H = Q_{23} = \left(\frac{mR}{M} T_R\right) \ln \frac{V_3}{V_2}
\]
Analysis of Process 4 \(\rightarrow\) 1 (Isothermal Compression at \(T_L\)) is similar to that of Process 2 \(\rightarrow\) 3 except the temperature remains constant at \(T_L\) and integration occurs from state 4 to state 1. The resulting equation similar to Eq. 10 is
\[
Q_{41} = \left(\frac{mR}{M} T_L\right) \frac{3}{2} \frac{dV}{V}
\]
Letting \(Q_L = Q_{41}\) results in
\[
Q_L = Q_{41} = \left(\frac{mR}{M} T_L\right) \ln \frac{V_1}{V_4}
\]
Using Eqs. 11 and 12, the ratio between \(Q_H\) and \(Q_L\) is
\[
\frac{Q_H}{Q_L} = \frac{T_R}{T_L} \frac{\ln \frac{V_3}{V_2}}{-\ln \frac{V_1}{V_4}}
\]
\[- \frac{mR}{M} \frac{T}{V} \, dV' = mc_c \, dT \]
\[- \frac{R}{M} \int_3^4 \frac{dV}{V} = \frac{4}{3} c_v \frac{dT}{T} = \int_{\tau_2}^{\tau_3} c_v \, dT \]
\[
\frac{R}{M} \ln \frac{V_4}{V_3} = \frac{T}{\tau_2} \frac{dT}{T}
\]

Equating Eq. 15 with Eq. 16 and manipulating algebraically leads to Eq. 17.

\[- \frac{R}{M} \ln \frac{V_2}{V_1} = \frac{R}{M} \ln \frac{V_4}{V_3} \]
\[-(\ln V_2 - \ln V_1) = (\ln V_4 - \ln V_3) \]
\[(\ln V_2 - \ln V_1) = (\ln V_4 - \ln V_3) \]
\[
\ln \frac{V_3}{V_2} = -(\ln V_1 - \ln V_4) \]
\[
\ln \frac{V_2}{V_4} = -\ln \frac{V_1}{V_4} \quad (17)
\]

Next consider isothermal Process 2 \(\rightarrow\) 3. The reversible heat transfer, \(Q_H\), is the integral of \(T dS\) and thus

\[
Q_H = \frac{3}{2} T dS = \frac{3}{2} (dU + pdV) \]

For an ideal gas at constant temperature, the change in internal energy is zero. Therefore,

\[
Q_H = \frac{3}{2} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{mR}{M} T_H \ln \frac{V_3}{V_2} \quad (18)
\]

Similarly for isothermal Process 4 \(\rightarrow\) 1,

\[
Q_L = \frac{1}{4} T dS = \frac{1}{4} (dU + pdV) \]

Again for an ideal gas at constant temperature, the change in internal energy is zero. Therefore,

\[
Q_L = \frac{1}{4} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{mR}{M} T_L \ln \frac{V_3}{V_4} \quad (19)
\]

The ratio of heat transfers is obtained using Eqs. 18 and 19.

\[
\frac{Q_H}{Q_L} = \frac{\left( \frac{mR}{M} T_H \ln \frac{V_3}{V_2} \right)}{\left( \frac{mR}{M} T_L \ln \frac{V_1}{V_4} \right)} = \frac{T_H}{T_L} \frac{\ln \frac{V_3}{V_2}}{\ln \frac{V_1}{V_4}} \quad (20)
\]

Substituting Eq. 17 into Eq. 20 produces

\[
\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \frac{\ln \frac{V_3}{V_2}}{\ln \frac{V_1}{V_4}} = \frac{T_H}{T_L} \frac{\ln \frac{V_3}{V_2}}{\ln \frac{V_1}{V_4}} \]

which again is equivalent to Eq. 1.

**REVERSE CARNOT CYCLE ANALYSIS**

This exercise can be extended to reverse Carnot cycles such as refrigeration and heat pump cycles as shown in Fig. 2.

![Figure 2: Pressure-Volume and Temperature-Entropy Graphs for the Reverse Carnot Cycle](image)

Start with the first Gibbs' equation written for a single component system, Eq. 14. Considering isothermal Process 1 \(\rightarrow\) 2 in the reverse Carnot cycle, the reversible heat transfer, \(Q_L\), is the integral of \(T dS\) and thus

\[
Q_L = \frac{2}{1} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{2}{1} (dU + pdV) \]

For an ideal gas at constant temperature, the change in internal energy is zero. Therefore,

\[
Q_L = \frac{2}{1} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{mR}{M} T_L \ln \frac{V_3}{V_2} \quad (21)
\]

Similarly for isothermal Process 3 \(\rightarrow\) 4 in the reverse Carnot cycle,

\[
Q_H = \frac{4}{3} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{4}{3} (dU + pdV) \]

For an ideal gas at constant temperature, the change in internal energy is zero. Therefore,

\[
Q_H = \frac{4}{3} \int_{V_3}^{V_4} \frac{dV}{V} = \frac{mR}{M} T_H \ln \frac{V_3}{V_2} \quad (22)
\]

Based on Eqs. 21 and 22, the ratio of the heat transfers becomes Eq. 23.
\[
\frac{Q_H}{Q_L} = \frac{m \frac{R}{M} T_H \ln \left( \frac{V_4}{V_3} \right)}{m \frac{R}{M} T_L \ln \left( \frac{V_2}{V_1} \right)} = \frac{T_H \ln \left( \frac{V_4}{V_3} \right)}{T_L \ln \left( \frac{V_2}{V_1} \right)}
\]  

(23)

Now consider isentropic Process 2 \(\rightarrow\) 3 and apply Eq. 14. The term \(T dS\) is zero and \(dU = mc_d dT\) for an ideal gas. Thus Eq. 14 reduces to

\[-p dV = mc_d dT\]

Substitution for \(p\) using Eq. 4, and integrating from state 2 to state 3 leads to Eq. 24.

\[-\frac{mR}{M} \frac{T}{V} dV = mc_d dT\]

\[-\frac{R}{M^2} \frac{3}{2} c_v \frac{dT}{T} = \frac{T}{T_L} c_v \frac{dT}{T}\]

\[-\frac{R}{M} \ln \left( \frac{V_3}{V_2} \right) = \frac{T}{T_L} c_v \frac{dT}{T}\]

(24)

The analysis of isentropic Process 4 \(\rightarrow\) 1 is analogous to that of isentropic Process 2 \(\rightarrow\) 3 and leads to Eq. 25.

\[-p dV = mc_d dT\]

\[-\frac{mR}{M} \frac{T}{V} dV = mc_d dT\]

\[-\frac{R}{M^2} \frac{4}{3} c_v \frac{dT}{T} = \frac{T}{T_H} c_v \frac{dT}{T}\]

\[-\frac{R}{M} \ln \left( \frac{V_1}{V_4} \right) = \frac{T}{T_H} c_v \frac{dT}{T}\]

(25)

Equating Eq. 24 with Eq. 25 and manipulating algebraically leads to Eq. 26.

\[-\frac{R}{M} \ln \left( \frac{V_3}{V_2} \right) = \frac{R}{M} \ln \left( \frac{V_1}{V_4} \right)\]

\[-(\ln V_3 - \ln V_2) = (\ln V_1 - \ln V_4)\]

\[(\ln V_4 - \ln V_3) = (\ln V_1 - \ln V_2)\]

\[\ln \frac{V_4}{V_3} = -\ln \frac{V_2}{V_1}\]

(26)

Substituting Eq. 26 into Eq. 23 produces

\[\frac{Q_H}{Q_L} = \frac{T_L \ln \left( \frac{V_2}{V_3} \right)}{T_L \ln \left( \frac{V_2}{V_1} \right)} = \frac{T_H \ln \left( \frac{V_2}{V_3} \right)}{T_L \ln \left( \frac{V_2}{V_1} \right)} = \frac{T_L}{T_L}\]

which is equivalent to Eq. 1. Note that reverse Carnot cycle analysis and Carnot cycle analysis both produce Eq. 1.

**PERFORMANCE PARAMETERS**

Performance parameters measure the ratio of the net useful effect desired to the "cost" to obtain that effect. Heat engine performance is expressed as efficiency while refrigeration cycle performance and heat pump cycle performance are expressed as coefficient of performance. In most texts the equations for cycle performance are expressed such that numerical substitution is in terms of magnitudes. This section presents an alternative methodology to determine cycle performance while maintaining sign convention consistency. This methodology is demonstrated for three cases: 1) all energy into a system is positive as described by Callen (1960) and the machinery is the system, 2) HIP to WIN and the machinery is the system, and 3) HIP to WIN and the system is defined as the sum of the machinery, the source, and the sink with each component associated with a useful effect energy transfer.

The method used in each case is to first apply a consistent sign convention from the perspective of the identified system. Next define the appropriate performance parameter equation in terms of the established sign convention. Apply conservation of energy to the cycle and solve for \(\eta_{NET}\) in terms of heat transfers. Substitute the result for \(\eta_{NET}\) into the performance parameter equation to develop the expression for the final performance parameter relationship. When solving for numerical answers, substitute values using the established sign convention. To determine maximum possible (Carnot) performance, apply Eq. 1 to the final performance parameter relationship.

The first two cases presented define the system as the machine itself as represented by the dashed circles in Figs. 3 through 8. The third case presents an alternative method in which the system is defined as the sum of the machinery, the source, and the sink with each component associated with a useful effect energy transfer as shown in Figs. 9 through 11. If consistency is established regardless of the sign convention and system designation incorporated, the final performance parameter relationships are identical in all three cases.  

**CASE 1 – ALL ENERGY IN IS POSITIVE and the MACHINERY is the SYSTEM.**

The Heat Engine (HE) for Case 1 is shown in Fig. 3. In the figure (as in Figs. 4 – 11), negative signs are shown before all energy transfers that are negative in value according to the respective sign convention.
The performance is measured by the efficiency, $\eta$. It is defined as

$$\eta = \frac{-W_{\text{NET}}}{Q_H}$$  \hspace{1cm} (27)

Since $\Sigma E_{\text{In}} = \Sigma E_{\text{Out}}$ for the cycle, then $Q_H = -W_{\text{NET}} + (-Q_L)$ or $-W_{\text{NET}} = Q_H + Q_L$. Consequently,

$$\eta = 1 + \frac{Q_L}{Q_H}$$  \hspace{1cm} (28)

Note that upon substitution of numerical values in accordance with the established sign convention that $\eta$ is a positive value in Eqs. 27 and 28.

For a Carnot engine, using the results from Eq. 1,

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}$$  \hspace{1cm} (29)

The Refrigeration (R) Cycle for Case 1 is shown in Fig. 4.

$$\beta = \frac{Q_L}{W_{\text{NET}}}$$  \hspace{1cm} (30)

Since $\Sigma E_{\text{In}} = \Sigma E_{\text{Out}}$ for the cycle, then $W_{\text{NET}} + Q_L = -Q_H$ or $W_{\text{NET}} = -Q_H - Q_L$. Consequently,

$$\beta = \frac{Q_L}{-Q_H - Q_L} = \frac{1}{-\frac{Q_H}{Q_L} - 1}$$  \hspace{1cm} (31)

Note that upon substitution of numerical values in accordance with the established sign convention that $\beta$ is a positive value in Eqs. 30 and 31.

For a Carnot refrigeration cycle, using the results from Eq. 1,

$$\beta_{\text{Carnot}} = \frac{1}{T_H - T_L} = \frac{T_L}{T_H - T_L}$$  \hspace{1cm} (32)

The Heat Pump (HP) Cycle for Case 1 is shown in Fig. 5.

$$\gamma = \frac{-Q_H}{W_{\text{NET}}}$$  \hspace{1cm} (33)

Since $\Sigma E_{\text{In}} = \Sigma E_{\text{Out}}$ for the cycle, then $W_{\text{NET}} + Q_L = -Q_H$ or $W_{\text{NET}} = -Q_H - Q_L$. Consequently,

$$\gamma = \frac{-Q_H}{-Q_H - Q_L} = \frac{1}{1 + \frac{Q_L}{Q_H}}$$  \hspace{1cm} (34)

Note that upon substitution of numerical values in accordance with the established sign convention that $\gamma$ is a positive value in Eqs. 33 and 34.

For a Carnot heat pump, using the results from Eq. 1,

$$\gamma_{\text{Carnot}} = \frac{1}{1 - \frac{T_L}{T_H}} = \frac{T_H}{T_H - T_L}$$  \hspace{1cm} (35)

CASE 2 – HP to WIN sign convention and the MACHINERY is the SYSTEM.

The Heat Engine for Case 2 is shown in Fig. 6.
Figure 6. Heat Engine is System with HIP to WIN Sign Convention

The performance is measured by the efficiency, \( \eta \). It is defined as

\[ \eta = \frac{W_{NET}}{Q_H} \]  

(36)

Since \( \sum_{i=1}^{n} \text{Energy}_{in} = \sum_{i=1}^{n} \text{Energy}_{out} \) for the cycle, then

\[ Q_H = W_{NET} + (-Q_L) \] or \( W_{NET} = Q_H + Q_L \). Consequently,

\[ \eta = 1 + \frac{Q_L}{Q_H} \]  

(28)

Note that upon substitution of numerical values in accordance with the established sign convention that \( \eta \) is a positive value in Eqs. 36 and 28.

For a Carnot engine, using the results from Eq. 1,

\[ \eta_{Carnot} = 1 - \frac{T_L}{T_H} \]  

(29)

The Refrigeration Cycle for Case 2 is shown in Fig. 7.

\[ \beta = -\frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} \]  

(31)

Note that upon substitution of numerical values in accordance with the established sign convention that \( \beta \) is a positive value in Eqs. 37 and 31.

For a Carnot refrigeration cycle, using the results from Eq. 1,

\[ \beta_{Carnot} = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_L}{T_H - T_L} \]  

(32)

The Heat Pump Cycle for Case 2 is shown in Fig. 8.

\[ \gamma = -\frac{Q_H}{W_{NET}} \]  

(38)

Since \( \sum_{i=1}^{n} \text{Energy}_{in} = \sum_{i=1}^{n} \text{Energy}_{out} \) for the cycle, then

\[ -W_{NET} + Q_L = -Q_H \] or \( W_{NET} = Q_H + Q_L \). Consequently,

\[ \gamma = \frac{-Q_H}{-Q_H - Q_L} = \frac{1}{1 + \frac{Q_L}{Q_H}} \]  

(34)

Note that upon substitution of numerical values in accordance with the established sign convention that \( \gamma \) is a positive value in Eqs. 38 and 34.

For a Carnot heat pump, using the results from Eq. 1,

\[ \gamma_{Carnot} = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_H}{T_H - T_L} \]  

(35)

CASE 3 – HIP to WIN sign convention and the SYSTEM is the sum of the machine, the source, and the sink. Case 3 considers a unique perspective in defining the system comprised of the machine and the reservoirs. A useful effect is associated with each component: \( W_{NET} \) with the
machine, $Q_H$ with the high temperature reservoir, and $Q_L$ with the low temperature reservoir.

The Heat Engine for Case 3 is shown in Fig. 9.

![Figure 9. Heat Engine with System Perspective Using HIP to WIN Sign Convention](image)

The performance is measured by the efficiency, $\eta$. It is defined as

$$\eta = \frac{W_{\text{NET}}}{-Q_H}. \quad (39)$$

Since $\Sigma Energy_{in} = \Sigma Energy_{out}$, the energy balance for the machine becomes $-Q_H = W_{\text{NET}} + Q_L$ or $W_{\text{NET}} = -Q_H - Q_L$. Consequently,

$$\eta = 1 + \frac{Q_L}{Q_H}. \quad (28)$$

Note that upon substitution of numerical values in accordance with the established sign convention that $\eta$ is a positive value in Eqs. 39 and 28.

For a Carnot engine, using the results from Eq. 1,

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}. \quad (29)$$

The Refrigeration Cycle for Case 3 is shown in Fig. 10.

![Figure 10. Refrigeration Cycle with System Perspective Using HIP to WIN Sign Convention](image)

The performance is measured by the coefficient of performance and is defined as

$$\beta = \frac{-Q_L}{W_{\text{NET}}}. \quad (40)$$

Since $\Sigma Energy_{in} = \Sigma Energy_{out}$, the energy balance for the machine becomes $-W_{\text{NET}} + (-Q_L) = Q_H$ or $-W_{\text{NET}} = Q_H - Q_L$. Consequently,

$$\beta = \frac{-Q_L}{Q_H - Q_L} = \frac{1}{Q_L - Q_H}. \quad (31)$$

Note that upon substitution of numerical values in accordance with the established sign convention that $\beta$ is a positive value in Eqs. 40 and 31.

For a Carnot refrigeration cycle, using the results from Eq. 1,

$$\beta_{\text{Carnot}} = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_L}{T_H - T_L}. \quad (32)$$

The Heat Pump Cycle for Case 3 is shown in Fig. 11.

![Figure 11. Heat Pump Cycle with System Perspective Using HIP to WIN Sign Convention](image)

The performance is measured by the coefficient of performance and is defined as

$$\gamma = \frac{Q_H}{-W_{\text{NET}}}. \quad (41)$$

Since $\Sigma Energy_{in} = \Sigma Energy_{out}$, the energy balance for the machine becomes $-W_{\text{NET}} + (-Q_L) = Q_H$ or $-W_{\text{NET}} = Q_H + Q_L$. Consequently,

$$\gamma = \frac{Q_H}{Q_H + Q_L} = \frac{1}{1 + \frac{Q_L}{Q_H}}. \quad (34)$$

Note that upon substitution of numerical values in accordance with the established sign convention that $\gamma$ is a positive value in Eqs. 41 and 34.

For a Carnot heat pump, using the results from Eq. 1,

$$\gamma_{\text{Carnot}} = \frac{1}{\frac{T_L}{T_H} - 1} = \frac{T_H}{T_H - T_L}. \quad (35)$$
If the system is well-defined, the choice of sign convention does not make any difference. The results for cycle performance are the same in all cases for the Heat Engine (Eq. 28), the Refrigeration Cycle (Eq. 31), and the Heat Pump Cycle (Eq. 34). Similarly, the results for Carnot cycle performance are the same in all cases for the Heat Engine (Eq. 29), the Refrigeration Cycle (Eq. 32), and the Heat Pump Cycle (Eq. 25).

CONCLUSIONS

The proof presented in this paper results in the relationship \(-Q_2/Q_1 = (T_3/T_1)\). The usefulness of this equation is demonstrated in analyses aimed at finding the performance parameter for several cycles using various sign conventions and system designations.

The three different cycle analyses presented in this paper show that the sign convention and system designation used in cycle analysis are inconsequential. The key is to maintain consistency in use of the chosen sign convention. If used precisely, the sign convention is an asset in developing performance equations. If used improperly, the sign convention indeed becomes an evil and potentially causes confusion for the teacher and the novice student of thermodynamics.

ACKNOWLEDGEMENT

The views expressed herein are those of the authors and do not purport to reflect the position of the United States Military Academy, the Department of the Army, or the Department of Defense.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>molecular mass</td>
<td>kg/mol</td>
</tr>
<tr>
<td>(C)</td>
<td>heat transfer</td>
<td>kJ</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>kJ/(mol - K)</td>
</tr>
<tr>
<td>S</td>
<td>entropy</td>
<td>kJ/K</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>U</td>
<td>internal energy</td>
<td>kJ</td>
</tr>
<tr>
<td>V</td>
<td>volume</td>
<td>m³</td>
</tr>
<tr>
<td>W</td>
<td>work</td>
<td>kJ</td>
</tr>
<tr>
<td>c</td>
<td>specific heat</td>
<td>kJ/(kg - K)</td>
</tr>
<tr>
<td>m</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>kPa</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)</td>
<td>high temperature reservoir</td>
</tr>
<tr>
<td>(L)</td>
<td>low temperature sink</td>
</tr>
<tr>
<td>(v)</td>
<td>constant volume</td>
</tr>
</tbody>
</table>

Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta)</td>
<td>efficiency</td>
</tr>
<tr>
<td>(\beta)</td>
<td>refrigeration cycle coefficient of performance</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>heat pump cycle coefficient of performance</td>
</tr>
</tbody>
</table>

REFERENCES


BIBLIOGRAPHY


Sussman, M. V., 1972, *Elementary General Thermodynamics*, Addison-Wesley, Reading MA.
ON THE TEACHING OF CONDENSATION HEAT TRANSFER

A. Özer Armas, Ph.D., P.E.
COL Daise D. Boettner, Ph.D.
MAJ Michael J. Benson, P.E.
MAJ Bret P. Van Poppel
Department of Civil and Mechanical Engineering
United States Military Academy at West Point
West Point, NY 10996
Tel.: 845-938-2600; Fax: 845-938-5522

ABSTRACT
The topic of condensation heat transfer is usually included in a chapter on Boiling and Condensation in most Heat Transfer textbooks. The assumptions made are those of laminar liquid film with constant thermo-physical properties, uniform vapor temperature equal to the saturation temperature of the vapor, negligible shear at the liquid-vapor interface, and negligible momentum and energy transfer by advection in the condensate film. The results presented are normally for the film thickness, the local convective heat transfer coefficient, and the Nusselt number. However, no means are presented to the student to determine if all of these simplifying assumptions are actually satisfied for a given problem. This investigation clarifies these points to improve teaching of the material and understanding by the student at the undergraduate and graduate level.

INTRODUCTION
Condensation phenomenon is discussed in almost all textbooks on heat transfer, both at the undergraduate and graduate levels, based on the initial work of Nusselt (1915) and (1916). Currently available textbooks include Incropera and DeWitt (2002), Kreith and Bohn (2001), Bejan (1998), Mills (1995), and some of the others listed in the Bibliography. These authors continue to make a number of assumptions for the solutions obtained. However, no textbook mentions how the student can check to see if ALL of these assumptions are satisfied prior to using the results obtained for the boundary layer thickness, the convective heat transfer coefficient and the Nusselt number. This paper demonstrates analytically the similarity based solution, the physical meaning of the assumptions, and the conditions that the student must verify prior to using the results.

DISCUSSION
As is the case with other convective phenomena, condensation is governed by the conservation equations of mass, momentum, and energy, as well as the equation of state for the substance. Therefore,

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 \quad (1) \]

\[ \frac{D\mathbf{V}}{Dt} = \mathbf{F}_{\text{body}} - \frac{1}{\rho} \nabla p + \mathbf{v} \nabla \cdot \mathbf{V} + \frac{1}{3} \mathbf{v} \nabla (\nabla \cdot \mathbf{V}) \quad (2) \]

\[ \text{ENERGY:} \quad \rho \frac{De}{Dt} = -\rho (\nabla \cdot \mathbf{V}) + \nabla \cdot (kVT) + \phi \quad (3) \]

where

\[ \phi = 2 \mu \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right)^2 + \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)^2 + \frac{2}{3} \mu \left( \frac{\partial u}{\partial x} + \frac{\partial u}{\partial x} \right)^2 \quad (4) \]

or

\[ \rho \frac{Di}{Dt} = \frac{De}{Dt} + \nabla \cdot (kVT) + \phi \quad (5) \]

with \( i = e + p/\rho \), and the

\[ \text{EQUATION OF STATE:} \quad p = p(\rho, T) \quad (6) \]
The fundamental solution to convective heat transfer problems may be obtained as:

1. Solutions of the governing equations using the concept of the boundary layer.
2. Dimensional analysis coupled with extensive experimental data and curve fitting techniques.
3. Using the approximate integral method.

The boundary layer solution to the convection problem is normally demonstrated under the assumptions of steady flow, incompressible fluid, constant dynamic viscosity and thermal conductivity, and for the case of an ideal gas with constant specific heats. Under these assumptions, the governing equations (1), (2), and (5) reduce to

\[
\text{MASS:} \quad \nabla \cdot \mathbf{V} = 0 \tag{7}
\]

\[
\text{MOMENTUM:} \quad (\mathbf{V} \cdot \nabla \mathbf{V}) = \mathbf{F}_{\text{BOD}} - \frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{V} \tag{8}
\]

\[
\text{ENERGY:} \quad \rho c_p (\mathbf{V} \cdot \nabla T) = k \nabla^2 T + \phi \tag{9}
\]

where \( \phi \) is obtained from equation (4) where the last term is eliminated because of equation (7). The equation of state remains unchanged.

Using order of magnitude analysis and for two-dimensional flow, equations (7) - (9) reduce to

\[
\text{MASS:} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{10}
\]

\[
\text{MOMENTUM-x:} \quad u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \nu \frac{\partial^2 u}{\partial y^2} \tag{11}
\]

\[
\text{MOMENTUM-y:} \quad \frac{\partial p}{\partial y} = 0 \tag{12}
\]

with the additional restriction that the Reynolds number at the end of the plate be equal to or greater than 100, \( RE_L \geq 100 \).

\[
\text{ENERGY:} \quad u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{u}{c_p} \frac{\partial p}{\partial x} + \alpha \frac{\partial^2 T}{\partial y^2} + \frac{\partial (\phi T)}{\partial y} \tag{13}
\]

with the additional restrictions that Eckert number,

\[
EC = \frac{U_o^2}{c_p (T_w - T_a)}
\]

is \( O(1) \) and the Péclet number is equal to or greater than 100, \( PE \geq 100 \). For \( EC \ll O(1) \), then the pressure and viscous terms drop out giving for the energy equation

\[
\text{ENERGY:} \quad u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \frac{\partial^2 T}{\partial y^2} \tag{14}
\]

For the condensation problem, the general assumptions are, Hsu (1963), Lienhard (1981) and others:

1. The temperature of the vapor, \( T_v \), is a constant.
2. The condensate film is laminar.
3. Since the kinematic viscosity of the vapor is much less than that of the liquid, there is no frictional resistance on the liquid at the interface with the vapor.
4. The inertia terms for the liquid are negligible, or

\[
\frac{u}{\partial x} + v \frac{\partial v}{\partial y} = 0 \tag{15}
\]

5. The convection term in the liquid film is also negligible, or

\[
\frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = 0 \tag{16}
\]

Assumptions (2), (4) and (5) must be satisfied before the result to be obtained is valid. This is the essence of this paper so that the student has a way of satisfying the assumptions prior to using the results that will be obtained for the film thickness, the convective heat transfer coefficient, and the Nusselt number.

Since there are vapor and liquid phases present at equilibrium, there must be two equations characterizing the physical problem, one for the liquid film and one for the vapor. However, the fact that the vapor temperature \( T_v \) is a constant, assumption (1), eliminates the energy equation for the vapor. Assumption (3) eliminates the inertia and frictional terms of the momentum equation for the vapor giving

\[
\frac{1}{\rho} \frac{\partial p}{\partial x} + g = 0
\]

or

\[
\frac{1}{\rho} \frac{\partial p}{\partial x} = -\frac{\rho_v}{\rho} g \tag{17}
\]

Substituting Equation (17) into the momentum equation for the liquid, Equation (11), results in

\[
u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} + g \left( \frac{\rho - \rho_v}{\rho} \right) \tag{18}
\]

The combination of equations (15) and (18), and (14) and (16) is actually given by White (1984); however, he too does not show the consequences of these limitations for use by the student. Actually, the material discussed by White (1984) is available in several articles by Rohsenow (1956) where he neglected the momentum changes at the start and never showed how one can calculate the validity of the assumption, by Sparrow and Gregg (1959) who neglected then retained the inertia terms for the liquid, they still did not show how one might check the conditions under which either case is valid, and by Chen (1961) who included the effect of the drag to an initially stationary body of vapor. The equations were obtained using the integral method and a perturbation procedure for numerical results. Again, no methods of checking the validity of assumptions made were included.

Since at equilibrium the densities of the liquid and the vapor, \( \rho \) and \( \rho_v \), respectively, are constants, the buoyancy-body force is independent of the temperature. In most cases, the density of the liquid is much larger than that of the vapor giving for the governing equations

\[
\text{MASS:} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{19}
\]
MOMENTUM: \[ u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} + g \]

ENERGY: \[ u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = k \frac{\partial^2 T}{\partial y^2} \]

with the boundary conditions of:

\[ y = 0 \quad u = v = 0 \quad T = T_w \]
\[ y = \delta \quad \frac{\partial u}{\partial y} = 0 \quad T = T_v \]
\[ x = 0 \quad \delta = 0 \]

since at the top of the plate where \( x = 0 \), \( T, u, v \) have no physical meaning. Now there are three equations with four unknowns; the mass, momentum, and energy equations with \( u, v, T \) and \( \delta \) as unknowns. Thus a fourth equation must be obtained to have a mathematically solvable system of four equations and four unknowns.

\[ \Theta = \frac{T - T_v}{T_w - T_v} \]

the mass conservation equation is identically satisfied because of the normal definition of the stream function. The transformed momentum and energy equations along with the boundary conditions become

\[ f'' + 3ff' - 2f^2 + 1 = 0 \]
\[ \Theta + 3\eta \frac{\partial \Theta}{\partial \eta} = 0 \]

with

\[ \eta = 0 \quad f = f' = 0 \quad \Theta = 1 \]
\[ \eta = \eta_\delta \quad f' = 0 \quad \Theta = 0 \]

where

\[ \eta_\delta = \left( \frac{g}{4\nu^2 x} \right)^{1/4} \delta \]

Barmeister (1983) does go through the similarity calculations and obtains equations (30); however, the analysis is not carried any further.

The PHYSICAL meaning of the terms in the transformed and untransformed equations is, respectively,

\[ \text{VISCOS FORCE:} \quad f'' = \nu \frac{\partial^2 u}{\partial y^2} \]

\[ \text{INERTIA FORCE:} \quad 3ff' - 2f^2 = u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \]

\[ \text{BODY FORCE:} \quad 1 = g \]

\[ \text{CONDUCTION:} \quad \Theta' = \alpha \frac{\partial^2 T}{\partial y^2} \]

\[ \text{CONVECTION:} \quad 3\eta \frac{\partial \Theta}{\partial \eta} = u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \]

This physical meaning is important since various terms will be dropped based on the assumptions made in the analysis that will follow.

In order for similarity to hold, all equations and boundary conditions should be independent of the variable \( x \). In order to show this, equation (26) must be transformed using equations (27)-(29). Thus, first transforming the conduction term into the liquid layer,

\[ k \left( \frac{\partial T}{\partial y} \right)_{y=\delta} d\xi = -k(T_w - T_v)\int_{y=\eta_\delta}^{y=\delta} \frac{\partial \Theta}{\partial \eta} \left( \frac{g}{4\nu^2 x} \right)^{1/4} d\eta \]

and assuming that \( \Theta(\eta_\delta) \) to be a constant, which it will have to be if \( \eta_\delta \) is to be a constant, and then integrating

\[ k \left( \frac{\partial T}{\partial y} \right)_{y=\delta} d\xi = -\frac{4}{3} k(T_w - T_v) \Theta(\eta_\delta) \left( \frac{g}{4\nu^2 x} \right)^{1/4} \]

Similarly,

\[ \rho \int_0^\infty ud\eta = \rho \int_0^\infty \int_0^\infty \int_0^{\lambda s} (2\xi x)^{1/2} f' \left( \frac{4\nu}{\xi} \right)^{1/4} d\eta \]

\[ = \rho (64g^{1/4} x^3)^{1/4} f(\eta_\delta) \]
since $f(0) = 0$. Equating the two terms, equations (34) and (35),

$$\frac{k(T_v - T_w)}{\nu Pr \phi} = -3 \frac{f(\eta_\delta)}{\Theta(\eta_\delta)}$$

(36)

Using the definition of the Prandtl number, $Pr = \frac{\mu}{\rho c_p k}$, then

$$\frac{c_p(T_v - T_w)}{l_\delta} = -3 Pr \frac{f(\eta_\delta)}{\Theta(\eta_\delta)}$$

(37)

which is a similar result obtained by Sparrow and Gregg (1959). Since $x$ no longer appears in equations (36) or (37), then $\eta_\delta$ is either a constant or $\delta \sim x^{1/4}$ for similarity to hold.

Thus, the governing set of equations and boundary conditions for condensation heat transfer now become

$$f'' + 3f' - 2(f')^2 + 1 = 0$$

$$\Theta + 3Pr \Theta' = 0$$

$$\frac{c_p(T_v - T_w)}{l_\delta} = -3Pr \frac{f(\eta_\delta)}{\Theta(\eta_\delta)}$$

(38)

$$\eta = 0 \quad f = f' = 0 \quad \Theta = 1$$

$$\eta = \eta_\delta \quad f'' = 0 \quad \Theta = 0$$

where the properties are those of the liquid since the vapor was at a constant temperature, $T_v$, non-viscous, and with negligible density compared to that of the liquid. Equation (38) is also obtained by Roshen and Choi (1961) without going further with any discussion.

The EXACT solution is obtained by choosing a value for $\eta_\delta$ for a given Prandtl number and solving the momentum and energy equations simultaneously. The result thus obtained is then substituted into the energy balance equation and the process is repeated until the value converges to the computed value of $\eta_\delta$.

However, a very meaningful APPROXIMATE solution can be obtained using power series for the velocity and temperature distributions that satisfy the boundary conditions at $\eta = 0$ as

$$f = C_1 \eta^2 - \frac{1}{6} \eta^3 + C_2 \eta^4 + ...$$

(39)

$$\Theta = 1 + C_2 \eta - Pr \frac{C_1 C_2}{4} \eta^4 + ...$$

(40)

where $C_1$ and $C_2$ are constants. For $\eta < 1$, then

$$f = C_1 \eta^2 - \frac{1}{6} \eta^3$$

(41)

$$\Theta = 1 + C_2 \eta$$

(42)

Note, however, that these distributions also satisfy

$$f'' + 1 = 0$$

(43)

for negligible inertia, and

$$\Theta' = 0$$

(44)

for negligible convection in the film such that all energy transfer is by conduction from the outside film to the plate surface.

For these solutions to be valid, the condition of $\eta < 1$ must be satisfied. For the condition of negligible inertia, the term

$$\frac{C^2}{30} \eta^5 \ll \frac{1}{6} \eta^3$$

(45)

or

$$\eta_\delta^3 \ll \frac{5}{C_i^2}$$

(46)

must be satisfied, AND for the condition of negligible convection,

$$Pr \frac{C_1 C_2}{4} \eta_\delta^4 \ll C_2 \eta_\delta$$

(47)

or

$$\eta_\delta^3 \ll \frac{4}{C_i Pr}$$

(48)

must be satisfied. These two conditions form the RESTRICTIONS of the above solutions and, therefore, analyses. Differentiating $f$, Equation (41), twice and evaluating at $\eta_\delta$ gives

$$f''(\eta_\delta) = 2C_1 - \eta_\delta.$$ Using the boundary condition at $\eta_\delta$, $f''(\eta_\delta) = 0$ Equation (38), then

$$C_1 = \frac{\eta_\delta}{2}$$

(49)

Substituting back into equation (41) gives for the distribution

$$f = \frac{\eta_\delta^3}{2} \left[ \frac{(\eta_\delta)^2}{\eta_\delta} - \frac{1}{3} \frac{T_v}{T_w} \right]$$

(50)

Since $\Theta$ is zero at $\eta_\delta$, then $C_2 = -\frac{1}{\eta_\delta}$ giving for the temperature distribution

$$\Theta = 1 - \frac{\eta}{\eta_\delta}$$

(51)

The energy balance equation requires the values of $f(\eta_\delta)$ and $\Theta'(\eta_\delta)$. Thus, upon substitution into equation (38),

$$\frac{c_p(T_v - T_w)}{l_\delta} = \frac{-Pr \eta^3}{3} \left[ -\frac{1}{\eta_\delta} \right] = Pr(\eta_\delta)^4$$

or solving for $\eta_\delta$

$$\eta_\delta = \left[ \frac{c_p(T_v - T_w)}{Pr l_\delta} \right]^{1/4}$$

(52)

Substituting for $\eta_\delta$ from equation (33) gives the boundary layer thickness as

$$\delta = \frac{4c_p T_v x (T_v - T_w)}{g Pr l_\delta}$$

(53)

which is a result given in almost all textbooks.

To determine the heat flux, $q^*$, $k \left[ \frac{\partial T}{\partial y} \right]_{y=0}$, using equations (29) and (33), the result becomes

$$q^* = -k(T_v - T_w) \Theta(0) \left( \frac{g}{4 \nu^2 \delta} \right)^{1/4}$$

(54)
For $\Theta(0) = -\frac{1}{\eta_\delta} = \left[ \frac{PRI_{f_2}}{c_p(T_w - T_v)} \right]^{1/4}$, as discussed by Sibson in Sparrow and Gregg (1959), the heat flux reduces to
\[ q^* = k(T_v - T_w) \left( \frac{gI_{f_2} PR}{4v^2 xc_p(T_v - T_w)} \right)^{1/4}. \]
Thus, the local NUSSELT number, $NU_x = \frac{k_x}{k}$, can be obtained as
\[ NU_x = \left( \frac{q^*}{T_v - T_w} \right)^{1/4} \] or
\[ NU_x = \left[ \frac{gPRI_{f_2} x^3}{4c_p(T_v - T_w)v^2} \right]^{1/4}. \] (55)

Using an alternate definition of the PRANDTL number,
\[ PR = \frac{\nu c_p}{k}, \]
then the local NUSSELT number becomes, as is found in almost all textbooks,
\[ NU_x = 0.7071 \left[ \frac{gPRI_{f_2} x^3}{4k(T_v - T_w)v^2} \right]^{1/4}. \] (56)

The range of applicability of this result is, therefore:

**NEGLIGIBLE INERTIA:** Using equations (46) and (49),
\[ \frac{c_p(T_v - T_w)}{PRI_{f_2}} \ll 20 < 2 \] (57)
This is reported by Sparrow and Gregg (1959) but not as a limitation for the final solution.

**NEGLIGIBLE CONVECTION:** Using equations (48) and (49),
\[ \frac{c_p(T_v - T_w)}{I_{f_2}} \ll 8 < 0.8 \] (58)
Thus, BOTH of these conditions, equations (57) and (58), MUST hold along with the LAMINAR FILM assumption before the boundary layer thickness, equation (53) or the $NU_x$ relationship, equation (56), would have any validity.

For the range of applicability for the laminar film condition and following Gidof (1957),
\[ RE_{D_H} = \frac{4gI_\delta}{v} < 2000 \] (59)
where $D_H$ is the hydraulic diameter equal to the ratio of the cross-sectional area of the conduit to the wetted perimeter.

Since the average velocity is given by $\bar{u} = \frac{1}{\delta} \int_0^\delta u dv$, then upon transformation, using equations (27) and (28), the value of $\bar{u}$ is obtained as
\[ \bar{u} = \left( \frac{64gI_2 x^3}{\delta} \right)^{1/4} = f(\eta_2) \] (60)

Using equations (50), (53), and (60), equation (59) reduces to
\[ \frac{c_p(T_v - T_w)}{PRI_{f_2}} > 4.293 \left( \frac{x^2}{v} \right)^{1/3} \] (61)

Therefore, in order to use equations (53), (55) or (56), the RESTRICTIVE conditions, the inequalities of equations (57), (58), and (61), must be satisfied. If any one of these conditions is not met, then the equations for the boundary layer thickness or the NUSSELT number, equations (53) and (56), respectively, cannot be used.

**CONCLUSIONS:**

Condensation heat transfer is an important topic in heat transfer particularly in the design of heat exchangers. Therefore, the results given in textbooks must be used in this design process. However, none of the textbooks in print go through the analysis showing the required restrictions on the applicability of the results to calculate the boundary layer thickness, the convective heat transfer coefficient, or the NUSSELT number. Equations (53), (55), and (56). Here, the three assumptions made to determine these equations that one finds in almost all textbooks are clearly identified and quantified for the student to satisfy before using any of the results.

In teaching this topic to our undergraduates, therefore, these restrictions should be mentioned and the results inserted into their textbooks. For the graduate student, their horizons would be expanded if they are made to go through these developments to better appreciate what is involved in analytical heat transfer analyses.

**ACKNOWLEDGEMENT**

The views expressed herein are those of the authors and do not purport to reflect the position of the United States Military Academy, the Department of the Army, or the Department of Defense.

The remarks of the reviewers are appreciated and have made a difference in the final form of the paper.

The first author, AOA, would like to acknowledge Professor Robert D. Cess of the State University of New York, Stony Brook who taught him to be thorough and correct in teaching of heat transfer.

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>specific heat</td>
<td>kJ/(kg K)]</td>
</tr>
<tr>
<td>D</td>
<td>substantial derivative</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>internal energy</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>EC</td>
<td>Eckert number</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>force vector</td>
<td>N</td>
</tr>
<tr>
<td>g</td>
<td>similarity velocity transform</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>gravity</td>
<td>m/s^2</td>
</tr>
<tr>
<td>i</td>
<td>convective heat transfer</td>
<td>W/(m^2 K)</td>
</tr>
<tr>
<td>k</td>
<td>enthalpy</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>m</td>
<td>mass</td>
<td>kg</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>kPa</td>
</tr>
<tr>
<td>P^2</td>
<td>Péclet number</td>
<td>(RE)(PR)</td>
</tr>
</tbody>
</table>
\[ \text{Prandtl number } = \frac{c_p \mu}{k} = \frac{\nu}{\alpha} = \frac{c_p \nu}{k} \]

\[ \text{Reynolds number } = \frac{\bar{v} \times c}{\nu} \]

\[ \text{temperature } = [\text{K}] \]

\[ \text{time } = [\text{s}] \]

\[ \text{velocity component in the x direction } = [\text{m/s}] \]

\[ \text{average velocity } = [\text{m/s}] \]

\[ \text{velocity component in the y direction } = [\text{m/s}] \]

\[ \text{volume } = [\text{m}^3] \]

\[ \text{velocity } = [\text{m/s}] \]

\[ \text{velocity component in the z direction } = [\text{m/s}] \]

\[ \text{direction } = [\text{m}] \]

\[ \text{direction } = [\text{m}] \]

Subscripts

\[ c \] characteristic hydraulic diameter

\[ D_H \] phase change

\[ l \] length

\[ p \] constant pressure

\[ v \] constant volume, vapor

\[ w \] wall

\[ \infty \] free stream

\[ \delta \] evaluated at the boundary layer thickness

Superscripts

\[ \cdot \] derivative with respect to time

Greek Symbols

\[ \alpha \] thermal diffusivity $[\text{m}^2/\text{s}]$

\[ \delta \] boundary layer thickness [m]

\[ \nabla \] vector operator

\[ \phi \] the term in equation (4)

\[ \psi \] similarity coordinate transform

\[ \Theta \] nondimensional temperature

\[ \mu \] dynamic viscosity $[\text{N-s/m}^2]$.

\[ \nu \] kinematic viscosity $[\text{m}^2/\text{s}]$

\[ \xi \] dummy variable

\[ \rho \] density $[\text{kg/m}^3]$

\[ \Psi \] stream function

REFERENCES


Nusselt, W., (1916), *Die Oberflächenentladung des Wasserdampfes*, *Zeitschrift für das Verein der deutscher Ingenieure*, 60, No. 28, pp. 541-546 and 569-575.


BIBLIOGRAPHY


ON EQUIVALENCY OF VARIOUS EXPRESSIONS FOR
SPEED OF WAVE PROPAGATION FOR
COMPRESSIBLE LIQUID FLOWS WITH HEAT TRANSFER

T. C. CHAWLA
Reactor Analysis and Safety Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

(Received 22 March 1978 and in revised form 31 March 1978)

Abstract—It is demonstrated that for a compressible flow model with heat transfer, the introduction of a specific state equation to supplement the continuity, momentum and enthalpy equations, leads to a very specific form of an expression for a speed of wave propagation. Consequently, the numerous expressions obtained for various choices of state equations are not easily identifiable and, therefore, can not be evaluated directly in terms of measurable properties. By utilizing the various thermodynamic relationships, we have shown that these expressions are all equivalent and are identifiable as isentropic sonic velocity. As a corollary to this demonstration, we have also obtained expressions in terms of measurable properties for various thermodynamic-state variables occurring in the coefficients of the governing equations. These expressions are required if loss in accuracy owing to noise introduced in the direct numerical differentiation of the derivatives that these state-variables represent is to be avoided.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>flow cross-sectional area;</td>
</tr>
<tr>
<td>$a_0$</td>
<td>speed wave propagation defined by equation (11);</td>
</tr>
<tr>
<td>$C_p$</td>
<td>specific heat at constant pressure;</td>
</tr>
<tr>
<td>$C_v$</td>
<td>specific heat at constant volume;</td>
</tr>
<tr>
<td>$c_s$</td>
<td>speed of wave propagation defined by equation (15);</td>
</tr>
<tr>
<td>$g$</td>
<td>acceleration due to gravity;</td>
</tr>
<tr>
<td>$h$</td>
<td>specific enthalpy;</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure;</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>heat flux;</td>
</tr>
<tr>
<td>$R_b$</td>
<td>heated or wetted perimeter;</td>
</tr>
<tr>
<td>$s$</td>
<td>specific entropy;</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature of a liquid coolant;</td>
</tr>
<tr>
<td>$t$</td>
<td>time;</td>
</tr>
<tr>
<td>$u$</td>
<td>specific internal energy;</td>
</tr>
<tr>
<td>$v$</td>
<td>fluid velocity;</td>
</tr>
<tr>
<td>$z$</td>
<td>coordinate in the vertical direction.</td>
</tr>
</tbody>
</table>

Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_p$</td>
<td>$-\frac{(\partial P/\partial T)_p}{\rho}$, coefficient of thermal expansion;</td>
</tr>
<tr>
<td>$\beta_T$</td>
<td>$\frac{(\partial P/\partial T)_p}{\rho}$, isothermal coefficient of bulk compressibility;</td>
</tr>
<tr>
<td>$\beta_s$</td>
<td>$\frac{(\partial P/\partial T)_s}{\rho}$, adiabatic coefficient of bulk compressibility;</td>
</tr>
<tr>
<td>$\gamma_T$</td>
<td>$\frac{(\partial P/\partial T)_p}{\rho}$, thermal pressure coefficient;</td>
</tr>
<tr>
<td>$\Lambda_T$</td>
<td>$\frac{(\partial h/\partial T)_p}{\rho}$;</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>$1/R_b$;</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>$\frac{(\partial s/\partial P)_p}{\rho}$;</td>
</tr>
<tr>
<td>$\rho$</td>
<td>fluid density;</td>
</tr>
<tr>
<td>$\tau_w$</td>
<td>wall shear stress;</td>
</tr>
<tr>
<td>$\Psi_w$</td>
<td>$ut\cdot S_w/A$;</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>speed of wave propagation as defined by equation (22).</td>
</tr>
</tbody>
</table>

INTRODUCTION

The compressible liquid flow with heat transfer occurs in numerous nuclear reactor applications. For example, loss of flow resulting from pipe rupture both in the case of boiling water and pressurized water reactors, and also in the case of liquid metal cooled fast breeder reactors (LMFBRs) requires the modeling of compressible liquid flow with heat transfer. The dynamics of the coolant, subsequently to the release of molten fuel in the coolant channels during a power transient in an LMFBR, are generally analyzed in terms of compressible coolant flow with heat transfer. The governing equations are solved either by the use of finite-difference methods or by the method of characteristics. In both schemes, one needs to determine the speed of wave propagation as a function of tabulated properties of the liquids. In the explicit form of finite-difference methods (such as Lax method, two step Lax–Wendroff difference method, donor-cell type different method), one needs speed of wave propagation to determine the size of time steps that satisfies stability criterion [1]. In the case of method of characteristics, the speed of wave propagation is required to determine the slopes of the characteristics. In this latter application, the form of the expression for the speed of wave propagation varies with the exact form of governing equations chosen for solution. Very frequently, these expressions have very diverse form and do not permit direct numerical evaluation in terms of the properties tabulated in the standard tables. In addition, the algebraic manipulation involved to obtain the govern-
ing equations in a form suitable for application of a given numerical method (such as the method of characteristics) leads to very complex forms of coefficients of the various terms of the resultant governing equations. These coefficients, generally, are both functions of flow parameters and of the physical properties of the coolant. The purpose of the present note is to demonstrate various expressions arrived at in most common formulations of the governing equations for compressible liquid flow with heat transfer are equivalent and are identifiable with very familiar expression, namely \( a^2 = \frac{(\partial P/\partial \rho)_s}{\rho} \) (see Nomenclature for definition of symbols) for the speed of sound defined for the isentropic process of state change and fluid flow. As a corollary to this demonstration, we will show how the various coefficients which depend only on the properties, can be expressed in a form suitable for direct numerical evaluation by the use of tabulated or measured properties.

**FORMULATION**

The most common form of the basic governing equations, which are utilized to describe flow through a coolant channel of constant cross-sectional area during a transient such as initiated by loss of flow due to pipe rupture, is [2–4]:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial z} &= 0, \quad (1) \\
\frac{\partial v}{\partial t} + \frac{\partial (\rho v^2)}{\partial z} &= -\frac{\partial P}{\partial z} - \rho g - \frac{S_{nu} a^2}{A}, \quad (2) \\
\frac{\partial h}{\partial t} + \frac{\partial (\rho h)}{\partial z} &= \rho \frac{\partial S_{nu}}{\partial A} + \frac{\partial P}{A} + v \frac{\partial P}{\partial z}, \quad (3)
\end{align*}
\]

The use of equation (1) into equations (2) and (3) yields,

\[
\begin{align*}
\rho \left( \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial z} \right) &= -\frac{\partial P}{\partial z} - \rho g - \frac{S_{nu} a^2}{A}, \quad (7) \\
\rho \left( \frac{\partial h}{\partial t} + v \frac{\partial h}{\partial z} \right) &= Q_w + \Phi_w + \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right), \quad (8a)
\end{align*}
\]

where

\[
Q_w = \frac{q_{sw} S_{nu}}{A}, \quad \Phi_w = \frac{\nu \sigma S_{nu}}{A}. \quad (8b)
\]

Combining equations (5) and (8) first to eliminate \( h \) between them and second to eliminate \( P \) between them:

\[
\begin{align*}
\frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} + \rho a^2 \frac{\partial v}{\partial z} + \frac{R_k a^2}{\rho} (Q_w + \Phi_w) &= 0, \quad (9) \\
\frac{\partial h}{\partial t} + v \frac{\partial h}{\partial z} + a^2 \frac{\partial v}{\partial z} &= \frac{R_k a^2}{\rho} (Q_w + \Phi_w), \quad (10)
\end{align*}
\]

The use of equation (1) into equation (2) yields,

\[
\begin{align*}
\rho \frac{\partial v}{\partial t} + \rho v \frac{\partial v}{\partial z} &= \frac{\partial P}{\partial z} - \rho g - \frac{S_{nu} a^2}{A}, \quad (11)
\end{align*}
\]

We will show, subsequently, that the above expression defines the isentropic sonic velocity corresponding to the system of equations (7), (9) and (10) which are explicit in \( v, P \) and \( h \). We may note here, that properties \( R_k \) and \( R_s \) as defined by equation (6) are not directly measurable properties. It is clear that the numerical evaluation of these properties is required not only for the determination of quantity \( a \) but also for determining coefficients in the governing equations (9) and (10).

**Explicit in variables \( \rho, v, P \)**

From the state equation (4c), we have

\[
\frac{dh}{dt} = \lambda_p \frac{dp}{dt} + \lambda_s dP. \quad (12)
\]

The use of equation (12) into equation (8) yields

\[
\begin{align*}
\mu \lambda_p \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right) + \left( \mu \lambda_s - 1 \right) \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right) &= Q_w + \Phi_w. \quad (13)
\end{align*}
\]

Eliminating the terms involving \( \rho \) in equation (13) by using equation (1), we obtain

\[
\begin{align*}
\left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right) + \rho c^2 \frac{\partial v}{\partial z} &= \frac{1}{\mu \lambda_s - 1} (Q_w + \Phi_w), \quad (14)
\end{align*}
\]

where

\[
c = \left( \frac{-\rho \lambda_p}{\rho \lambda_s - 1} \right)^{1/2}. \quad (15)
\]

The above expression also defines isentropic sonic velocity, although the form of the expression is not a very familiar one. In the subsequent analysis, we demonstrate that the above is indeed isentropic sonic velocity. Once again, properties \( \lambda_p \) and \( \lambda_s \) are not directly measurable quantities, therefore, unless we can demonstrate that expression (15) indeed repre-
sents an isentropic sonic velocity, we will not be able to calculate satisfactorily the numerical values for the quantity \( c \). Thus, if one wants to utilize the system of equations (1), (7) and (14) which are explicit in \( \rho, v \) and \( P \), one must numerically evaluate the quantity \( c \) as defined by expression (15).

**Explicit in variables \( v, P, T \)**

From state equation (4b), we can write

\[
\frac{\partial P}{\partial T} = \rho \frac{\partial v}{\partial T} + P \frac{\partial \rho}{\partial T} = 0.
\]

The use of equation (16) into equation (1) yields

\[
\rho \sigma_p \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial z} \right) + \rho \rho_t \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right) + \rho \frac{\partial v}{\partial z} = 0.
\]

From state equation (4d), we have

\[
\frac{dh}{\partial T} = C_p \frac{\partial T}{\partial T} + \Lambda_T \frac{\partial P}{\partial P}.
\]

The use of equation (18) into equation (8) gives

\[
\rho C_p \left( \frac{\partial T}{\partial t} + v \frac{\partial T}{\partial z} \right) + \left( \rho \Lambda_T - 1 \right) \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial z} \right) = Q_w + \Phi_w.
\]

The combination of equations (17) and (19) gives

\[
\rho \sigma_p \frac{\partial \rho}{\partial t} + \frac{\partial P}{\partial T} + \rho \rho_t \frac{\partial \rho}{\partial P} = 2 \frac{\partial \Omega}{C_p} (Q_w + \Phi_w),
\]

where

\[
\Omega = \frac{1}{\left( \rho \rho_t + \rho \Lambda_T - 1 \right)}^{1/2}
\]

Equations (20), (21) together with equation (7) represents a system of equations that are explicit in \( P, T \) and \( v \). This system has necessitated the introduction of parameter \( \Omega \) as defined by equation (22). Although not recognizable as it is defined in the form (22), but it will be shown subsequently that \( \Omega \) is the isentropic sonic velocity. We, also, further recognize in view of the third term of equation (21) the need for numerical evaluation of quantity \( \Lambda_T \).

**EVALUATION OF VARIOUS PARAMETERS IN TERMS OF MEASURABLE PROPERTIES**

Various thermodynamic-state variables such as \( a, c, \Omega, K_p, \Lambda_p, \Lambda, \omega, \) and \( R_s \) as introduced previously must be expressed in terms of measurable or derived properties for their evaluation.

**Parameters \( R_s \) and \( \lambda_p \)**

From the definition of the parameter \( R_s \) as given by equation (6) and from the definitions of \( \sigma_p \) and \( C_p \), we can write

\[
R_s = \left( \frac{\partial \rho}{\partial T} \right)_P \left( \frac{\partial T}{\partial \rho} \right)_P = -\frac{\rho \sigma_p}{C_p}.
\]

From equation (23a), we obtain

\[
\lambda_p = -\frac{C_p}{\rho \sigma_p}.
\]

Equation (23) will permit us to determine \( R_s \) and \( \lambda_p \) since \( \rho, C_p \) and \( \sigma_p \) are either tabulated in properties tables (see for example Padilla [5]) or can be derived from other measurable properties [5, 6].

**Parameters \( R_s \) and \( \lambda_p \)**

From equations (4a) and (12), we can obtain

\[
R_p = \left( \frac{\partial P}{\partial T} \right)_P = -\frac{\rho h}{\rho \sigma_p}.
\]

The use of thermodynamic relationship

\[
h = u + P/R
\]

yields

\[
\left( \frac{\partial h}{\partial P} \right)_P = \frac{C_v}{\gamma_v} - \frac{1}{R_p}.
\]

From the state equations (4), one can readily derive.

\[
\gamma_v = \left( \frac{\partial P}{\partial T} \right)_P = \frac{\rho h}{P \sigma_p}.
\]

Substituting for \( \gamma_v \) from equation (27) and for \( C_v = C_p \beta_v / \beta_T \) (see [6] for the derivation of this relationship) into equation (26), we have

\[
\left( \frac{\partial h}{\partial P} \right)_P = \frac{\beta_v}{P \sigma_p} + \frac{1}{R_p}.
\]

The use of the following relationship whose derivation can be found in [6] and [7]

\[
\beta_T - \beta_v = \frac{\rho T_p^2}{\rho C_p}
\]

into equation (28) yields finally

\[
\lambda_p = \left( \frac{\partial h}{\partial P} \right)_P = \frac{\rho T_p^2}{\rho C_p} \beta_v + \frac{1}{R_p}.
\]

Substituting equations (23), (30) and (29) into equation (24) gives

\[
R_p = \rho \sigma_p + \frac{\sigma_p}{C_p}
\]

The relationships (30) and (31) will enable us to evaluate \( \lambda_p \) and \( R_p \), respectively, in terms of either directly measurable properties or properties that can be derived from other measurable properties (see for
example [5]). For example, $\beta$, is directly measurable or can be determined from the measurements of sonic velocity [5, 6].

The use of equation (31) and (23a) into equation (11) gives

$$a = \frac{1}{(R_p + \frac{1}{\rho})^{1/2}} = \frac{1}{(\rho \beta_p)^{1/2}} = \frac{\partial P}{\partial \rho}^{1/2}.$$

(32)

The substitution of equations (23b), (30) and (29) into equation (15) yields

$$c = \frac{(\rho \beta_p)}{(\rho \beta_p - 1)^{1/2}} = \frac{\partial P}{\partial \rho}^{1/2}.$$  

(33)

Clearly, expressions (11) and (15) have become identifiable namely, each of them defines isentropic sonic velocity.

Substituting the following relation for $\Lambda_T$, whose derivation can be found in [6],

$$\Lambda_T = \frac{\partial \Lambda}{\partial P} = \frac{1}{(1 - T G L^*)},$$

(34)

and equation (29) into equation (22) gives

$$\Omega = \frac{1}{(\rho \beta_p)^{1/2}},$$

(35)

The expression (22), for $\Omega$, thus, becomes recognizable.

CONCLUSIONS

By utilizing various thermodynamic relations, we have been able to demonstrate that the various expressions for the speed of wave propagation introduced due to specific choices of a state equation, are identifiable with isentropic sonic velocity and, therefore, can be evaluated in terms of measurable properties. We have also derived expressions for various thermodynamic-state variables occurring in the coefficients of the governing equation, in terms of measurable and/or derived properties. The need for such expressions can hardly be overemphasized in view of the fact that direct numerical calculations of the derivatives that these state variables represent will introduce noise and, therefore, their accuracy will be suspect.

Acknowledgement—My special thanks are to Mamoru Ishii for his comments on the manuscript. Some useful discussions with Adrian Tenter are greatly appreciated. The work was performed under the auspices of the U.S. Department of Energy.

REFERENCES
Об эквивалентном характере выражений для скорости распространения волны в потоке сжимаемой жидкости при наличии теплообмена

Аннотация — Показано, что при описании течения сжимаемой жидкости с теплообменом добавление конкретного уравнения состояния к уравнениям сохранения массы, импульса и энергии приводит к очень специфической форме выражения для скорости распространения волны. Вследствие этого многочисленные выражения, полученные при использовании различных уравнений состояния, оказываются трудно идентифицируемыми и непригодными для проведения расчетов в терминах непосредственно измеряемых величин. Используя различные термодинамические соотношения, авторы показали, что все эти выражения являются эквивалентными и определяют из энтропическую скорость звука. Для подтверждения данного вывода получены выражения в терминах непосредственно измеряемых величин для различных термодинамических параметров, входящих в коэффициенты исходных уравнений. Эти выражения требуются в тех случаях, когда необходимо избежать потери точности из-за возникающих погрешностей при прямом численном дифференцировании производных, представленных указанными параметрами состояния.
ON EQUIVALENCY OF VARIOUS EXPRESSIONS FOR SPEED OF WAVE PROPAGATION FOR COMPRESSIBLE LIQUID FLOWS WITH HEAT TRANSFER

T. C. CHAWLA
Reactor Analysis and Safety Division, Argonne National Laboratory, Argonne, Il. 60439, U.S.A.

(Received 22 March 1978 and in revised form 31 March 1978)

Abstract—It is demonstrated that for a compressible flow model with heat transfer, the introduction of a specific state equation to supplement the continuity, momentum and enthalpy equations, leads to a very specific form of an expression for a speed of wave propagation. Consequently, the numerous expressions obtained for various choices of state equations are not easily identifiable and, therefore, can not be evaluated directly in terms of measurable properties. By utilizing the various thermodynamic relationships, we have shown that these expressions are all equivalent and are identifiable as isentropic sonic velocity. As a corollary to this demonstration, we have also obtained expressions in terms of measurable properties for various thermodynamic-state variables occurring in the coefficients of the governing equations. These expressions are required if less in accuracy owing to noise introduced in the direct numerical differentiation of the derivatives that these state-variables represent is to be avoided.

NOMENCLATURE

\( A \) 
flow cross-sectional area;

\( a \) 
speed wave propagation defined by equation (11);

\( C_p^* = (\frac{\partial H}{\partial T})_p \) 
specific heat at constant pressure;

\( C_v^* = (\frac{\partial u}{\partial T})_v \) 
specific heat at constant volume;

\( c \) 
speed of wave propagation defined by equation (15);

\( g \) 
acceleration due to gravity;

\( h \) 
specific enthalpy;

\( P \) 
pressure;

\( Q_\infty = \frac{q_S}{A} \) 
heat flux;

\( R_h \) 
(\( \frac{\partial P}{\partial T} \))_h;

\( R_v \) 
(\( \frac{\partial P}{\partial T} \))_v;

\( S_h \) 
heated or wetted perimeter;

\( s \) 
specific entropy;

\( T \) 
temperature of a liquid coolant;

\( t \) 
time;

\( u \) 
specific internal energy;

\( v \) 
fluid velocity;

\( z \) 
coordinate in the vertical direction.

Greek symbols

\( \tau_x \) 
wall shear stress;

\( \Phi_x \) 
\( \frac{u_x}{S_w/A} \);

\( \omega \) 
speed of wave propagation as defined by equation (22).

INTRODUCTION

The compressible liquid flow with heat transfer occurs in numerous nuclear reactor applications. For example, loss of flow resulting from pipe rupture both in the case of boiling water reactors and also in the case of liquid metal cooled fast breeder reactors (LMFBs) requires the modeling of compressible liquid flow with heat transfer. The dynamics of the coolant, subsequent to the release of molten fuel in the coolant channels during a power transient in an LMFB, are generally analyzed in terms of compressible coolant flow with heat transfer. The governing equations are solved either by the use of finite-difference methods or by the method of characteristics. In both schemes, one needs to determine the speed of wave propagation as a function of tabulated properties of the liquids. In the explicit form of finite-difference methods (such as Lax method, two step Lax–Wendroff difference method, donor-cell type different method), one needs speed of wave propagation to determine the size of time steps that satisfies stability criterion [1]. In the case of method of characteristics, the speed of wave propagation is required to determine the slopes of the characteristics. In this latter application, the form of the expression for the speed of wave propagation varies with the exact form of governing equations chosen for solution. Very frequently, these expressions have very diverse form and do not permit direct numerical evaluation in terms of the properties tabulated in the standard tables. In addition, the algebraic manipulation involved to obtain the govern-
ing equations in a form suitable for application of a given numerical method (such as the method of characteristics) leads to very complex forms of coefficients of the various terms of the resultant governing equations. These coefficients, generally, are both function of flow parameters and of the physical properties of the coolant. The purpose of the present note is to demonstrate various expressions arrived at in most common formulations of the governing equations for compressible liquid flow with heat transfer are equivalent and are identifiable with very familiar expression, namely $a^2 = \frac{\partial P}{\partial \rho}$, (see Nomenclature for definition of symbols) for the speed of sound defined for the isentropic process of state change and fluid flow. As a corollary to this demonstration, we will show how the various coefficients which depend only on the properties, can be expressed in a form suitable for direct numerical evaluation by the use of tabulated or measured properties.

FORMULATION

The most common form of the basic governing equations, which are utilized to describe flow through a coolant channel of constant cross-sectional area during a transient such as initiated by loss of flow due to pipe rupture, is [2-4]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho v) = 0,$$

(1)

$$\frac{\partial}{\partial t}(\rho v) + \frac{\partial}{\partial x}(\rho v^2) = \frac{\partial P}{\partial x} - \rho g - \frac{S_x \tau_x}{A},$$

(2)

$$\frac{\partial}{\partial t}(\rho h) + \frac{\partial}{\partial x}(\rho h) = \frac{q_x S_x}{A} - \frac{v \tau_x S_x}{A} + \frac{\partial P}{\partial x} + \frac{\partial P}{\partial t} + \frac{\partial P}{\partial z},$$

(3)

$$\rho = \rho(h, P),$$

(4a)

or

$$\rho = \rho(T, P),$$

(4b)

or

$$h = h(T, P).$$

(4d)

If we utilize the first equation of state (4a), we can make equations (1)-(3) explicit in variables $\rho$, $v$, and $P$. The use of third state equation (4c) will render equations (1)-(3) explicit in $\rho$, $v$, and $P$. Depending upon the choice of a specific form of state equation as we will illustrate below, we arrive at different expressions for the speed of wave propagation.

Explicit in variable $v$, $P$, $h$

The use of first state equation (4a) in equation (1) gives

$$R_x \left( \frac{\partial h}{\partial t} + v \frac{\partial h}{\partial x} \right) + R_v \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} \right) + \frac{\partial \psi}{\partial x} = 0,$$

(5)

where

$$R_x = \left( \frac{\partial P}{\partial h} \right)_v, \quad R_v = \left( \frac{\partial P}{\partial P} \right)_h.$$

The use of equation (1) into equations (2) and (3) yields,

$$\rho \left( \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} \right) = -\frac{1}{\rho} \frac{\partial P}{\partial x} - g - \frac{S_x \tau_x}{A},$$

(7)

$$\rho \left( \frac{\partial h}{\partial t} + v \frac{\partial h}{\partial x} \right) = Q_x + \Phi_x + \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} \right),$$

(8a)

where

$$Q_x = \frac{q_x S_x}{A}, \quad \Phi_x = \frac{v \tau_x S_x}{A}. \tag{8b}$$

Combining equations (5) and (8) first to eliminate $h$ between them and second to eliminate $P$ between them:

$$\frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} + \rho a^2 \frac{\partial h}{\partial t} + \rho g \frac{\partial h}{\partial x} + \rho \frac{\partial a^2}{\partial x} = 0,$$

(9)

$$\frac{\partial h}{\partial t} + v \frac{\partial h}{\partial x} + \frac{\partial h}{\partial x} = \frac{a^2 \frac{\partial P}{\partial x}}{\rho},$$

(10)

where

$$a = \frac{1}{\left(1 + \frac{R_x}{R_v} \frac{S_x}{P_x} \right)^{1/2}}.$$  

(11)

We will show, subsequently, that the above expression defines the isentropic sonic velocity corresponding to the system of equations (7), (9) and (10) which are explicit in $\rho$, $v$, and $h$. We may note here, that properties $R_x$ and $R_v$ as defined by equation (6) are not directly measurable properties. It is clear that the numerical evaluation of these properties is required not only for the determination of quantity $a$ but also for determining coefficients in the governing equations (9) and (10).

Explicit in variables $\rho$, $v$, $P$.

From the state equation (4c), we have

$$dh = \lambda_x dp + \lambda_v dp.$$  

(12)

The use of equation (12) into equation (8) yields

$$\rho \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} \right) + (\rho a^2 - 1) \left( \frac{\partial P}{\partial t} + v \frac{\partial P}{\partial x} \right) = Q_x + \Phi_x.$$  

(13)

Eliminating the terms involving $\rho$ in equation (13) by using equation (1), we obtain

$$\frac{\partial h}{\partial t} + v \frac{\partial h}{\partial x} + \rho \frac{\partial h}{\partial x} = \frac{1}{1 - \rho \lambda_x} (Q_x + \Phi_x).$$  

(14)

where

$$c = \left( \frac{\rho \lambda_x}{1 - \rho \lambda_x} \right)^{1/2}.$$  

(15)

The above expression also defines isentropic sonic velocity, although the form of the expression is not a very familiar one. In the subsequent analysis, we demonstrate that the above is indeed isentropic sonic velocity. Once again, properties $\lambda_x$ and $\lambda_v$ are not directly measurable quantities, therefore, unless we can demonstrate that expression (15) indeed repre-
sents an isentropic sonic velocity, we will not be able to calculate satisfactorily the numerical values for the quantity \( c \). Thus, if one wants to utilize the system of equations (1), (17) and (14) which are explicit in \( p \) and \( \rho \), one must numerically evaluate the quantity \( c \) as defined by expression (15).

**Explicit in variables \( v, P, T \)**

From state equation (4b), we can write

\[
\frac{\partial \rho}{\partial p} = -\rho \sigma_\rho \frac{\partial T}{\partial \rho} + \rho \beta \frac{\partial P}{\partial \rho}.
\]  

(16)

The use of equation (16) into equation (1) yields

\[-\rho \sigma_\rho \left( \frac{\partial T}{\partial t} + \frac{\partial T}{\partial z} \right) + \rho \beta \frac{\partial P}{\partial \rho} \left( \frac{\partial P}{\partial t} + \frac{\partial P}{\partial z} \right) + \rho \frac{\partial \rho}{\partial \rho} = 0.\]

(17)

From state equation (4d), we have

\[d_{\rho} = C_p \frac{\partial T}{\partial \rho} + \lambda \frac{\partial P}{\partial \rho}.
\]  

(18)

The use of equation (18) into equation (8) gives

\[
\rho C_p \left( \frac{\partial T}{\partial t} + \frac{\partial T}{\partial z} \right) + \rho \lambda \left( \frac{\partial P}{\partial \rho} \right) = Q_w + \Phi_w.
\]

(19)

The combination of equations (17) and (19) gives

\[
\frac{\partial P}{\partial \rho} + \frac{\partial \rho}{\partial z} = \rho \lambda \frac{\partial T}{\partial \rho} - \rho \lambda \frac{\partial T}{\partial \rho} = \frac{\rho \lambda \Omega^2}{C_p} (Q_w + \Phi_w),
\]  

(20)

where

\[
\Omega = \frac{1}{\left( \rho \beta + \rho \lambda \Omega^2 \frac{\sigma_\rho}{C_p} \right)^{1/2}}
\]  

(22)

Equations (20), (21) together with equation (7) represents a system of equations that are explicit in \( P, T \) and \( \rho \). This system has necessitated the introduction of parameter \( \Omega \) as defined by equation (22). Although not recognizable as it is defined in the form \( \Omega \), but it will be shown subsequently that \( \Omega \) is the isentropic sonic velocity. We also, further recognize in view of the third term of equation (21) the need for numerical evaluation of quantity \( \lambda \).

**EVALUATION OF VARIOUS PARAMETERS IN TERMS OF MEASURABLE PROPERTIES**

Various thermodynamic-state variables such as \( \alpha, \Omega, \Gamma, \lambda, \rho, \lambda_\rho, \lambda_t, \) and \( R_s \) as introduced previously must be expressed in terms of measurable or derived properties for their evaluation.

**Parameters \( R_s \) and \( \lambda_\rho \)**

From the definition of the parameter \( R_s \), we can write

\[R_s = \left( \frac{\partial p}{\partial T} \right)_T \left( \frac{\partial T}{\partial \rho} \right)_p = -\frac{\rho \sigma_\rho}{C_p}.
\]  

(23a)

From equation (23a), we obtain

\[\lambda_\rho = -\frac{C_p}{\rho \sigma_\rho}.
\]  

(23b)

Equation (23) will permit us to determine \( R_s \) and \( \lambda_\rho \) since \( \rho, C_p, \sigma_\rho \), and \( \sigma_\rho \) are either tabulated in properties tables (see for example Padilla [5]) or can be derived from other measurable properties [5, 6].

**Parameters \( \lambda_t \) and \( \gamma \)**

From equations (4a) and (12), we can obtain

\[\lambda_t = \left( \frac{\partial p}{\partial T} \right)_T = -\left( \frac{\partial h}{\partial P} \right)_T = -R_s \left( \frac{\partial h}{\partial P} \right)_T.
\]  

(24)

The use of thermodynamic relationship

\[h = u + P/\rho
\]  

(25)

yields

\[\left( \frac{\partial h}{\partial P} \right)_T = \frac{C_v}{\gamma} + \frac{1}{\rho}
\]  

(26)

From the state equations (4), one can readily derive

\[\gamma = \left( \frac{\partial P}{\partial T} \right)_T = -\left( \frac{\partial P}{\partial P} \right)_T = \frac{\sigma_\rho}{\beta_\rho}.
\]  

(27)

Substituting for \( \gamma \) from equation (27) and for \( C_v \) \( = C_p \beta_t \beta_r \) (see [5] for the derivation of this relationship) into equation (25), we have

\[\left( \frac{\partial h}{\partial P} \right)_T = \frac{C_v}{\gamma} + \frac{1}{\rho} \frac{\sigma_\rho}{\beta_\rho}.
\]  

(28)

The use of the following relationship whose derivation can be found in [6] and [7]

\[\beta_r - \beta_t = \frac{\gamma C_v}{\rho C_p}
\]  

(29)

into equation (28) yields finally

\[\lambda_\rho = \left( \frac{\partial h}{\partial P} \right)_T = \left( \frac{\partial \rho}{\partial T} \right)_T + \frac{1}{\rho} \frac{\sigma_\rho}{\beta_\rho}.
\]  

(30)

Substituting equations (23), (30) and (29) into equation (24) gives

\[R_s = \rho \beta_t + \frac{\sigma_\rho}{C_p}.
\]  

(31)

The relationships (30) and (31) will enable us to evaluate \( \lambda_\rho \) and \( R_s \), respectively, in terms of either directly measurable properties or properties that can be derived from other measured properties (see for
example [5]. For example, \(\beta_p\) is directly measurable or can be determined from the measurements of sonic velocity [5, 6].

The use of equation (31) and (23a) into equation (11) gives

\[
e = \frac{1}{\left(\frac{R_s + \frac{R_s}{\rho}}{\rho}\right)^{1/2}} = \frac{1}{\left(\frac{\rho R_s}{\rho}\right)^{1/2}} = \left(\frac{\partial P}{\partial \rho}\right)_p^{1/2} \sqrt{m} \tag{32}
\]

The substitution of equations (23b), (30) and (29) into equation (15) yields

\[
c = \left(\frac{-\rho \beta_p}{\rho \beta_p - 1}\right)^{1/2} = \frac{1}{\left(\frac{\rho R_s}{\rho}\right)^{1/2}} = \left(\frac{\partial P}{\partial \rho}\right)_p^{1/2} \sqrt{m} \tag{33}
\]

Clearly, expressions (11) and (15) have become identifiable namely, each of them defines isentropic sonic velocity.

Substituting the following relation for \(\Lambda_r\) whose derivation can be found in [6],

\[
\Lambda_r = \left(\frac{\partial P}{\partial \rho}\right)_r = \frac{1}{\rho} \sqrt{1 - \frac{\beta_p}{\rho}} \tag{34}
\]

and equation (29) into equation (22) gives

\[
\Omega = \frac{1}{\left(\frac{\rho R_s}{\rho}\right)^{1/2}} = \left(\frac{\partial P}{\partial \rho}\right)_p^{1/2} \sqrt{m} \tag{35}
\]

The expressions (22) for \(\Omega\) thus, becomes recognizable.

CONCLUSIONS

By utilizing various thermodynamic relations, we have been able to demonstrate that the various expressions for the speed of wave propagation introduced due to specific choices of state equations, are identifiable with isentropic sonic velocity and, therefore, can be evaluated in terms of measurable properties. We have also derived expressions for various thermodynamic-state variables occurring in the coefficients of the governing equation, in terms of measurable and/or derived properties. The need for such expressions can hardly be overemphasized in view of the fact that direct numerical calculations of the derivatives that these state variables represent will introduce noise and, therefore, their accuracy will be suspect.

Acknowledgments—My special thanks are to Mamoru Ishii for his comments on the manuscript. Some useful discussions with Adrian Tenner are greatly appreciated. The work was performed under the auspices of the U.S. Department of Energy.

REFERENCES


SUR L’EQUIVALENCE DE PLUSIEURS EXPRESSIONS DE LA VITESSE DE PROPAGATION D’UNE ONDE POUR DES ECOULEMENTS DE LIQUIDES COMPRESSIBLES AVEC TRANSFERT DE CHALEUR

Résumé—On montre que pour un modèle d’écoulement compressible avec transfert de chaleur, l’introduction d’une équation d’état spécifique en supprimant des équations de continuité, de quantité de mouvement et d’enthalpie, conduit à une forme très spécifique d’expression pour la vitesse de propagation d’une onde. En conséquence, les nombreuses expressions obtenues pour différents choix d’équations d’état ne sont pas aisément identifiables et ne peuvent être évaluées directement en fonction des propriétés mesurables. En utilisant les relations de la thermodynamique, il est montré que ces expressions sont toutes équivalentes et identifiables à la vitesse de son isentropique. Comme corollaire de cette démonstration, des expressions sont obtenues en termes de propriétés mesurables pour plusieurs variables thermodynamiques d’état intervenant dans les coefficients des équations du problème. Ces expressions sont nécessaires si l’on veut éviter la perte de précision introduite dans la différentiation numérique directe de grandeurs dérivées que les variables d’état représentent.

ZUR GLEICHWERTIGKEIT VERSCHIEDENER AUSDRÜCKE FÜR DIE GESCHWINDIGKEIT DER WELLENLEITUNG BEI KOMPRESSIBLEN FLÜSSIGKEITSSSTRÖMUNGEN MIT WÄRMEÜBERGANG

Zusammenfassung—Es wird gezeigt, daß die Einführung einer spezifischen Zustandsgleichung zur Ergänzung der Kontinuitäts-, Impuls- und Enthalpiegleichungen bei dem Modell einer kompressiblen Strömung mit Wärmeübergang zu einer sehr spezifischen Gleichungsgestalt für die Wellenleistungsgeschwindigkeit führt. Folglich lassen sich die zahlreichen Ausdrücke, die man bei Verwendung der unterschiedlichen Zustandsgleichungen erhält, nicht einfach als gleich erster und dritter Ordnung identifizieren.
On the use of Jacobians to reduce thermodynamic derivatives

C. W. SOMERTON, and Ö. A. ARNAS, Mechanical Engineering Department, Louisiana State University, Baton Rouge, LA 70803, USA

Original received 26th October 1983
Amended 16th July 1984

INTRODUCTION

One of the main topics covered in an elementary thermodynamics course is the development of relationships among thermodynamic properties. Chief among these relationships are, of course, the Maxwell relations. The purpose behind teaching thermodynamic relations is to demonstrate how unmeasurable thermodynamic properties, such as internal energy or Helmholtz potential, can be calculated from experimental measurements. The reduction of thermodynamic partial derivatives to measurable quantities is the key to this demonstration.

Most thermodynamic texts employ reduction methodologies that, at the best, have no clear-cut procedure and, in many cases, are totally haphazard and random. Teaching reduction via these methodologies is very difficult, since it is rarely satisfying to tell students that if they work enough problems they will eventually get a handle on it. Fortunately, there is an alternative method in which the reduction of partial derivatives can be achieved rapidly and elegantly by the use of Jacobians. This method was developed by Shaw [1]. What we present here is a systematic procedure that has proved very successful in teaching the method to students. It is surprising, after seeing the method in action, to realize that the method is not presented in some of the most classical textbooks of thermodynamics such as Zemansky [2] and Van Wylen and Sonntag [3]. The apparent neglect of this powerful method in such texts is what has provided the motivation for this paper.

CRITERIA FOR REDUCTION

The question as to what is meant by the reduction of a thermodynamic partial derivative must be addressed before we proceed with a presentation of the Jacobian method. The objective of reduction is to obtain an expression for a thermodynamic partial derivative in terms of measurable quantities. If we restrict our attention to simple systems, then all the thermodynamic properties only four can be measured directly: pressure, temperature, volume, and mass. Indirectly, we can also experimentally determine the specific heats $c_p$ and $c_v$. 

0306-4190/85/0001-009 $2.00 International Journal of Mechanical Engineering Education Vol 13 No 1
We now restrict our attention to a single-component simple system. This eliminates mass as an independent parameter and dictates our extensive parameters to be on a per unit mass basis. Thus, pressure, temperature, and specific volume become the 'measurable' thermodynamic properties. Of these three, only two are independent since an equation of state provides a relationship among the three. We choose to use temperature and pressure as our two independent variables. It is important to note that these two variables appear as coefficients in the equation of the first differential of the internal energy. That is,

\[ du = T ds - p dv \]  

where

\[ T = \left( \frac{\partial u}{\partial s} \right)_v \quad \text{and} \quad p = - \left( \frac{\partial u}{\partial v} \right)_s \]

Thus our two independent variables correspond to the first order partial derivatives of the first differential of \( u \). When we consider the reduction of first order partial derivatives, we must have a base set of independent first derivatives. Since the functional form of the internal energy represents the fundamental relation for the system and hence provides us with all thermodynamic knowledge about the system and changes in the system, then we can determine the number of elements of this base set by considering the equation of the second differential of the internal energy,

\[ d^2 u = \left( \frac{\partial^2 u}{\partial s^2} \right)_v (d s)^2 + 2 \left( \frac{\partial^2 u}{\partial s \partial v} \right)_{v-s} (d s)(d v) \]

\[ + \left( \frac{\partial^2 u}{\partial v^2} \right)_s (d v)^2 \]

where we have used the notation

\[ \left( \frac{\partial^2 u}{\partial s \partial v} \right)_{v-s} = \left( \frac{\partial}{\partial s} \left( \frac{\partial u}{\partial v} \right)_s \right)_{v} \]

This equation shows that we should have a base set of three independent first derivatives. The set we choose are:

Specific Heat at Constant Pressure:

\[ c_p = T \left( \frac{\partial s}{\partial T} \right)_p \]

Coefficient of Thermal Expansion

\[ \alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \]

Isothermal Compressibility

\[ \kappa_T = - \frac{1}{v} \left( \frac{\partial u}{\partial p} \right)_T \]
On the use of Jacobians to reduce thermodynamic derivatives

Finally, for the reduction of second derivatives we must also have a base set of these derivatives. With pressure and temperature as the independent variables, we can form the set

\[
\begin{align*}
\left( \frac{\partial \alpha}{\partial \tau} \right)_T, & \quad \left( \frac{\partial \alpha}{\partial \ell} \right)_p, \quad \left( \frac{\partial \alpha}{\partial T} \right)_p, \\
\left( \frac{\partial \kappa}{\partial \ell} \right)_T, & \quad \left( \frac{\partial \kappa}{\partial T} \right)_p, \quad \left( \frac{\partial \kappa}{\partial \ell} \right)_T
\end{align*}
\]

As was done in the case of equation (3), we consider the equation of the third differential of internal energy.

\[
d^3 u = \left( \frac{\partial^3 u}{\partial s^3} \right)_v (ds)^3 + 2 \left( \frac{\partial^2 u}{\partial s \partial y} \right)_{v-s} (ds)^2 (dv) + 2 \left( \frac{\partial^2 u}{\partial \ell \partial y} \right)_{v-s} (dv)^2 + \left( \frac{\partial^3 u}{\partial \ell^3} \right)_s (dv)^3
\]

(9)

By analogy, therefore, we should have a base set of four independent second derivatives. This means that two of the six second derivatives of equation (8) are redundant. It can be shown that an appropriate base set of four independent second derivatives is

\[
\begin{align*}
\left( \frac{\partial \alpha}{\partial \tau} \right)_T, & \quad \left( \frac{\partial \alpha}{\partial \ell} \right)_p, \quad \left( \frac{\partial \alpha}{\partial T} \right)_p, \\
\left( \frac{\partial \kappa}{\partial \ell} \right)_T, & \quad \left( \frac{\partial \kappa}{\partial T} \right)_p, \quad \left( \frac{\partial \kappa}{\partial \ell} \right)_T
\end{align*}
\]

(10)

A summary of our reduction criteria is given in Table 1. One final point involves the exclusion of the entropy in complete reduction criteria. The entropy will often appear through the Jacobian reduction method. When this occurs the additional equation

\[
s - s^0 = \int_{T^0}^T \frac{c_p}{T} \, dT - \int_{p^0}^p c_v \, dp
\]

(11)

should be included if we are to have reduction in a rigorous sense.

### Table 1

<table>
<thead>
<tr>
<th>Base derivatives for reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base zero derivatives</td>
</tr>
<tr>
<td>Base first derivatives</td>
</tr>
<tr>
<td>Base second derivatives</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
THE METHOD

The method developed by Shaw [1] is based upon a determinant of a specific form called a Jacobian and defined as

$$\frac{\partial (u, v, \ldots, w)}{\partial (x, y, \ldots, z)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \cdots & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} & \cdots & \frac{\partial v}{\partial z} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} & \cdots & \frac{\partial w}{\partial z} \end{vmatrix} \quad (12)$$

The property that makes a Jacobian profitable for reduction purposes is that it may be used to represent a partial derivative. That is,

$$\left( \frac{\partial u}{\partial x} \right)_{y \ldots z} = \frac{\partial (u, y, \ldots, z)}{\partial (x, y, \ldots, z)} \quad (13)$$

We may prove this easily by writing in determinant notation

$$\frac{\partial (u, y, \ldots, z)}{\partial (x, y, \ldots, z)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \cdots & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} & \cdots & \frac{\partial v}{\partial z} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial z}{\partial x} & \frac{\partial z}{\partial y} & \cdots & \frac{\partial z}{\partial z} \end{vmatrix} \quad (14)$$

but since \(x, y, \ldots, z\) are our independent variables then

$$\frac{\partial y}{\partial x} = \frac{\partial z}{\partial y} = \ldots = 0 \quad (15)$$

so that

$$\frac{\partial (u, y, \ldots, z)}{\partial (x, y, \ldots, z)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \cdots & \frac{\partial u}{\partial z} \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{vmatrix} \quad (16)$$

or by expanding the determinant

$$\frac{\partial (u, y, \ldots, z)}{\partial (x, y, \ldots, z)} = \left( \frac{\partial u}{\partial x} \right)_{y \ldots z} \quad (17)$$

which is our property.
Three other properties that will be of use are:

(i) Element Interchange

\[
\frac{\partial (u, v, \ldots, w)}{\partial (x, y, \ldots, z)} = - \frac{\partial (v, u, \ldots, w)}{\partial (x, y, \ldots, z)}
\]  \hspace{1cm}  (18)

(ii) Chain Rule

\[
\frac{\partial (u, v, \ldots, w)}{\partial (x, y, \ldots, z)} = \frac{\partial (u, v, \ldots, w)}{\partial (r, s, \ldots, t)} \cdot \frac{\partial (r, s, \ldots, t)}{\partial (x, y, \ldots, z)}
\]  \hspace{1cm}  (19)

(iii) Reciprocity

\[
\frac{\partial (u, v, \ldots, w)}{\partial (x, y, \ldots, z)} = \left[ \frac{\partial (x, y, \ldots, z)}{\partial (u, v, \ldots, w)} \right]^{-1}
\]  \hspace{1cm}  (20)

The first property can clearly be proved from determinant operations, while the second two properties come from direct analogy to ordinary derivatives.

With this background we can now present a cookbook procedure for the reduction of derivatives using Shaw's Jacobian methodology.

Step 1: If the derivative consists of a thermodynamic potential (a Legendre transformation of internal energy such as enthalpy, Gibbs function, etc.) or the internal energy, bring it to the numerator and eliminate it by the use of the appropriate defining differential equation for that variable. For example, for the Gibbs function we would use

\[
dg = -sdT + vdp
\]  \hspace{1cm}  (21)

Step 2: Write the derivative(s) in Jacobian notation.

Step 3: Introduce p and T as the independent variables.

Step 4: Reduce the Jacobian(s) by

(a) Maxwell relations

The two most commonly used ones will be

\[
\left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial p}{\partial T} \right)_s \hspace{1cm} \text{ (22)}
\]

\[
\left( \frac{\partial s}{\partial v} \right)_p = \left( \frac{\partial p}{\partial T} \right)_s \hspace{1cm} \text{ (23)}
\]

(b) Definitions of \(c_p\), \(\alpha\), and \(\kappa_T\).

(c) Calculating the determinant.

---

...By following these steps the proper reduction of all thermodynamic derivatives will be assured. It should be noted that Step 1 can become rather involved since, as will be shown, bringing a variable to the numerator will often involve a considerable number of Jacobian operations. If we are dealing with a second or higher order derivative it is useful to introduce a Step 0.

Step 0: Introduce the definition of the first derivative, carry out the chain rule, reverse the order of differentiation, and see if simplification occurs.
EXAMPLE 1: REDUCTION OF A FIRST DERIVATIVE

A first derivative that commonly appears in thermodynamics is the specific heat at constant volume, given by

\[ c_v = \frac{T}{\left( \frac{\partial s}{\partial T} \right)_v} \]  

By reducing the derivative \((\partial s/\partial T)_v\), we will be able to obtain the well-known relationship for \(c_v\) as a function of \(C_v\), \(\alpha\), and \(kT\). We proceed by following our step-by-step outline. We first write the derivative in Jacobian notation

\[ \left( \frac{\partial s}{\partial T} \right)_v = \frac{\partial (s, \nu)}{\partial (T, \nu)} \]  

and introduce \(p\) and \(T\)

\[ = \frac{\partial (s, \nu)}{\partial (p, T)} \frac{\partial (T, \nu)}{\partial (p, T)} \]  

and interchange the elements of the numerator of the second Jacobian

\[ = \frac{\partial (p, T)}{\partial (p, T)} \frac{\partial (s, \nu)}{\partial (p, T)} \]  

The second Jacobian can be written as a derivative

\[ = \frac{\partial (s, \nu)}{\partial (p, T)} \left( \frac{\partial s}{\partial p} \right)_T \]  

However, by definition

\[ \kappa_T = -\frac{1}{v} \left( \frac{\partial s}{\partial p} \right)_T \]  

so that

\[ \left( \frac{\partial s}{\partial T} \right)_v = \frac{1}{\kappa_T^v} \frac{\partial (s, \nu)}{\partial (p, T)} \]  

The remaining Jacobian cannot be written as a derivative. Thus, we must reduce it by calculating the determinant. In determinant form, we have

\[ \left( \frac{\partial s}{\partial T} \right)_v = \frac{1}{\kappa_T^v} \left| \begin{array}{cc} \partial s/\partial p & \partial s/\partial T \\ \partial s^v/\partial p & \partial s^v/\partial T \end{array} \right| \]  

Calculating the determinant

\[ = \frac{1}{\kappa_T^v} \left[ \left( \frac{\partial s}{\partial p} \right)_T \left( \frac{\partial s}{\partial T} \right)_p - \left( \frac{\partial s}{\partial p} \right)_T \left( \frac{\partial s}{\partial T} \right)_p \right] \]
On the use of Jacobians to reduce thermodynamic derivatives

Using the Maxwell relation for the first derivative

\[
\frac{\partial s}{\partial p}_T = -\frac{\partial v}{\partial T}_p
\]  \hspace{1cm} (33)

and then using our three definitions

\[c_p = T \frac{\partial s}{\partial T}_p\]  \hspace{1cm} (34)

\[\alpha = \frac{1}{\nu} \frac{\partial v}{\partial T}_p\]  \hspace{1cm} (35)

\[\kappa T = -\frac{1}{\nu} \frac{\partial v}{\partial p}_T\]  \hspace{1cm} (36)

we may write

\[
\frac{\partial s}{\partial T}_\nu = \frac{1}{\kappa T} \left[ -\alpha^2 \nu^2 + \frac{\nu}{\kappa T} \frac{\partial c_p}{\partial T}_h \right]
\]  \hspace{1cm} (37)

or finally we may find

\[
c_\nu = T \frac{\partial s}{\partial T}_\nu = c_p - \frac{\alpha^2 \nu T}{\kappa T}
\]  \hspace{1cm} (38)

which is the well known relationship we were seeking.

**EXAMPLE 2: REDUCTION OF A SECOND DERIVATIVE**

In thermodynamic analysis it often becomes important to reduce second derivatives to measurable quantities. This is especially true of stability analyses. In this section we consider a throttling process where we need to know how the specific heat at constant pressure varies with temperature. Thus we wish to reduce \((\partial c_p/\partial T)_h\).

Employing Step 0 we introduce

\[
c_p = T \frac{\partial s}{\partial T}_p
\]  \hspace{1cm} (39)

to obtain

\[
\frac{\partial c_p}{\partial T}_h = \left( \frac{\partial}{\partial T} \left[ T \frac{\partial s}{\partial T}_p \right] \right)_h
\]  \hspace{1cm} (40)

carrying out the chain rule

\[
= \left( \frac{\partial s}{\partial T}_p \frac{\partial T}{\partial T}_h \right)_h + T \left( \frac{\partial}{\partial T} \left[ T \frac{\partial s}{\partial T}_p \right] \right)_h
\]  \hspace{1cm} (41)
interchanging the order of differentiation and noting \((\partial T / \partial T)_h = 1\), we obtain

\[
\left( \frac{\partial c_p}{\partial T} \right)_h = \left( \frac{\partial s}{\partial T} \right)_T + T \left( \frac{\partial^2 s}{\partial T \partial T} \right)_h
\]

(42)

which does not lend itself to a further simplification. However, note that if we were reducing \((\partial c_p / \partial T)_h\), the second term would be zero after interchanging the order of differentiation so that Step 0 would have produced a very simplified form.

Continuing, our next step is to bring the enthalpy to the numerator. To achieve this we begin by writing the derivative in Jacobian notation

\[
\left( \frac{\partial c_p}{\partial T} \right)_h = \frac{\partial c_p(h)}{\partial (T,h)}
\]

(43)

We introduce \(p\) and \(T\)

\[
= \frac{\partial c_p(h)}{\partial (T,p)} \frac{\partial (T,h)}{\partial (T,p)}
\]

(44)

interchange elements of both numerator and denominator of second Jacobian

\[
= \frac{\partial c_p(h)}{\partial (T,p)} \frac{\partial (h,T)}{\partial (p,T)}
\]

(45)

write first Jacobian in determinant form and second as a derivative

\[
= \begin{vmatrix}
\frac{\partial c_p}{\partial T} & \frac{\partial c_p}{\partial p} \\
\frac{\partial h}{\partial T} & \frac{\partial h}{\partial p}
\end{vmatrix}
\begin{pmatrix}
\frac{\partial h}{\partial p} \\
\frac{\partial h}{\partial T}
\end{pmatrix}
\]

(46)

calculating the determinant

\[
= \left[ \frac{\partial c_p}{\partial T}_p \left( \frac{\partial h}{\partial p} \right)_T - \frac{\partial c_p}{\partial p}_T \left( \frac{\partial h}{\partial T} \right)_p \right] \left[ \frac{\partial h}{\partial p} \right]^{-1}
\]

(47)

The first derivative is a 'base' second derivative. Thus we are left with reducing the three remaining derivatives. For the derivatives of \(h\) we use the appropriate differential equation

\[
dh = T ds + v dp
\]

(48)

to obtain

\[
\left( \frac{\partial h}{\partial T} \right)_p = T \left( \frac{\partial s}{\partial T} \right)_p = c_p
\]

(49)

\[
\left( \frac{\partial h}{\partial p} \right)_T = T \left( \frac{\partial s}{\partial p} \right)_T
\]

(50)

or using the Maxwell relation

\[
\left( \frac{\partial s}{\partial p} \right)_T = \left( \frac{\partial v}{\partial T} \right)_p
\]

(51)
and the definition
\[ \alpha = \frac{1}{\nu} \left( \frac{\partial \nu}{\partial T} \right)_p \] (52)

we can write
\[ \left( \frac{\partial h}{\partial p} \right)_T = \nu (1 - T \alpha) \] (53)

For \((\partial c_p / \partial p)_T\) we begin by substituting in for \(c_p\)
\[ \left( \frac{\partial c_p}{\partial p} \right)_T = \left( \frac{\partial}{\partial p} \left[ T \left( \frac{\partial \nu}{\partial T} \right)_p \right] \right)_T \] (54)

interchanging the differentiation
\[ = T \left( \frac{\partial}{\partial T} \left( \frac{\partial \nu}{\partial p} \right)_T \right)_p \] (55)

and using
\[ \left( \frac{\partial \nu}{\partial p} \right)_T = - \left( \frac{\partial \nu}{\partial T} \right)_p = - \nu \] (56)

we obtain
\[ \left( \frac{\partial c_p}{\partial p} \right)_T = - T \left( \frac{\partial \alpha}{\partial T} \right)_p \] (57)

applying the chain rule
\[ = - T \alpha \left( \frac{\partial \nu}{\partial T} \right)_p - \left( \frac{\partial \alpha}{\partial T} \right)_p \] (58)

or by definition
\[ = - T \nu \left[ \alpha^2 + \left( \frac{\partial \alpha}{\partial T} \right)_p \right] \] (59)

Finally, we obtain
\[ \left( \frac{\partial c_p}{\partial T} \right)_h = \left( \frac{\partial c_p}{\partial T} \right)_p + \frac{c_p T}{(1 - \alpha T)} \left[ \alpha^2 + \left( \frac{\partial \alpha}{\partial T} \right)_p \right] \] (60)

**JACOBIAN REDUCTION FOR MORE COMPLEX SYSTEMS**

The power of the Jacobian reduction method can be demonstrated once again when more complex thermodynamic systems are considered. Multi-component, electromagnetic, and deformable solid systems can all be treated by Jacobians as outlined above with the following modifications.
(1) Designate additional independent parameters.
(2) Identify additional base derivatives.
(3) Recognize that the Jacobian may now be an \([n \times n]\) determinant.
(4) Identify the additional Maxwell relations.

CONCLUDING REMARKS

The authors have attempted to bring attention to the Jacobian reduction method for thermodynamic partial derivatives. We hope that by reading this paper the method will gain further recognition and use, and that instructors will be encouraged to teach the method in basic thermodynamic courses. Guggenheim [4] dismisses the Jacobian method as at times being merely amusing. This comment holds some merit since some of the identities obtained are not useful. But the power of the method is clear and can prove very useful in thermodynamic research as one of the authors has shown [5].

REFERENCES