

# THE GRADUATE STUDENT VERSUS THERMODYNAMICS

JOSEPH J. MARTIN

*University of Michigan,  
Ann Arbor, Mich.*



Joseph J. Martin was educated at Iowa State, Rochester, and Carnegie-Mellon University (Sc.D. '47). He is professor and associate director of Institute of Science and Technology at University of Michigan. Presently he is a vice-president of ASEE and a Director of AIChE.

Thermodynamics has the reputation, enviable or not, of being a worthy adversary for those who dare to engage it in battle. For most young proteges there are many rounds of rough in-fighting before mastery of the subject can be claimed. This is not because of its sheer logic, for mathematics is undoubtedly the queen of the sciences in this respect, and mathematics does not seem to offer the same degree of difficulty. Rather, it is more probably due to the extreme range of application of thermodynamic principles. Although Webster says that "thermodynamics is the science which treats of the mechanical action or relations of heat," it is much more appropriate to say that thermodynamics is the science of energy and entropy which is involved in every equilibrium state of matter and every process or change that occurs in the real ponderable universe.

As an undergraduate the young protege is exposed to the so-called "laws of thermodynamics," of which there are just four as follows:

**Zerth.** If a thermometer shows the same reading when in separate contact with two objects, no change occurs when the two objects are touched to each other.

**First.** Energy and mass are simultaneously conserved (accountable) in all processes and individually conserved in most cases.

**Second.** Actual processes occur in one direction and the initial conditions will never be restored without the aid of some outside agent.

**Third.** The entropy of a pure substance in perfect crystalline form vanishes at the absolute zero of temperature.

The zerth and second laws are quite acceptable to the undergraduate because he has had some experience with thermometers and because he has learned the irreversible ways of mother nature from the time of his first broken dish or balloon to the time he has burned the last drop of gasoline in his car many miles from a service station. The first law is palatable because energy and mass balances are mathematically neat, but the protege is often shaky on the general concept

of energy. He finds it difficult to explain the nature of internal energy or to tell just where energy is stored when a weight is lifted in a gravitational field. The third law makes sense to him only insofar as he understands the abstract quantity, entropy, and the absolute temperature scale.

It is generally not the laws of thermodynamics which present the greatest difficulty to the novice in the field, but the hundreds of equations which have been developed to permit quantification of the elementary principles embodied in the laws themselves. Fortunately, however, there are just four basic equations from which all others are derived by suitable mathematical manipulation. These four questions do not have a one to one correspondence with the four laws, but collectively they incorporate the first three laws within their structures. The four equations are:

## The Fundamental Property Relation of Matter (Gibbs Equation),

$$du = Tds - PdV + \sum_{i=1}^N \mu_i dm_i \quad (1)^*$$

## The Energy Balance on a System,\*\*

$$d(U + mu^2/2 + mgz)_{sys} = \delta Q - \delta W + \sum_{j=1}^K (\bar{H} + u^2/2 + gz)_{j} \delta m_j \quad (2)$$

\*See the Nomenclature at the end for the definition of symbols.

\*\*A system is any portion of the universe chosen for analysis, and may have many distinct parts.

The Entropy Balance on a System,

$$dS_{\text{sys}} = \sum_{i=1}^M (\delta Q/T)_i + \delta LW/T_o + \sum_{j=1}^K \bar{s}_j \delta m_j \quad (3)$$

The Mass Balance on a System,

$$dm_{\text{sys}} = \sum_{j=1}^K \delta m_j \quad (4)$$

Although it may appear to be an oversimplification of the subject, there is little question but what complete understanding of the four basic equations amounts to a mastery of classical thermodynamics. The equations are, therefore, introduced to the protege at an early stage, even though it is quite unlikely that in a single course he will perceive all of their underlying implications. The graduate student who is exposed to one or more succeeding courses will gradually gain a more complete understanding of the extreme power and utility of the four equations to describe the thermodynamic character of all processes and all equilibrium states of matter.

The first of the basic equations is probably the most important and the protege learns that a uniform mass of matter has the extensive thermodynamic properties, internal energy, entropy, volume, and mass of each component, and the intensive properties (potentials), temperature, pressure, and chemical potential of each component.\* The point to be emphasized is that these properties are not completely independent, but are interlocked through Eqn. (1). Any change in the condition or state of matter will cause changes in the thermodynamic properties, but the changes cannot occur indiscriminately; they must occur in accordance with this differential equation. In the deduction of the several terms in the equation, the inclusion of entropy is paramount. It is done in one approach by saying that for a simple heat transfer to the exclusion of any other effect the change of entropy is the change of internal energy divided by temperature, or  $dS=dU/T$ . This makes S extensive in the same manner as U. The desirability of defining entropy this way is best understood by noting that, for example, when a hot object is touched to a cold object in isolated conditions, the energy balance shows nothing is lost since  $dU_{\text{Both}}=dU_{\text{H}}+dU_{\text{C}}=0$ . Yet experience and intuition tell us that something has changed and the ability to do work has been lost. Calculat-

\*Equation (1) is the ordinary version of the fundamental property relation. Additional terms of the form, (intensive) d (extensive) may readily be added to it to account for the more unusual effects such as surface, elongation or tensile, electric, and magnetic.

**Thermodynamics is the science of energy and entropy which is involved in every equilibrium state of matter and every process that occurs in the real universe.**

ing  $dU/T$  (i.e., entropy change) for both objects shows  $(dU/T)_{\text{Both}} = (dU/T) + (dU/T)_{\text{C}} = dS_{\text{Both}} > 0$  because  $dU_{\text{H}} = -dU_{\text{C}}$  and  $T_{\text{H}} > T_{\text{C}}$ . The change in entropy,  $dS$ , provides a quantitative measure of the irreversibility of the heat transfer. Its relation to the work lost is given by Eqn. (3).

The unusual mathematical character of Eqn. (1) being an exact differential and homogeneous of the first degree permits it to be integrated to

$$U = TS - PV + \sum_{i=1}^N \mu_i m_i \quad (5)$$

and then differentiated to

$$0 = s dT - v dP + \sum_{i=1}^N m_i d\mu_i \quad (6)$$

which is the Gibbs-Duhem equation that is worthy of extended contemplation by the protege. Because U, TS, and PV often occur together as in (5), it is convenient to define  $H = U + PV$ ,  $A = U - TS$ , and  $G = H - TS$ , but it is obvious that although very handy and efficient, H, A, and G are not fundamental properties. By rules of partial differentiation and the definition of heat capacity as

$$C_x = T(dS/dT)_x \quad (7)$$

it is possible to put Eqn. (1) in such seemingly unrelated forms as

$$d\bar{s} = C_p dT/T - (d\bar{v}/dT)_p dP \quad (8)$$

$$\Delta \bar{H} = T \Delta \bar{v} (dP/dT)_{\text{sat}} \quad (9)$$

and many others. In fact, the bulk of thermodynamics involves the application of Eqn. (1) in different ways to a wide variety of situations involving ponderable matter.

In the second basic equation, the energy balance, the protege notes how heat and work are introduced with arbitrary signs, and the reason for distinguishing flows of energy to the system by "δ", and changes of energy within the system by "d". The most common applications of the equation are in three integrated forms:

Closed System,

$$Q - W = \Delta U_{\text{sys}} \quad (10)$$

Steady-Flow System,

$$\dot{Q} - \dot{W} = \Delta \dot{H} + \Delta(u^2/2) + g\Delta Z \quad (11)$$

Single-Flow System,

$$\int \underline{H} \delta m + Q - W = \left[ (\underline{U}m)_f - (\underline{U}m)_i \right]_{\text{sys}} \quad (12)$$

Of course, the energy balance may take many other forms by proper specialization of Eqn. (2) for particular cases.

The third basic equation, the entropy balance, is useful for calculation of the work lost in real irreversible processes and for analysis of idealized reversible processes. The protege is quite aware that a tank of compressed air can do useful work by connecting it to an expansion engine and that such work can be forever lost by allowing the air to leak out instead of flowing through the engine. He is equally aware that an outside agent must do work on the air that leaked out in order to get it back into the tank. He will readily appreciate that this work of restoration under certain ideal conditions is the work lost during the irreversible leaking process.

For many applications the entropy balance is applied to closed systems as a simple integral,

$$\int T ds_{\text{sys}} = Q + LW \quad (13)$$

In this form it is seen that for a non-flow reversible process (no lost work) the heat transfer equals the  $\int T ds$ . If in addition there is no heat transfer (adiabatic as well as reversible), the  $\int T ds$  vanishes and the process is isentropic. When Eqn. (3) is applied to a reversible heat engine operating in a steady state (no lost work, no change of entropy of the system—the engine, no mass flow—only heat and work flow),

$$\sum_i (\delta Q/T)_i = 0 = \delta Q_h/T_h + \delta Q_l/T_l$$

This may be combined with the energy balance,  $\delta Q_h + \delta Q_l - \delta W_r = 0$ , to give

$$\delta W_r = \delta Q_h \left( \frac{T_h - T_l}{T_h} \right) = \delta Q_l \left( \frac{T_h - T_l}{T_l} \right) \quad (14)$$

which is the Carnot relation that is utilized in the analysis of heat engines and heat transfer processes. Here it is desirable that the protege become familiar with heat engine cycles that are used in steam plants, gas turbines, and reciprocating internal combustion engines. The concept of available energy should be included also.

The energy and entropy balances may be combined in another manner by eliminating  $Q$  between Eqn. (11) and Eqn. (13) applied to a unit mass of flowing material, and utilizing the definition of

$$\underline{G} = \underline{H} - T\underline{S} \text{ or } \Delta \underline{G} = \Delta \underline{H} - \int T ds - \int s dT, \text{ so that} \quad (15)$$

$$-\underline{LW} - \underline{W} = \Delta \underline{G} + \int s dT + \Delta(u^2/2) + g\Delta Z$$

By using the property relation,  $\Delta G = \int V dp - \int S dT$ , which is just a case of Eqn. (1) for the unit mass, another energy-entropy balance form is

$$-\underline{LW} - \underline{W} = \int v dp + \Delta(u^2/2) + g\Delta Z \quad (16)$$

which is Bernoulli's equation. This equation has proven extremely useful in the treatment of a wide variety of fluid flow problems, particularly those in which there is friction lost work. For a reversible process no work is lost and (16) becomes

$$-\underline{W}_r = \int v dp + \Delta(u^2/2) + g\Delta Z \quad (17)$$

while (15) becomes

$$-\underline{W}_r = \Delta \underline{G} + \int s dT + \Delta(u^2/2) + g\Delta Z \quad (18)$$

The last two equations find applications in the flow work concept of equilibrium between two states. By this concept if two states are in equilibrium, no work can be obtained from a transfer or flow of mass between them. Direct use of the equations furnishes an analysis of non-isothermal equilibrium, which is equilibrium superimposed on a steady-state irreversible heat transfer. Most applications, however, are to isothermal equilibrium so that Eqn. (18) is written

$$0 = \Delta \underline{G}_T + \Delta(u^2/2) + g\Delta Z = \Delta \underline{G}_T + m\Delta(u^2/2) + mg\Delta Z \quad (19)$$

If component A in a mixture is free to move between two states in equilibrium, (19) may be written

$$0 = \Delta \bar{G}_{A,T} + \Delta(u^2/2) + g\Delta Z \quad (20)$$

This is the key equation of phase equilibrium and to understand its implications, it is necessary to become familiar with partial extensive properties as derivatives of any extensive property with respect to mass of component A at constant  $T, P$ , and masses of all other components. For free energy, as an example,  $\bar{G}_A = (dG/dm_A)_{T,P,m_B}$  (21)

This may be compared with the property relation (1) to show that  $G_A \equiv \mu_A$  (22)

Further comparison with (5) shows that

$$G = m_A G_A + m_B G_B + \dots \quad (23)$$

When one has gained confidence that a partial property of a component of a mixture is essentially the same as the unit mass property of a pure substance, he sees how most of the equations for pure and mixture components are interchangeable. For example, by proper manipulation of the fundamental property relation (1) he can get both

$$\left[ \frac{d(G/T)}{dT} \right]_P = \frac{-\underline{H}}{T^2} \quad (24)$$

and

$$\left[ \frac{d(\bar{G}_A/T)}{dT} \right]_P = \frac{-\bar{H}_A}{T^2} \quad (25)$$

which are Gibbs-Helmholtz equations.

The protege's level of sophistication in thermodynamics is advancing rapidly if he fully comprehends the definition and use of fugacity and activity through the equations,

$$d\bar{G}_A = RT d \ln \bar{f}_A \text{ where } \bar{f}_A \rightarrow P_A \text{ as } P \rightarrow 0 \quad (26)$$

and

$$\bar{G}_A = \bar{G}_A^\circ + RT \ln \frac{\bar{f}_A}{\bar{f}_A^\circ} = \bar{G}_A^\circ + RT \ln a_A \quad (27)$$

Here integration has been conducted isothermally from a chosen standard state\* to any state. When Eqns. (23) and (27) are applied to a reaction,  $aA + bB \rightleftharpoons cC + dD$ , at a given temperature and no kinetic or potential effects, Eqn. (18) yields

$$-W_r = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = \Delta G^\circ + RT \ln J_a \quad (28)$$

At equilibrium where  $W_r = 0$ , this becomes

$$\Delta G^\circ = -RT \ln K_a \quad (K_a = J_{a_{\text{Equilibrium}}}) \quad (29)$$

Then substituting Eqns. (8) and (25) into the temperature derivative of (29), and integrating between two temperatures, the following equation for situations without appreciable latent heat effects can be obtained by a person who has a good grasp of the subject,

$$\ln \frac{K_{a_2}}{K_{a_1}} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \int_{T_1}^{T_2} \frac{(C_{P_{\text{Prod}}} - C_{P_{\text{React}}}) dT}{RT^2} \quad (30)$$

At the same time this move is made, it is desirable that the protege learn how to use certain tabular values of thermodynamic functions so that he can evaluate

$$\left( \frac{\Delta G^\circ}{T} \right)_T = -R \ln K_a = \sum_{\text{Prod}} \left( \frac{G_T^\circ - H_T^\circ}{T} + \frac{\Delta H_f^\circ}{T} \right) - \sum_{\text{React}} \left( \frac{G_T^\circ - H_T^\circ}{T} + \frac{\Delta H_f^\circ}{T} \right) \quad (31)$$

The protege's knowledge should extend to electrochemical reactions, so that he understands the relations involving electrical work and voltage, such as

$$W = N\mathcal{F}\mathcal{E} \quad (32)$$

$$\frac{d(\mathcal{E}_r^\circ/T)}{dT} = \frac{\Delta H^\circ}{N\mathcal{F}T^2} \quad (33)$$

$$N\mathcal{F}\mathcal{E}_r^\circ = RT \ln K_a \quad (34)$$

\*Standard state is a state of the material at the temperature of interest and usually at a given pressure or other conditions that determine the state.

The entropy balance is useful for calculations of the work lost in real irreversible processes and for analysis of idealized reversible processes.

and

$$N\mathcal{F}\mathcal{E}_r = N\mathcal{F}\mathcal{E}_r^\circ - RT \ln J_a \quad (35)$$

By defining the activity coefficient,  $\gamma_i = \bar{f}_i/x_i f_i^\circ$ , it is desirable to be able to proceed from Eqn. (6) to get

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0 \quad (36)$$

$$\int_0^1 \ln \frac{\gamma_A}{\gamma_B} dx_A = 0 \quad (37)$$

and

$$\ln \gamma_A^\infty = \int_{\gamma_B=1}^{\gamma_B^\infty} \frac{x_B}{x_A} d \ln \gamma_B \quad (38)$$

Rewriting Eqn. (20). for simple phase equilibria.

$$\bar{G}_A^\alpha = \bar{G}_A^\beta \quad (39)$$

and utilizing (27), the extremely useful relation,

$$\bar{f}_A^\alpha = \bar{f}_A^\beta \quad (40)$$

is obtained. From the definition of the activity coefficient the equation for liquid-vapor-equilibrium is often shown as

$$(\gamma_A x_A f_A^\circ)^{\text{liq}} = (\gamma_A y_A f_A^\circ)^{\text{vapor}} \quad (41)$$

For ideal solutions the protege learns that if he appreciates the significance of assuming  $\bar{v}_A = v_A$ , he can derive

$$\bar{f}_A = y_A f_A \quad (42)$$

$$\Delta G_{\text{mix}}^{\text{ideal}} = RT(n_A \ln x_A + n_B \ln x_B) \quad (43)$$

Equally useful relations for enthalpy and entropy may be obtained.

For non-ideal solutions it is desirable to see how

$$\Delta G_{\text{Ex}} = \Delta G_{\text{mix}} - \Delta G_{\text{ideal}} = RT(n_A \ln \gamma_A + n_B \ln \gamma_B) \quad (44)$$

and for regular solutions how

$$\Delta G_{\text{mix}}^{\text{reg}} = x_A(1-x_A)\omega + RT(x_A \ln x_A + x_B \ln x_B) \quad (45)$$

The empirical and semi-theoretical techniques for obtaining activity coefficients or required PVT behavior or an empirical constant such as  $\omega$  must be introduced at each step in which real problems are considered. Calculation of actual situations leads to the application, employment, and even development of correlations of the properties of matter. It behooves the protege to master many of these in the course of mastering the fundamentals of thermodynamics.

Nothing has been said about the fourth basic equation since it is generally used directly as is. Clearly, however, if an application is contemplated to an extremely high energy process, such as a nuclear reaction or high velocity particles, the Einstein relation,  $E = mc^2$ , must be employed. In such a case the individual mass and energy balances must be modified to allow for the equivalence of mass and energy.

NOMENCLATURE	
A	Helmholtz free energy, U-TS
a	Activity, $\xi/t^\circ$
c	Heat capacity, $T(dS/dT)$
F	Faraday number
f	Fugacity
G	Gibbs free energy, H-TS
g	Acceleration of gravity
H	Enthalpy
$J_a$	Ratio of activities $a_{C,D}^a/a_{A,B}^a$
$K_a$	Equilibrium ratio of activities
LW	Lost work
m	Mass
N,n	Number of moles
P	Pressure
P	Partial pressure
Q	Quantity of heat
S	Entropy
T	Temperature
U	Internal Energy
u	Velocity
V	Volume
W	Work
x	Mole fraction
Y	Mole fraction
Z	Height above datum plane
$\alpha, \beta$	Phases
$\gamma$	Activity coefficient
$\mu$	Chemical potential
$\omega$	Constant for regular solutions
—	Below an extensive property makes it per unit mass
—	Above an extensive property makes it a partial property of a mixture.
□	Denotes vapor pressure, as $P^\square$ .

Several example problems and solutions are presented in the following section.

## ChE problems for teachers

The following problems with solutions were submitted by Professor J. J. Martin.

No. 1. One hundred million standard cubic feet (60°F, 1 atm) per day of radioactive waste gas at 1000°F must be released at a height of 400 ft. above the ground to avoid contamination of the surrounding area. A circular stack of uniform diameter is to be used. A draft at the base of the stack of 1 in. of water will be required (pressure inside stack base is 1 in. H<sub>2</sub>O less than barometric pressure). The barometric pressure at the base of the stack is 740 mm Hg and the ambient temperature 60°F. The gas has a molecular weight of 32 and may be considered an ideal gas. What diameter will be required?

The lost work of gas flowing through the stack may be approximated by the equation:

$$LW = \frac{0.032 \text{ lu}^2}{g_c D}$$

LW = lost work in ft-lb<sub>F</sub>/lb<sub>M</sub>

l = height in ft

D = diameter in ft

u = velocity in feet per sec

$g_c$  = conversion factor from lb<sub>M</sub> to lb<sub>F</sub>

Solution: For barometric pressure at top consider a stagnant column of air outside the stack. Since it is at equilibrium (no flow) with no kinetic effects, Eqn. (17) applies as

$$0 = \int_{\text{base}}^{\text{top}} \frac{RT}{P} dP + g\Delta Z$$

$$RT \ln \frac{P_{\text{top}}}{P_{\text{base}}} = -g\Delta Z$$

$$\text{so } (10.73)(520) \ln \frac{P_{\text{top}}}{740} = - \frac{(400)(29)}{144}$$

$$\text{and } P_{\text{top}} = 729.41 \text{ mm Hg}$$

The pressure inside the base of the stack is

$$P_{\text{in base}} = 740 - \frac{(25.4)(1)}{13.6} = 738.13 \text{ mm Hg}$$

The gas velocity inside the stack at an average pressure of 734 mm Hg is

$$u = \frac{10^8 (760)(1460)(4)}{24(3600)(520)(734)\pi D^2} = \frac{4290 \text{ ft}}{D^2 \text{ sec}}$$

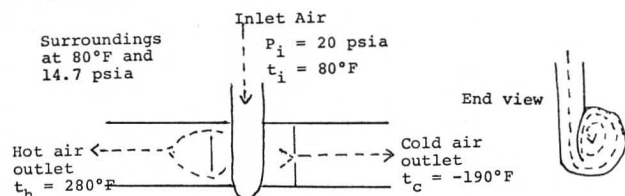
For flow inside the stack with no kinetic effects and no work, Eqn. (16) applies as

$$-LW = \int \frac{RT}{P} dP + g\Delta Z$$

$$\text{Thus, } - \frac{(0.032)(400)(4290)^2}{32.17 D^4} = \frac{(10.73)(1460)(144)}{(32)} \ln \frac{729.41}{738.13} + 400$$

$$\text{Solving } D = 7.2 \text{ ft}$$

No. 2. A Ranque-Hilsch vortex cylinder is a device to expand a stream of air in steady flow from high pressure and ambient temperature down to two streams at atmospheric pressure, one of which is at low temperature and the other at high temperature. Air enters the cylinder through a tangential tube, creating a vortex from which the hot air is withdrawn from the outer periphery and the cold air is withdrawn from the central region, as shown below. In a certain test of the equipment the temperatures and pressures were measured and reported to be as indicated on the diagram. The mass flow rate of the hot air was stated to be 1.35 times that of the cold air. Show by calculations whether the reported measurements are possible.



Solution: Apply the energy balance Eqn. (2) to the whole device. Assuming negligible kinetic and potential effects, and

$$\delta Q = \delta W = dE_{\text{sys}} = 0,$$

$$\sum_j H_j \delta m_j = 0 \text{ or } (H\delta m)_i = (H\delta m)_h + (H\delta m)_c$$

$$\text{Let } \delta m_h = 1.35, \delta m_c = 1.0, \delta m_i = 2.35$$

Taking the reference state of air at 80°F and 20 psia, and assuming ideal gas behavior with  $C_p = 7.0$  Btu/lb mole-°R,

$$H_i = 0, H_h = 7(280-80) = 1400, \text{ and } H_c = 7(-190-80) = -1890$$

Substituting in the energy balance

$$0 = (1400)(1.35) + (-1890)(1) = 0. \text{ So energy balance OK.}$$

Apply the entropy balance as

$$dS = \frac{\delta LW}{T_0} + \sum_j S_j \delta m_j = 0 \text{ for steady state}$$

or

$$- \frac{\delta LW}{T_0} = (S\delta m)_i - (S\delta m)_h - (S\delta m)_c$$