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Chapter 1

THE FIRST LAW OF THERMODYNAMICS

The utilization of naturally occurring sources of energy for doing work and for converting raw materials into useful products probably constitutes the greatest contribution that the engineer makes to society. Engineering techniques and processes have relieved man from the rigors of exhausting manual labor and have freed him from the limitations of his immediate environment. They have made available food, clothing and shelter that are more satisfactory than those found in nature and have made possible the transportation of these life necessities to areas where they do not occur naturally. As a result, civilized societies have spread over all the inhabitable areas of the earth, and with the development of commercial space transportation, they may eventually spread to other planets.

The rapid pace of technological development of the past two hundred years could not have occurred without the clarification and definition of the different forms of energy and the formulation of quantitative relationships governing the transformation of one form of energy into another. The body of knowledge which was gradually and painstakingly accumulated over many years has been reduced to a set of laws and now constitutes the subject matter of classical thermodynamics. A clear understanding of thermodynamic principles is essential for the appreciation of past developments and for continued progress in the field of engineering.

The laws of classical thermodynamics are based upon direct empirical observations; and as such, they are entirely independent of any theories which have been or will be proposed for the physical nature of matter and energy. The quantitative relationships based upon the laws of classical thermodynamics may be expressed in terms of experimentally measurable properties.

Contrary to the usual connotation of the term "dynamics", classical thermodynamics is concerned only with energy transformations and their effect upon the measurable macro or bulk properties of a system without regard to the detailed mechanism by which the transformations take place. A mechanistic interpretation of such transformations can be made only through the use of an acceptable model or theory of the nature of matter and energy. However, since

a mechanistic interpretation does provide a deeper insight and a better understanding of otherwise abstract empirical relations, elementary principles of the quantum and statistical mechanics may be used to interpret changes in the macro or bulk properties of a system in terms of its micro or molecular properties. The use of these theories in the development and interpretation of thermodynamic relations has given rise to a distinct discipline termed "statistical thermodynamics", which is particularly useful in interpreting the thermodynamic functions of internal energy and entropy and in providing a criterion for the establishment of an equilibrium state.

The laws and relations of classical thermodynamics will first be discussed from an empirical point of view. They will then be developed and interpreted on the basis of statistical thermodynamics.

1-1. The Conservation Laws of Mass and Energy

The concept of energy evolved slowly over a period of centuries. The elementary human senses could easily observe that a body in motion behaved and reacted unlike a body at rest; a hot body felt and behaved unlike a cold body. Even certain bodies at rest could be made to release energy in the form of heat by using them as fuel for a fire.

Although the qualitative observations could be made easily, the interpretations remained vague and confused, as exemplified by the phlogistic theory which conceived of heat as a fluid analogous to water. Only with the advent of quantitative measurements of the past two hundred years have the concepts of energy been clarified and clearly defined. It can now be demonstrated experimentally that mass and energy are interconvertible and that the totality of mass and energy is conserved in all known transformations. The concept of mass and energy conservation is now accepted as a fundamental law of nature and forms the basis for the First Law of Thermodynamics.

Although mass and energy are not independent, the change in mass due to energy changes is negligible except for extremely high energy reactions. For example, the mass change corresponding to an energy change of 1,000,000 Btu of energy may be calculated from the Einstein relation

$$\Delta E = \Delta mc^2$$

to be approximately 2.6×10^{-8} lb. For this reason, mass and energy may be considered to be independent for all physical processes and for those chemical processes involving the ordinary valence forces. For these cases, a conservation law of mass may be stated independently of the conservation law of energy.

Energy may be neither created nor destroyed.

Mass may be neither created nor destroyed.

These statements may be used independently without measurable error in the

majority of engineering applications and have been adopted as the First Law of Thermodynamics.

Experimental evidence indicates that energy may manifest itself in several different forms. For example, the energy of a mass and its measurable properties such as temperature and pressure may be altered by the application of heat or work. Proper application of the First Law requires a clear recognition of these various forms of energy.

1-2. Internal Energy

From a macroscopic point of view, the energy of a system which is inherent in its mass is termed the "internal energy". Internal energy is a property of mass which is completely defined by the state of the system and is therefore known as a "state or point function". The change in internal energy between two defined states of a mass is a fixed quantity and is independent of the mechanism producing the change.

From a microscopic or molecular point of view, the internal energy of a mass is the summation of all kinetic and potential energies of the particles making up that mass. In general, this energy is partitioned among the potential and kinetic energies of particles within the nucleus of each atom, the potential and kinetic energies of vibration of atoms within a molecule, the relative kinetic energies of rotation of groups of atoms within the molecule, the kinetic energies of rotation or translation of the molecule as a unit and, finally, any potential energies between molecules within the system.

The various types of internal energy may be roughly classified as "temperature independent" and "temperature dependent". Within the ranges of temperature and pressure normally encountered in engineering practice, the electronic and nuclear energies are essentially temperature independent and constitute the internal energy of a mass at the absolute zero of temperature. The energies of translation, rotation and vibration are temperature dependent and account for that portion of the internal energy which a body contains above absolute zero. This portion of the internal energy is commonly referred to as "thermal energy" and is of primary interest in thermodynamics.

At the present time, the absolute values of the electronic and nuclear energies cannot be determined, but changes in the values of these energies may be evaluated empirically from heats of formation or combustion data for the specific compounds involved. On the other hand, considerable progress has been made in determining the values of the different types of thermal energy. For example, on the basis of the classical kinetic theory of gases the average translational internal energy of an ideal gas is calculated to be $\frac{3}{2}RT$. Since the translation of a molecule in field-free space possesses 3 degrees of freedom (1 for each coordinate axis), $\frac{1}{2}RT$ of internal energy may be assigned to each degree of freedom.

A semi-quantitative determination of the average internal energies of rotation and vibration is possible if each degree of freedom for rotation is assigned $\frac{1}{2}RT$ of energy, and each degree of vibration is assigned $1RT$ of energy ($\frac{1}{2}RT$ each for potential and kinetic energy of vibration). In determining the total degrees of freedom, in a molecule each atom is considered as a mass point having 3 degrees of freedom. Therefore, a molecule containing n atoms will have $3n$ degrees of freedom. The monatomic molecule then possesses a total of 3 degrees of freedom, all of which are translational. If we consider an atom as a mass point without dimensions, a monatomic molecule possesses no rotational or vibrational energy. The diatomic molecule possesses a total of 6 degrees of freedom of which 3 are translational, 2 are rotational (neglecting spinning of atoms on the bond axis) and 1 is vibrational. The nonlinear triatomic molecule possesses a total of 9 degrees of freedom of which three are translational, 3 are

TABLE 1-1 CLASSICAL CONTRIBUTIONS TO MOLECULAR INTERNAL ENERGY

	Monatomic		Diatomic		Nonlinear Triatomic	
	\mathcal{F}	E/RT	\mathcal{F}	E/RT	\mathcal{F}	E/RT
Translation	3	$\frac{3}{2}$	3	$\frac{3}{2}$	3	$\frac{3}{2}$
Rotation	0	0	2	1	3	$\frac{3}{2}$
Vibration	0	0	1	1	3	3
Total	3		6		9	

\mathcal{F} = Degrees of freedom

E = Internal Energy

rotational, and 3 are vibrational. Table 1-1 lists the classical contribution of each degree of freedom to the internal energy for the monatomic, diatomic, and nonlinear triatomic molecules on the basis of classical theory.

The classical concepts of internal energy are partially confirmed by empirical data on heat capacities. The term "heat capacity" was used originally to indicate the quantity of heat necessary to change the temperature of a unit mass of material one degree. However, the heat capacity was found to be a function of the particular conditions under which the heat was added. For example, the quantity of heat required to raise a unit mass of gas one degree was found to be considerably greater if the gas expanded under a constant pressure during the heating process than that required if the gas was confined to a fixed volume. Also the particular temperature level at which the heat was added influenced the result. For these reasons several different types of heat capacities have been used, each identified with a particular type of heating process.

At the present time, the quantity of energy contained in a mass is identified as internal energy rather than as heat, and the term "heat capacity" has lost its historical significance. Nevertheless, the term is still used extensively to designate a well-defined property of mass. Of immediate interest is the constant-volume heat capacity, defined as the rate of change of the internal energy of a unit mass with respect to temperature under constant volume conditions.

$$C_v = (\partial E / \partial T)_v \quad (1-1)$$

The partial derivative may be a function of both temperature and pressure.

Since C_v measures the rate of change of the internal energy with respect to temperature under constant volume conditions, approximate values of C_v may be obtained directly by differentiation of the internal energy terms in Table 1-1 with respect to temperature. The results are summarized in Table 1-2.

TABLE 1-2 HEAT CAPACITIES OF IDEAL GASES
calories/(gram mole) ($^{\circ}\text{K}$) or Btu/(lb mole) ($^{\circ}\text{R}$)

	Monatomic		Diatomic		Triatomic	
	C_v	C_p	C_v	C_p	C_v	C_p
Translation	3	5	3	5	3	5
Rotation	0	0	2	2	3	3
Room Temperature and Below	—	—	—	—	—	—
Vibration	3	5	5	7	6	8
Very High Temperatures	0	0	2	2	6	6
	—	—	—	—	—	—
	3	5	7	9	12	14

Values of C_p for ideal gases may be obtained from C_v through the relation

$$C_p = C_v + R$$

where R has a numerical value of 1.987 cal/(gram mole) ($^{\circ}\text{K}$).

For a monatomic molecule, the classical theory predicts a C_v of 3 cal/(gram mole) ($^{\circ}\text{K}$) and a C_p of about 5 cal/(gram mole) ($^{\circ}\text{K}$) which is independent of temperature; this prediction is in agreement with experiment. According to the classical theory, the C_v of a diatomic molecule should be 7 cal/(gram mole) ($^{\circ}\text{K}$) and C_p should be about 9 cal/(gram mole) ($^{\circ}\text{K}$). Actually the C_p of most diatomic molecules is about 7 cal/(gram mole) ($^{\circ}\text{K}$) at room temperature and approaches 9 as a limit at high temperatures. This indicates that the vibrational energy of a diatomic molecule is usually small at room temperature, but it increases gradually with temperature until the full contribution of $1R$ per vibrational degree of freedom to the heat capacity is obtained at high temperature.

If the vibrational contribution is assumed negligible at room temperature, C_p for a nonlinear triatomic molecule should be 8 cal/(gram mole) ($^{\circ}\text{K}$) at room temperature and should approach 14 as a maximum at high temperature. This prediction is in close agreement with experiment.

1-3. Heat

The internal energy of a mass may be altered by the addition or removal of energy in the form of heat. By definition, heat is a form of energy in the process of being transferred from one region to another under the influence of a temperature difference. The rate of transfer is proportional to the temperature difference. According to this definition, it is incorrect to speak of the energy contained in a mass of material as heat. Energy may be transferred to the mass as heat, but upon entering the mass it is converted into internal energy and is not stored as heat.

Heat is a form of energy in transit, and its direct evaluation must depend upon the particular mechanism of transfer. Since classical thermodynamics is not particularly concerned with the mechanisms of heat conduction, convection and radiation, the quantity of heat transferred can be evaluated thermodynamically only by observing the effect of the heat transfer process upon the properties of a system and its surroundings.

1-4. Work

The internal energy of a mass may also be altered by the addition or removal of energy in the form of work. By definition, work is a form of energy in the process of being transferred by the action of a force through a displacement. Both a force and a displacement must be present in order to transfer energy in the form of work.

A common form of work encountered in engineering practice results from a change in the volume of a system produced by the action of an external pressure. In this case, the force acting may be evaluated by the product of the external pressure and the area over which it acts. The displacement is conveniently evaluated as the volume change divided by the cross-sectional area. Therefore, the work done is equal to the product of the force (pA) and the displacement ($\Delta v/A$), or

$$w = (pA)(\Delta v/A) = p\Delta v \quad (1-2)$$

where p is a *constant* pressure acting during the volume change Δv .

If the volume change is carried out in several stages for which there is a constant discrete acting pressure for each stage, the total work done is the sum of the $p\Delta v$ products for all stages.

$$w = \sum p_i \Delta v_i \quad (1-3)$$

If the acting pressure varies continuously during the volume change, the work done is given by the integral

$$w = \int_{v_1}^{v_2} p \, dv \quad (1-4)$$

The evaluation of the integral requires a known relation between the acting external pressure and the volume of the system at all points during the process.

Work, like heat, is a form of energy in transit, and its evaluation depends upon the particular mechanism by which it is transferred. For example, work is performed by the isothermal expansion of one mole of an ideal gas from ten atm to one atm. However, the exact amount of work produced depends upon the particular path followed during the expansion, as illustrated in Example 1-1.

Example 1-1

Determine the amount of work performed by the isothermal expansion of 1 mole of an ideal gas from 10 atm to 1 atm along each of the following paths.

Path (a). The gas is allowed to expand in one step from 10 atm to 1 atm against a constant external pressure of 1 atm.

Path (b). The expansion is carried out in two steps. In the first step, the gas is expanded from 10 atm to 5 atm against a constant external resisting pressure of 5 atm. In the second step, the gas is expanded from 5 atm to 1 atm against a constant external pressure of 1 atm.

Path (c). The expansion is carried out in three steps. In the first step, the gas is expanded from 10 to 5 atm against a constant external pressure of 5 atm; in the second step, it is expanded from 5 to 2 atm against a constant external pressure of 2 atm. In the third step, the gas is expanded from 2 atm to 1 atm against a constant external pressure of 1 atm.

Path (d). The expansion is carried out in nine steps by progressively reducing the external pressure in increments of 1 atm.

Path (e). The expansion is carried out in an infinite number of steps by allowing the external pressure to become only infinitesimally smaller than the internal pressure in each successive step.

The expansion done in each step is calculated as the product of the constant external pressure and the volume change. In this example, the external pressure is always the final pressure of a given expansion step. For this case, the work done is given by Eq. (1-2).

$$w = p_2 \Delta v$$

For 1 mole of an ideal gas

$$\Delta v = RT/p_2 - RT/p_1 = -RT(p_2 - p_1)/p_2 p_1$$

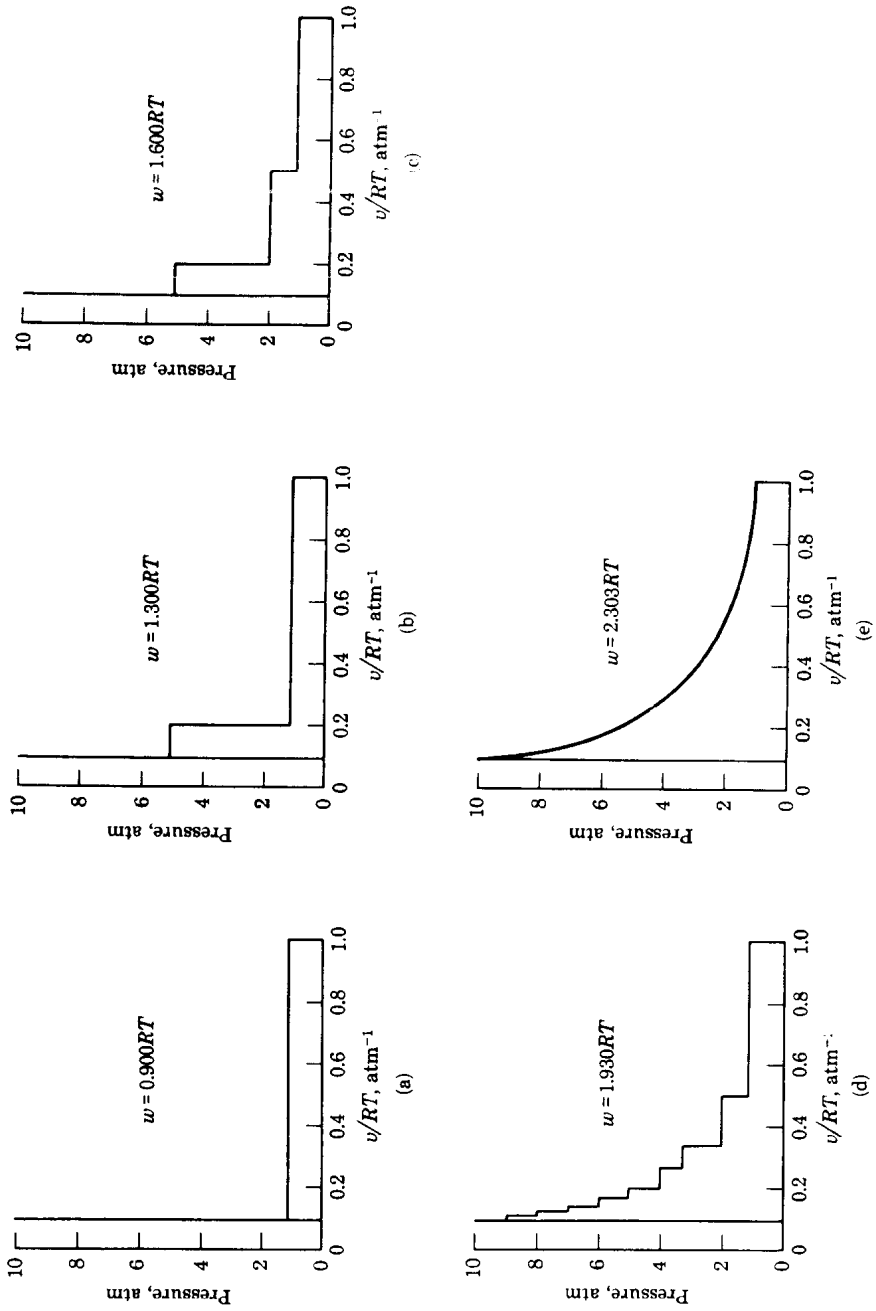


Fig. 1-1 Isothermal Expansion Work for an Ideal Gas

where p_2 and p_1 represent the final and initial pressures in the cylinder respectively. The work performed per step is then

$$w = -RT(p_2 - p_1)/p_1 = -RT\Delta p/p_1$$

and the total work for each path is

$$w = -RT \sum \Delta p/p_i$$

The calculations for the work done in each step of the different paths are summarized below. The results are shown graphically in Figs. 1-1a through 1-1e.

<i>Path</i>	p_1	p_2	w/RT
a	10	1	0.900
b	10	5	0.500
	5	1	0.800
			1.300
c	10	5	0.500
	5	2	0.600
	2	1	0.500
			1.600
d	10	9	0.100
	9	8	0.111
	8	7	0.125
	7	6	0.143
	6	5	0.167
	5	4	0.200
	4	3	0.250
	3	2	0.334
	2	1	0.500
			1.930
e	In the limit as the Δp per step approaches zero, the total work done approaches		
	$-RT \int_{p_2}^{p_1} dp/p$		
	$= RT \ln(p_1/p_2)$		
	$= RT \ln(10)$		
	$= 2.303RT$		

In Path (a) the work obtained is $0.900RT$. In Path (b) the work obtained is $1.300RT$. In Path (c) the work obtained is $1.600RT$. If the expansion is carried out in nine steps as in Path (d), the work obtained is $1.930RT$. Evidently the amount of work obtained increases as the number of steps increases. In the limit of an infinite number of steps, the external pressure is essentially equal to the internal pressure at all times and the internal pressure may be substituted for the external pressure in the integral. Under these conditions, the amount of work obtained is $2.303RT$. This represents the maximum amount of work obtainable from the isothermal expansion of 1 mole of an ideal gas from 10 atm to 1 atm.

The essential conditions for obtaining the maximum work from a system require that the driving force and the resisting force be essentially balanced at all times. Such a process is referred to as an "equilibrium" or "reversible" process since only an infinitesimal change in either the driving or the resisting force will cause the process to reverse its direction. Such a process represents a limiting condition which can be approached but never reached in actual practice. It serves as a standard or reference process with which the performance of actual processes may be compared.

1-5. Energy Balances

The application of the energy conservation law to a specific system is referred to as an "energy balance" and is merely an accounting of the energy which enters, leaves and accumulates within the system during a particular process. In engineering practice, the two types of processes most frequently encountered are the "batch" process and the "steady-state flow" process. A batch process is one in which no material is added to or removed from the system during the process. A steady-state flow process is one in which material is introduced into the system at a constant mass rate and removed at the same mass rate; there is no accumulation of mass within the system during the process.

In a batch process, energy may be added to or removed from the system in either of two ways; namely, as heat or as work. If Q designates the net heat added to a system, w the net work done by the system, and ΔE the net increase in internal energy, an energy balance for a batch process may be represented by the relation

$$Q = w + \Delta E \quad (1-5)$$

Although heat and work are forms of energy in transit and consequently are functions of the particular path or mechanism of transfer, the difference between Q and w is completely fixed by the initial and final states of the system and is independent of any intermediate stages of processes involved.

In the steady-state flow process, two additional types of energy change are involved owing to possible changes in velocity and elevation of the material as it passes through the system. The change in kinetic energy between the inlet and outlet of the system is represented by

$$m(u_2^2 - u_1^2)/2g_c$$

where m is the mass of material passing through the system per unit time, u is its linear velocity and g_c is a dimensional constant to convert from mass to force dimensions. The change in potential energy owing to any change in elevation between inlet and outlet is represented by

$$m(z_2 - z_1)g/g_c$$

where z represents the elevation with respect to a reference plane of equipotential energy, and g is the local acceleration of gravity.

In addition, a distinction is usually made between the mechanical or shaft work transferred across the boundaries of the system and the work done on the system by the fluid as it enters and leaves at the system boundaries. In this case, the total work done by a unit mass of fluid passing through the system would be

$$w_{\text{total}} = w_s + p_2v_2 - p_1v_1 \quad (1-6)$$

where w_s represents mechanical or shaft work transferred across the system boundaries by some mechanical device such as a pump or turbine, p_2v_2 is the work performed by the system when a unit mass leaves, and p_1v_1 is the work performed upon the system when the unit mass enters; p represents the pressure on the fluid and v the volume of a unit mass. The pv term is sometimes referred to as "flow work".

A complete energy balance for a steady-state flow process based on a unit mass of fluid per unit time is then represented by the equation

$$Q = w_s + \Delta(pv) + \Delta E + \Delta(u^2/2g_c) + \Delta zg/g_c \quad (1-7)$$

In this equation, the summation of ΔE and $\Delta(pv)$ appears. Quite frequently this summation can be evaluated directly without calculating either ΔE or $\Delta(pv)$ individually. For this reason, the summation has been labeled the "change in enthalpy", defined by the equation

$$\Delta H = \Delta E + \Delta(pv) \quad (1-8)$$

In terms of the enthalpy change, the total energy balance per unit mass of fluid for a steady-state flow process becomes

$$Q = w_s + \Delta H + \Delta(u^2/2g_c) + \Delta zg/g_c \quad (1-9)$$

1-6. Bernoulli Equation

If attention is focused on a unit mass of material passing through a steady-state flow process, an energy balance for the unit mass is given by Eq. (1-5). If all processes occurring in the steady-state process were reversible, the work done on the unit mass could be evaluated in terms of the system pressure according to Eq. (1-4).

$$w_{rev} = \int p \, dv \quad (1-10)$$

Since the work is not actually performed along a reversible path, the amount of work done will be reduced by a quantity F representing energy dissipated as friction. The energy balance for the unit mass may then be written in the form

$$Q - \Delta E = w = \int p \, dv - F$$

Substituting for $(Q - \Delta E)$ in Eq. (1-7),

$$\int p \, dv = w_s + \Delta(pv) + \Delta(u^2/2g_c) + \Delta z(g/g_c) + F \quad (1-11)$$

Through the use of the mathematical relation

$$\Delta(pv) = \int p \, dv + \int v \, dp$$

Eq. (1-11) may be written in the form

$$-\int v \, dp = w_s + \Delta(u^2/2g_c) + \Delta z(g/g_c) + F \quad (1-12)$$

Eq. (1-12) is the conventional form of the Bernoulli equation for a steady-state flow system.

An evaluation of the energy dissipated as friction requires a detailed knowledge of the process mechanism and lies beyond the scope of thermodynamics. A thermodynamic analysis is primarily concerned with the maximum shaft work done by a process. The maximum shaft work is obtained in a reversible process for which F is zero. In cases where the kinetic and potential energy changes are negligible, Eq. (1-12) reduces to the following expression for the maximum or reversible shaft work.

$$w_s = -\int v \, dp \quad (1-13)$$

1-7. Energy Changes in Single-Phase Systems of Constant Composition

(a) *Constant-Volume Process.* The change in the internal energy of a mass is most conveniently evaluated in the terms of the constant-volume heat capacity defined by Eq. (1-1). Therefore, for a constant-volume process

$$\Delta E = \int C_v \, dT \quad (1-14)$$

The work done during a constant-volume batch process is zero because there are no displacements involved. Therefore, the heat added during a constant-volume process may be related to the change in internal energy by combining Eqs. (1-5) and (1-14).

$$Q = \Delta E = \int C_v dT \quad (1-15)$$

Since $\Delta(pv)$ is equal to $v\Delta p$ for a constant-volume process, the change in enthalpy may be evaluated by combining Eqs. (1-8) and (1-14).

$$\Delta H = \int C_v dT + v\Delta p \quad (1-16)$$

For liquids and solids undergoing only moderate pressure changes, the $v\Delta p$ term is usually negligible relative to the change in internal energy and

$$\Delta H \simeq \Delta E \quad (1-17)$$

For one mole of an ideal gas however, $v\Delta p$ is equal to $R\Delta T$ in a constant-volume process and

$$\Delta H = \int C_v dT + \int R dT = \int (C_v + R) dT = \int C_p dT \quad (1-18)$$

(b) *Constant-Pressure Process.* For a constant-pressure process, the change in enthalpy is most conveniently evaluated from the constant-pressure heat capacity. By definition,

$$C_p = (\partial H / \partial T)_p \quad (1-19)$$

Therefore, for a constant-pressure process,

$$\Delta H = \int C_p dT \quad (1-20)$$

Since both the work done in a constant-pressure batch process and $\Delta(pv)$ are equal to $p\Delta v$, the heat added may be related to the change in enthalpy by combining Eqs. (1-5), (1-8), and (1-20).

$$Q = \Delta E + p\Delta v = \Delta H = \int C_p dT \quad (1-21)$$

Since the volumetric thermal expansion of liquids and solids is quite small, the term $p\Delta v$ is usually negligible relative to ΔE so that

$$Q = \Delta H \simeq \Delta E \quad (1-22)$$

For 1 mole of an ideal gas, $p\Delta v$ is equal to $R\Delta T$ in a constant-pressure process, and

$$Q = \Delta H = \Delta E + R\Delta T \quad (1-23)$$

The combination of Eqs. (1-20) and (1-23) yields

$$Q = \int C_p dT = \Delta E + \int R dT \quad (1-24)$$

from which

$$\Delta E = \int (C_p - R) dT = \int C_v dT \quad (1-25)$$