

# ENGINEERING THERMODYNAMICS

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by

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## PREFACE

The basic concepts of thermodynamics are sufficiently broad in scope to cover a wide range of applications in physics, chemistry, and engineering. As a result, many diverse points of view have developed which quite naturally are related to the particular application under consideration. Nevertheless, it should be possible at the introductory level to concentrate on the basic concepts and to introduce such applications as those relating to conversion of thermal energy into work, heat, and mass transfer processes and chemical reaction systems as specific examples.

This book is designed to serve as an introductory text on the basic principles of thermodynamics with elementary applications in the several fields of engineering. Since the laws of thermodynamics are based upon direct experimental observation of bulk properties, they are empirical in nature. Although applications based on these laws can be formulated in concise, quantitative mathematical terms, thermodynamic quantities such as temperature, pressure, energy and entropy cannot be interpreted physically without reference to an acceptable theory on the structure of matter.

The use of a structural theory of matter to interpret thermodynamic quantities does not in itself negate or detract from the empirical development of thermodynamic relations. Any derived relations based on a structural model of matter which may be identified with empirical thermodynamic relations serves only to support the assumed structural model. However, an interpretation of the thermodynamic quantities in terms of the structural theory can be significant and revealing.

The situation is analogous to observing the time of sunrise daily over a period of several years at several locations on the surface of the earth. The empirical data could be correlated and the time of sunrise expressed as a mathematical function of the day of the year, latitude, longitude, and elevation. Such a correlation would be useful in a number of applications, but it would provide no information on the nature of the system which produced the observable data. The correlation could be interpreted only with reference to a physical model of the solar system. On the basis of a correct model, an equation could be derived which would predict the time of sunrise on a given day at a specific location. If such a prediction corresponded with the empirical correlation, it would serve to confirm the assumed model of the solar system and could be used to interpret the empirical data.

Within the framework of this philosophy, the elementary concepts of quantum and statistical mechanics are introduced to interpret the empirical properties of classical thermodynamics. The quantum concept of energy levels is used to interpret the internal energy function. Statistical theories are used to indicate that the thermodynamic energy and entropy are average or statistical properties of a bulk system. This approach supplies a significant insight into the Second Law concepts plus a solid foundation for the Third Law and an absolute entropy scale. Methods of numerical evaluation of the heat capacity and absolute entropy of ideal gases are also presented. Numerical values of absolute entropy are essential for analysis of chemical reaction systems. Once these basic concepts have been considered, the engineering applications are carried out in terms of the conventional thermodynamic relations.

The book is divided into two major sections. Chapters 1 through 6 treat the basic concepts and interpretations with evaluations and applications to pure component or constant composition systems. These chapters include the bulk of material which should be common to all fields of engineering. Chapters 7 through 10 introduce the composition variable and consider applications to phase and chemical equilibrium systems. In order to maintain the treatment at an elementary level, the subject matter has been limited in scope and many specialized applications have been purposely omitted.

Although the material presented is neither new nor unique, it is felt that the organization provides a continuous train of thought from fundamental concepts to applications which is not found in existing texts. Chapter 1 provides an early introduction to thermodynamic reasoning and calculations based only on the conservation laws of mass and energy. The material in Chapter 2 is considered as reference material where expressions for quantized energy levels are derived in sufficient detail to make clear the reasoning and assumptions involved as well as the mathematical manipulation. Although a background in differential equations is necessary for a detailed study of the mathematical development, the results obtained may be applied without reference to the derivations. A thorough appreciation of the statistical distributions developed in Chapter 3 is essential to the concept of the internal energy and entropy functions. The Maxwell-Boltzmann distribution in particular provides the basis for the statistical evaluation of the thermodynamic properties. Chapter 4 considers the application of the statistical concepts to the evaluation of thermodynamic properties with numerical calculations for the ideal gas system. In Chapter 5 methods are presented for the evaluation of changes in the thermodynamic properties of non-ideal fluids through the use of empirical  $pVT$  data and equations of state.

The discussion of the Second Law of Thermodynamics in Chapter 6 is based directly on the statistical concepts introduced in Chapters 3 and 4. Since

the entropy function has already been identified as a point function, the analyses of reversible heat engine cycles and irreversible processes follow as natural applications of the basic principles.

The elementary properties of solutions are introduced in Chapter 7, and the criteria of equilibrium are established in Chapter 8. Applications to phase and chemical equilibrium systems involving changes in the composition variable are considered in Chapters 9 and 10.

In attempting to cover numerical applications in several diverse fields, the problem of units arises. There is at present no consistent set of units which is common to all applications. However, the conversion of units from one system to another is confusing, wasteful of time and energy, and fundamentally unnecessary. Therefore, conversion of units is minimized in this text by adopting a consistent set of units for a given problem. The choice of units is usually dictated by the data available. In the majority of cases, the metric system is preferred, with energy expressed in units of calories, mass in grams, and temperature in degrees Kelvin (or centigrade). Wherever the English system appears desirable, energy is expressed in units of Btu, mass in pounds, and temperature in degrees Rankine (or Fahrenheit). Conversion between the two systems is rarely necessary. Fortunately, a number having units of cal/(gram mole) ( $^{\circ}\text{K}$ ) has the same numerical value in Btu/(lb mole) ( $^{\circ}\text{R}$ ). Therefore, the heat capacity and entropy functions have the same numerical value in both systems.

The author wishes to express his appreciation to his colleagues Professors Wilbur H. Parks and Arlie E. Paige for their interest, encouragement and suggestions made during the preparation of the material; to the several classes of students covering different branches of engineering who involuntarily served as guinea pigs and either knowingly or unknowingly assisted immeasurably in the text organization; and finally to his wife for her faithful cooperation and untiring efforts in the preparation of the manuscript.

M. T. HOWERTON

# CONTENTS

CHAPTER	PAGE
PREFACE	vii
1 THE FIRST LAW OF THERMODYNAMICS	
1-1. THE CONSERVATION LAWS OF MASS AND ENERGY	2
1-2. INTERNAL ENERGY	3
1-3. HEAT	6
1-4. WORK	6
1-5. ENERGY BALANCES	10
1-6. BERNOULLI EQUATION	12
1-7. ENERGY CHANGES IN SINGLE-PHASE SYSTEMS OF CONSTANT COMPOSITION	12
1-8. VARIATION OF HEAT CAPACITY WITH TEMPERATURE	20
1-9. ENERGY CHANGES IN A SINGLE-PHASE, STEADY-STATE FLOW SYSTEM OF CONSTANT COMPOSITION	24
1-10. ENERGY CHANGES IN PHASE TRANSITION	30
1-11. ENERGY CHANGES IN CHEMICAL REACTIONS	33
NOMENCLATURE	38
PROBLEMS	38
2 INTERNAL ENERGY LEVELS	41
2-1. INTERNAL ENERGY	41
2-2. THE QUANTUM THEORY	42
2-3. WAVE PROPAGATION THROUGH AN ELASTIC MEDIUM	43
2-4. WAVE EQUATION FOR ATOMIC SYSTEMS	45
2-5. TRANSLATIONAL ENERGY OF THE FREE PARTICLE	48
2-6. TRANSLATIONAL ENERGY LEVELS OF A PARTICLE IN A BOX	48
2-7. ENERGY LEVELS OF A RIGID ROTATOR	50
2-8. ENERGY LEVELS OF THE HARMONIC OSCILLATOR	54
NOMENCLATURE	60
PROBLEMS	62

3	STATISTICAL DISTRIBUTIONS	63
3-1.	ONE PARTICLE SITE PER ENERGY LEVEL	64
3-2.	SEVERAL PARTICLE SITES PER ENERGY LEVEL	65
3-3.	BOLTZMANN DISTRIBUTION	69
3-4.	FERMI-DIRAC DISTRIBUTION	71
3-5.	BOSE-EINSTEIN DISTRIBUTION	72
3-6.	BOLTZMANN DISTRIBUTION AS AN APPROXIMATION FOR INDISTINGUISHABLE PARTICLES	75
3-7.	EVALUATION OF $\lambda$	76
3-8.	TRANSLATIONAL PARTITION FUNCTION	76
3-9.	DEGENERACY OF TRANSLATIONAL ENERGY LEVELS	77
3-10.	EVALUATION OF $\mu$	78
3-11.	PARTITION FUNCTION FOR A RIGID ROTATOR	80
3-12.	PARTITION FUNCTION FOR HARMONIC OSCILLATOR	81
	NOMENCLATURE	87
	PROBLEMS	88
4	STATISTICAL EVALUATION OF THERMODYNAMIC FUNCTIONS	89
4-1.	INTERNAL ENERGY	89
4-2.	HEAT CAPACITY	93
4-3.	NUMBER OF ARRANGEMENTS FOR THE MOST PROBABLE DISTRIBUTION	102
4-4.	ENERGY CHANGES IN A CLOSED SINGLE-PHASE SYSTEM OF FIXED COMPOSITION	104
4-5.	HEAT	106
4-6.	WORK	106
4-7.	ENTROPY	106
4-8.	ENTHALPY	120
4-9.	THE FREE-ENERGY FUNCTIONS	120
	NOMENCLATURE	122
	PROBLEMS	123
5	EMPIRICAL EVALUATION OF THERMODYNAMIC FUNCTIONS	124
5-1.	THE PHASE RULE	124
5-2.	DERIVATION OF DIFFERENTIAL EQUATIONS	124

5-3.	INTEGRATION OF FIRST-ORDER PARTIAL DIFFERENTIAL EQUATIONS	130
5-4.	EXPERIMENTAL $PVT$ DATA	132
5-5.	ALGEBRAIC EQUATIONS OF STATE	137
5-6.	GENERALIZED COMPRESSIBILITY FACTORS	142
5-7.	THERMODYNAMIC CHARTS AND TABLES	158
	NOMENCLATURE	166
	PROBLEMS	166
6	THE SECOND LAW OF THERMODYNAMICS	168
6-1.	THE SECOND LAW OF THERMODYNAMICS	168
6-2.	SPONTANEOUS TRANSFER OF HEAT	169
6-3.	SPONTANEOUS EXPANSION OF FLUIDS	170
6-4.	SPONTANEOUS IRREVERSIBLE MIXING OF TWO IDEAL GASES	172
6-5.	REVERSIBILITY	173
6-6.	CONVERSION OF THERMAL ENERGY INTO WORK	174
6-7.	REVERSIBLE HEAT-ENGINE CYCLES	176
6-8.	AVAILABILITY	179
6-9.	UNAVAILABLE ENERGY	181
6-10.	THERMODYNAMIC ANALYSIS OF PROCESSES	185
	NOMENCLATURE	188
	PROBLEMS	188
7	THERMODYNAMIC PROPERTIES OF SOLUTIONS	190
7-1.	SINGLE-PHASE SOLUTIONS OF VARIABLE COMPOSITION	190
7-2.	PARTIAL MOLAL QUANTITIES	191
7-3.	EFFECT OF COMPOSITION ON PARTIAL MOLAL QUANTITIES	192
7-4.	THE CHEMICAL POTENTIALS	195
7-5.	EVALUATION OF PARTIAL MOLAL QUANTITIES	198
	NOMENCLATURE	210
	PROBLEMS	210
8	CRITERION OF EQUILIBRIUM	211
8-1.	GENERAL CRITERION OF EQUILIBRIUM	211
8-2.	CRITERION OF THERMAL EQUILIBRIUM	212
8-3.	CRITERION OF PHASE EQUILIBRIUM	213



8-4.	CRITERION OF PHASE EQUILIBRIUM IN TERMS OF THE PARTITION FUNCTION	214
8-5.	CRITERION OF EQUILIBRIUM IN TERMS OF THE HELMHOLTZ FREE ENERGY	215
8-6.	CRITERION OF PHASE EQUILIBRIUM IN TERMS OF THE CHEMICAL POTENTIAL	216
8-7.	CRITERION OF PHASE EQUILIBRIUM IN TERMS OF FUGACITY	216
8-8.	CRITERION OF CHEMICAL EQUILIBRIUM	222
8-9.	EVALUATION OF THE FUGACITY	222
8-10.	EVALUATION OF THE ACTIVITY COEFFICIENT	233
8-11.	EFFECT OF TEMPERATURE ON THE FUGACITY AND THE ACTIVITY COEFFICIENT	237
	NOMENCLATURE	238
	PROBLEMS	239
9	PHASE EQUILIBRIUM	240
9-1.	SOLID-VAPOR EQUILIBRIUM OF A PURE COMPONENT	240
9-2.	VAPOR-PHASE ADSORPTION ON SOLID SURFACES	244
9-3.	VAPOR-LIQUID EQUILIBRIUM FOR PURE COMPONENTS	248
9-4.	VAPOR-LIQUID EQUILIBRIUM IN MIXTURES	249
	NOMENCLATURE	268
	PROBLEMS	269
10	CHEMICAL EQUILIBRIUM	270
10-1.	EVALUATION OF THE CHEMICAL EQUILIBRIUM CONSTANT	271
10-2.	DETERMINATION OF EQUILIBRIUM COMPOSITION	275
10-3.	SIMULTANEOUS REACTIONS	282
10-4.	ADIABATIC REACTION TEMPERATURE	289
	NOMENCLATURE	295
	PROBLEMS	296
	BIBLIOGRAPHY	296
	APPENDIX	299
	INDEX	311

# *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  $2.6 \times 10^{-8}$  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  $\Delta v$ .

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

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



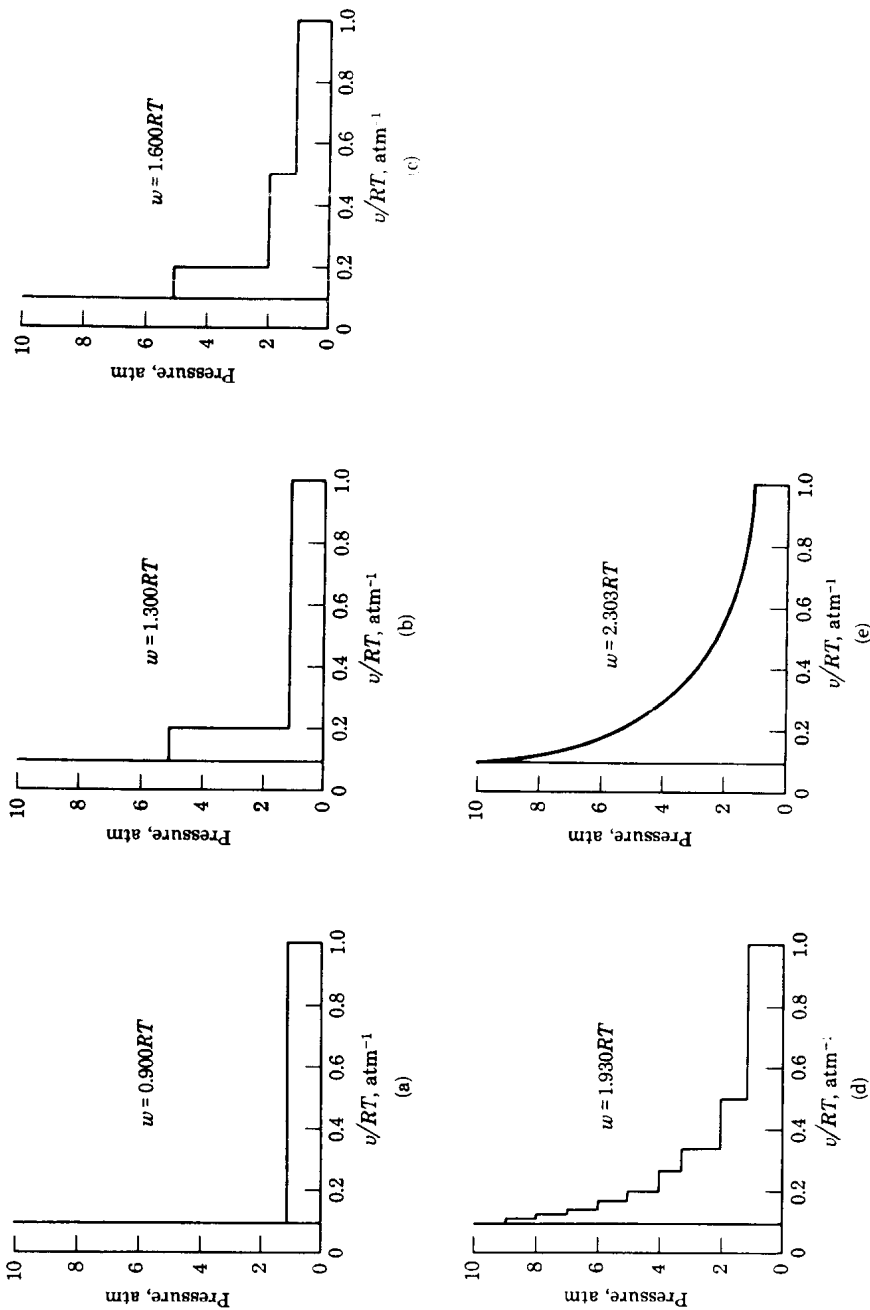


Fig. 1-1 Isothermal Expansion Work for an Ideal Gas