CHAPTER II

THE FIRST PRINCIPLE OF THERMODYNAMICS

2.1. Internal Energy

Let us consider a system which undergoes a change while contained in an adiabatic enclosure. This change may be brought about by different processes. For instance, we may increase the temperature T_1 of a given mass of water to a temperature $T_2 > T_1$ by causing some paddles to rotate in the water, or by letting electrical current pass through a wire immersed in the water. In both cases external forces have performed a certain amount of work upon the system.

Experience shows that the work done by external forces adiabatically on the system A_{ad} (that is, the system being enclosed in adiabatic walls) in order to bring about a certain change in its state is independent of the path. In other words, A_{ad} has the same value for every (adiabatic) process causing the same change, and it depends only on the initial and final states of the system. A_{ad} can therefore be expressed by the difference in a state function:

$$A_{\text{ad}} = \Delta U \tag{1}$$

and this function U is called the *internal energy* of the system. It follows that for a cycle, $A_{\text{ad}}=0$, and that for an infinitesimal process $\delta A_{\text{ad}} = \mathrm{d}U$ is an exact differential, which can be expressed by

$$\mathrm{d}U = \left(\frac{\partial U}{\partial X}\right)_Y \mathrm{d}X + \left(\frac{\partial U}{\partial Y}\right)_X \mathrm{d}Y \tag{2}$$

as a function of whatever independent variables X, Y are chosen.

The internal energy is defined by (1) except for an arbitrary constant that may be fixed by choosing a reference state. This indetermination is not important, because Thermodynamics only considers the variations in U rather than its absolute value. However, in order to have a unique constant, it is necessary that any state may in principle be related to the same reference state through an adiabatic process. This can always be done. As an example, let us consider an ideal gas. Let E_0 be the chosen reference state, plotted on a p, V diagram (Figure II-1); C is the curve describing the states that may be reached from E_0 by adiabatic expansion or compression. Let us consider any state E_1 of the plane pV at the right of C. E_1 can be reached from E_0 by an infinite number of adiabatic paths; for instance, if the gas is held in an adiabatic container of variable volume (such as an insulating cylinder with a frictionless piston), it can be made to follow the path E_0E' at V=const., and then $E'E_1$ at p=const.,

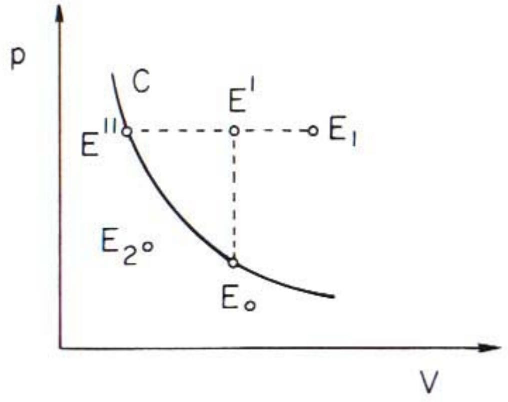

Fig. II-1. Reference state and adiabatic paths.

by having an electric current flow through an inserted resistance while the piston is first held at a fixed position and then left mobile with a constant pressure upon it. Or else it can be made to follow the path E_0E'' by increasing the pressure (with infinite slowness) and the $E''E_1$ at $p=$const. (as before for the path $E'E_1$).

The points of the plane pV at the left of C, such as E_2, cannot be reached adiabatically from E_0; it can be shown that this would be against the Second Principle. But these points can be related to E_0 be inverting the sense of the process (i.e., reaching E_0 from E_2).

Thus we can fix the arbitrary constant by choosing a single reference state, and relating all other states of the system to that one, for which we set $U=0$ (Figure II-2).

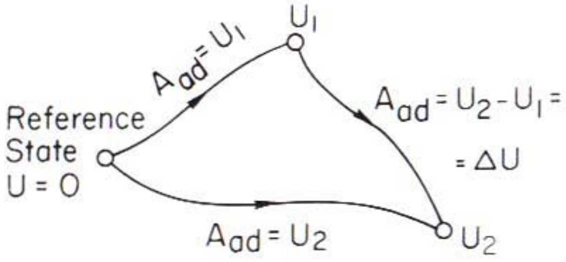

Fig. II-2. Reference state for internal energy.

2.2. Heat

If we now consider a non-adiabatic process causing the same change, we shall find that the work performed on the system will not be the same:

$$A \neq A_{\mathrm{ad}}. \tag{3}$$

We define the *heat* Q absorbed by the system as the difference

$$Q = \Delta U - A. \tag{4}$$

Or, for an infinitesimal process:

$$\delta Q = \mathrm{d}U - \delta A\,. \tag{5}$$

In the adiabatic case, $\delta Q = 0$ by definition.

U is a property of the system, and $\mathrm{d}U$ is an exact differential. Neither δA nor δQ are exact differentials, and neither A nor Q are *properties* of the system. In view of the importance of this basic distinction, we shall make at this stage a digression, in order to bring in a short review of related mathematical concepts.

Let δz be a differential expression of the type

$$\delta z = M\,\mathrm{d}x + N\,\mathrm{d}y \tag{6}$$

where x and y are independent variables, and M and N are coefficients which in general will be functions of x and y. If we want to integrate Equation (6), we shall have the expressions

$$\int M(x, y)\,\mathrm{d}x, \qquad \int N(x, y)\,\mathrm{d}y$$

which are meaningless unless a relation $f(x, y) = 0$ is known. Such a relation prescribes a path in the x, y plane, along which the integration must be performed. This is called a *line integral*, and its result will depend on the given path.

It may be, as a particular case, that

$$M = \frac{\partial z}{\partial x}, \qquad N = \frac{\partial z}{\partial y}\,. \tag{7}$$

We then have

$$\delta z = \frac{\partial z}{\partial x}\,\mathrm{d}x + \frac{\partial z}{\partial y}\,\mathrm{d}y = \mathrm{d}z \tag{8}$$

and δz is therefore an *exact* or *total differential*, which we write $\mathrm{d}z$. In this case, the integration will give

$$\int_1^2 \delta z = z(x_2, y_2) - z(x_1, y_1) = \Delta z \tag{9}$$

or else

$$z = z(x, y) + C \tag{10}$$

where C is an integration constant. z is then a *point function* which depends only on the pair of values (x, y), except for an additive constant. When the integral (9) is taken along a closed curve in the plane x, y, so that it starts and ends at the same point (runs over a cycle), Equation (9) takes the form

$$\oint \delta z = 0\,. \tag{11}$$

In order to check if a given expression (6) obeys condition (7), it would be necessary to know the function z. It may be easier to apply the theorem of the crossed derivatives

$$\frac{\partial^2 z}{\partial y\, \partial x} = \frac{\partial^2 z}{\partial x\, \partial y} \tag{12}$$

(assuming continuity for z and its first derivatives). That is:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}. \tag{13}$$

Equation (13) is therefore a necessary condition for Equation (7) to hold. It is also sufficient for the existence of a function that obeys it, because we can always find the function

$$z = \int M \,\mathrm{d}x + \int N \,\mathrm{d}y - \iint \frac{\partial M}{\partial y} \,\mathrm{d}x \,\mathrm{d}y + \text{const.} \tag{14}$$

which, with Equation (13), satisfies Equations (7).

Therefore, Equations (7), (9), (10), (11) and (13) are equivalent conditions that define z as a point function.

If δz is not an exact differential, a factor λ may be found (always in the case of only two independent variables) such that $\lambda \delta z = \mathrm{d}u$ is an exact differential. λ is called an *integrating factor*.*

The importance that these concepts have for Thermodynamics lies in that state functions like the internal energy are, by their definition, point functions of the state variables. The five conditions above mentioned for z to be a point function find therefore frequent application to thermodynamic functions.

On the other hand, as mentioned before, δA and δQ are not exact differentials.

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* These concepts may perhaps become clearer through an elementary example. Let

$$\delta z = 2y \,\mathrm{d}x + x \,\mathrm{d}y$$

which we want to integrate between $x = 0$, $y = 0$ and $x = 2$, $y = 2$, and let us choose two arbitrary paths (a) and (b).

(a) The path is defined by $y = x$. Then $\delta z = 3x\, dx$, which is immediately integrable between the two limits, giving $(3/2)\, x^2|_0^2 = 6$.

(b) Increase x from 0 to 2 at constant $y = 0$. The integration of δz along this step will give 0. Then increase y to 2 while keeping $x = 2$. This will give 4, which is the total change between the two points, different from the change obtained in (a).

An infinite number of other paths could be devised, with variable results. Obviously, no point function can be defined from δz.

On the other hand, δz admits an integrating factor $\lambda = x$. Thus

$$x\delta z = 2xy\, dx + x^2\, dy = d(x^2 y),$$

which is an exact differential. Its integral between the limits gives $(2^2 \times 2) - (0 \times 0) = 8$. The same result is obtained if a line integration is performed along the paths (a), (b) or any other. In this case we have a point function, which is $f(x, y) = x^2 y$.

Thus, an expression like

$$A = -\int_{\mathrm{i}}^{\mathrm{f}} p\,\mathrm{d}V \tag{15}$$

for the work of expansion, is meaningless if it is not specified how p depends on V along the process.

It is clear, from definition (5) or (4), that exchanging heat is, like performing work, a way of exchanging energy. The definition gives also the procedure for measuring heat in mechanical units. We may cause the same change in a system by an adiabatic process or by a process in which no work is performed. In the first case $\Delta U = A_{\mathrm{ad}}$, and in the second, $\Delta U = Q_{\mathrm{A}=0}$; as ΔU only depends on the initial and final states, we have $A_{\mathrm{ad}} = Q_{\mathrm{A}=0}$, which measures $Q_{\mathrm{A}=0}$ by the value of A_{ad}. This will be clearer by an example. Let our system be a mass of water, which we bring from 14.5 to 15.5°C. The first procedure will be to cause some paddles to rotate within the water (as in the classical experiment of Joule) with an appropriate mechanical transmission; A_{ad} may then be measured by the descent of some known weights. The second procedure will be to bring the water into contact with another body at a higher temperature, without performing any work; we say, according to the definition, that $Q_{\mathrm{A}=0}$ is the heat gained by our system in this case. If we refer these quantities to one gramme of water, $Q_{\mathrm{A}=0}$ is by definition equal to 1 cal, and A_{ad} will turn out to be equal to 4. 1855 J. This value is usually known as the *mechanical equivalent of heat*; it amounts to a conversion factor between two different units of energy.

The determination of Q for processes at constant volume or at constant pressure, in which no work is performed upon or by the system except the expansion term (when pressure is kept constant) has been the subject of Calorimetry. Its main experimental results can be briefly summarized as follows:

(1) If in a process at constant pressure no change of physical state and no chemical reactions occur in a homogeneous system, the heat absorbed is proportional to its mass and to the variation in temperature:

$$\delta Q_{\mathrm{p}} = c_{\mathrm{p}} m\,\mathrm{d}T \tag{16}$$

where the subindex p indicates that the pressure is kept constant, and the proportionality factor c_{p} is called the *specific heat capacity* (at constant pressure). The product $c_{\mathrm{p}}m$ is called the *heat capacity* of the system.

Similarly, at constant volume:

$$\delta Q_{\mathrm{v}} = c_{\mathrm{v}} m\,\mathrm{d}T. \tag{17}$$

(2) If the effect of the absorption of heat at constant pressure is a change of physical state, which also occurs at constant temperature, Q is proportional to the mass that undergoes the change:

$$\delta Q = l\,\mathrm{d}m. \tag{18}$$

The proportionality factor l is called the *latent heat* of the change of state.

(3) If the effect of the absorption of heat, either at constant pressure or at constant volume, is a chemical reaction, Q is proportional to the mass of reactant that has reacted and the proportionality factor is called the *heat of reaction* (referred to the number of moles indicated by the chemical equation) at *constant pressure*, or at *constant volume*, according to the conditions in which the reaction is performed. Heats of reaction have a sign opposite to that of the previous convention, i.e. they are positive if the heat is evolved (lost by the system). We will not be concerned with chemical reactions or their thermal effects.

The specific heat capacity and the latent heat may be referred to the mole instead of to the gramme. They are then called the *molar heat capacities* (or simply *heat capacities*) (at constant pressure C_p and at constant volume C_v) and the *molar heat* L of the change of state considered. In this case, formulas (16)–(18) become

$$\delta Q_p = C_p n \, dT \tag{16'}$$

$$\delta Q_v = C_v n \, dT \tag{17'}$$

$$\delta Q = L \, dn \tag{18'}$$

2.3. The First Principle. Enthalpy

The equation

$$dU = \delta A + \delta Q \tag{19}$$

is the mathematical expression of the First Principle of Thermodynamics.* When applied to an isolated system ($dU = 0$), it states the principle of conservation of energy.

We have used the 'egotistical convention' in defining A as the work performed on the system. It is also customary to represent the work done by the system on its surroundings by W. Obviously, $A = -W$.

In the atmosphere we shall only be concerned with one type of work: that of expansion. Therefore

$$\delta A = -p \, dV . \tag{20}$$

It is convenient to define another state function, besides U: the *enthalpy* H (also called *heat content* by some authors)

$$H = U + pV .$$

Introducing these relations, we shall have as equivalent expressions of the first principle:

$$dU = \delta Q - p \, dV \tag{21}$$

$$dH = \delta Q + V \, dp \tag{22}$$

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* We prefer the more appropriate denomination of '*Principles*' to that commonly used of '*Laws*'.

or their integral expressions

$$\Delta U = Q - \int p \, \mathrm{d}V \tag{23}$$

$$\Delta H = Q + \int V \, \mathrm{d}p . \tag{24}$$

The same expressions will be used with small letters when referred to the unit mass:

$$\mathrm{d}u = \delta q - p \, \mathrm{d}v \tag{25}$$

etc.

We must remark that Equation (20), and therefore Equations (21) and (22), assume the process to be quasi-static, if p is to stand for the internal pressure of the system. Otherwise, p is the external pressure exerted on the system.

2.4. Expressions of Q. Heat Capacities

Let us consider first a homogeneous system of constant composition. If we now write δQ from Equation (21) or (22), and replace the total differentials $\mathrm{d}U$, $\mathrm{d}V$, $\mathrm{d}H$ and $\mathrm{d}p$ by their expressions as functions of a chosen pair of variables, we find.

$$\text{Variables } T, V: \quad \delta Q = \left(\frac{\partial U}{\partial T}\right)_\mathrm{V} \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_\mathrm{T} + p\right] \mathrm{d}V \tag{26}$$

$$\text{Variables } T, p: \quad \delta Q = \left[\left(\frac{\partial U}{\partial T}\right)_\mathrm{p} + p\left(\frac{\partial V}{\partial T}\right)_\mathrm{p}\right] \mathrm{d}T + \left[\left(\frac{\partial U}{\partial p}\right)_\mathrm{T} + p\left(\frac{\partial V}{\partial p}\right)_\mathrm{T}\right] \mathrm{d}p \tag{27}$$

$$\text{Variables } T, p: \quad \delta Q = \left(\frac{\partial H}{\partial T}\right)_\mathrm{p} \mathrm{d}T + \left[\left(\frac{\partial H}{\partial p}\right)_\mathrm{T} - V\right] \mathrm{d}p . \tag{28}$$

Equation (27), as well as others that can be derived in a similar way, will be of no particular value to us, but it illustrates, by comparison with Equations (26) and (28), the fact that simpler expressions are obtained when the function U is associated with the independent variable V and when H is associated with p.

For a process of heating at constant volume, we find from Equation (26):

$$C_\mathrm{V} = \frac{\delta Q_\mathrm{V}}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_\mathrm{V} \tag{29}$$

or

$$c_\mathrm{v} = \left(\frac{\partial u}{\partial T}\right)_\mathrm{v} . \tag{29'}$$

And for constant pressure, from Equation (28):

$$C_p = \frac{\delta Q_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p \tag{30}$$

and

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p . \tag{30'}$$

The expressions of δQ also allow us to give values for the heat of change of volume, and of change of pressure, at constant temperature. From Equation (26):

$$\frac{\delta Q_T}{dV} = \left(\frac{\partial U}{\partial V}\right)_T + p$$

and from Equation (28):

$$\frac{\delta Q_T}{dp} = \left(\frac{\partial H}{\partial p}\right)_T - V .$$

2.5. Calculation of Internal Energy and Enthalpy

Equations (29) and (30) can be directly integrated along processes at constant volume and at constant pressure, respectively, to find U and H, if C_v and C_p are known as functions of T:

$$U = \int C_v \, dT + \text{const.} \qquad \text{(at constant volume)} \tag{31}$$

$$H = \int C_p \, dT + \text{const.} \qquad \text{(at constant pressure)} \tag{32}$$

C_v and C_p, as determined experimentally, are usually given by polynomic expressions, such as

$$C = \alpha + \beta T + \gamma T^2 + \ldots \tag{33}$$

for given ranges of temperatures.

The calculation of U and H for the general case when both T and V (or T and p) change must await consideration of the Second Principle (cf. Chapter III, Section 8).

Let us now consider two rigid containers linked by a connection provided with a stopcock. One of them contains a gas and the other is evacuated. Both are immersed in a common calorimeter. If the stopcock is opened, so that the gas expands to the total volume, it is found that the system (gas contained in both containers) has exchanged no heat with its surroundings. As there is no work performed (the total volume of the system remained constant), we have*:

$$Q = 0; \qquad A = 0; \qquad \Delta U = 0.$$

Actually this experiment, which was performed by Joule, was later improved by Joule and Thomson, who found a small heat exchange (Joule-Thomson effect). However, the effect vanishes for ideal gas behavior. In fact, if the equation of state $pV = R^*T$ is accepted as the definition of ideal gas, it may be shown, with the aid of the second principle, that this must be so**. Therefore the previous result is exact for ideal gases. As p changed during the process, we conclude that *U for an ideal gas* is only a function of T:

$$U = U(T)$$

and the partial derivatives of the previous formulas become total derivatives:

$$(34) \qquad C_V = \frac{\mathrm{d}U}{\mathrm{d}T}; \qquad c_v = \frac{\mathrm{d}u}{\mathrm{d}T}. \qquad (34')$$

Similarly, $H = U + pV = U + R^*T = H(T)$; therefore

$$(35) \qquad C_p = \frac{\mathrm{d}H}{\mathrm{d}T}; \qquad c_p = \frac{\mathrm{d}h}{\mathrm{d}T}. \qquad (35')$$

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* As the gas in the container, where it was originally confined, expands into the other, work is done by some portions of the gas against others, while their volumes are changing. These are internal transfers not to be included in A. This is an example demonstrating that systems must be defined carefully and clearly when considering a thermodynamic process; the system in this case is best defined as all the gas contained within the *two* containers (whose total volume is constant).

** It will be seen (Chapter III, Section 5) that for a reversible process

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V = T\,\mathrm{d}S - R^*T\frac{\mathrm{d}V}{V}$$

where S is the entropy. Dividing by T:

$$\frac{\mathrm{d}U}{T} = \mathrm{d}S - R^*\,\mathrm{d}\ln V.$$

$\mathrm{d}S$ is an exact differential, by the Second Law, and so is the last term. Therefore $(\mathrm{d}U/T)$ is also an exact differential, which may be written (by developing $\mathrm{d}U$):

$$\frac{\mathrm{d}U}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_p \mathrm{d}T + \frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_T \mathrm{d}p.$$

Applying to $(\mathrm{d}U/T)$ the condition of equality of crossed second derivatives

$$\frac{1}{T}\frac{\partial^2 U}{\partial p\,\partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial p}\right)_T + \frac{1}{T}\frac{\partial^2 U}{\partial T\,\partial p}$$

or

$$\left(\frac{\partial U}{\partial p}\right)_T = 0$$

and

$$U = U(T).$$

It can readily be derived that

$$C_p - C_v = R^*; \qquad c_p - c_v = R. \tag{36, 36'}$$

(36) (36′)

Heat capacities of gases can be measured directly, and the corresponding coefficients for introduction into Equation (33) can be determined experimentally in order to represent the data over certain temperature intervals. For simple gases as N_2, O_2, Ar, however, the data are nearly constant for all the ranges of temperature and pressure values in which we are interested. This agrees with the theoretical conclusions from Statistical Mechanics, which indicate the following values (*):

Monatomic gas: $C_v = \frac{3}{2}R^*; \qquad C_p = C_v + R^* = \frac{5}{2}R^*$

Diatomic gas: $C_v = \frac{5}{2}R^*; \qquad C_p = \frac{7}{2}R^*.$

We shall define the ratio coefficients

$$\varkappa = R^*/C_p = R/c_p; \qquad \eta = C_p/C_v = c_p/c_v.$$

For dry air, considered as a diatomic gas (neglecting the small proportion of Ar, CO_2, and minor components), we should expect:

$$\varkappa_d = 2/7 = 0.286; \qquad \eta_d = 7/5 = 1.400$$

$$c_{v_d} = 718\ \mathrm{J\ kg^{-1}\,K^{-1}} = 171\ \mathrm{cal\ kg^{-1}\,K^{-1}}$$

$$c_{pd} = 1005\ \mathrm{J\ kg^{-1}\,K^{-1}} = 240\ \mathrm{cal\ kg^{-1}\,K^{-1}}.$$

These values are in good agreement with experience, as can be seen from the values of c_{pd} from Table II-1.

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* According to the principle of equipartion of energy, the average molecular energy is given by

$$\bar{\varepsilon} = rkT/2$$

where r is the number of squared terms necessary to express the energy:

$$\varepsilon = \sum_1^r \tfrac{1}{2}\lambda_i \xi_i^2$$

k is Boltzmann's constant, λ_i are constants, and ξ_i are generalized coordinates or momenta. If no potential energy has to be considered, the ξ_i are all momenta and the number r is equal to the *degrees of freedom* of the molecules, as the number of generalized coordinates needed to determine their position: 3 for a monatomic gas, and two more (angular coordinates to give the orientation) for diatomic molecules; it is here assumed that the effect of vibration of the diatomic molecules may be neglected, which is true for N_2 and O_2 in the range of temperatures in which we are interested.

$$U = N_A\bar{\varepsilon} = \frac{r}{2}R^*T$$

$$C_v = \frac{dU}{dT} = \frac{r}{2}R^*$$

(N_A = Avogadro's number).

TABLE II-1

c_{p_d} in IT cal kg^{-1} K^{-1}

p(mb)	t(°C)			
	− 80	− 40	0	+ 40
0	239.4	239.5	239.8	240.2
300	239.9	239.8	239.9	240.3
700	240.4	240.1	240.1	240.4
1000	241.0	240.4	240.3	240.6

For simple ideal gases in general, and for a wide range of temperatures, the specific heats can be considered as constant, and the expressions of the internal energy and the enthalpy can be obtained by integrating Equations (34) and (35):

$$U = C_v T + a \tag{37}$$

$$H = C_p T + a\,. \tag{38}$$

Taking $H - U$, and noticing that

$$(C_p - C_v)T = R^* T = pV\,,\,.$$

it may be seen that the additive constant a, although arbitrary, must be the same for both functions.

Within this approximation, the two expressions (21) and (22) of the First Principle may be written as

$$\delta Q = C_v\,\mathrm{d}T + p\,\mathrm{d}V \tag{39}$$

and

$$\delta Q = C_p\,\mathrm{d}T - V\,\mathrm{d}p\,. \tag{40}$$

2.6. Latent Heats of Pure Substances. Kirchhoff's Equation

In general, from the expressions (21) and (22) of the First Principle, we can see that the heat absorbed by a system in a reversible process at constant volume Q_v (the subscript indicating the constancy of that variable) is measured by the change in internal energy and the heat at constant pressure Q_p by the change in enthalpy:

$$\delta Q_v = \mathrm{d}U \tag{41}$$

$$\delta Q_p = \mathrm{d}H\,. \tag{42}$$

In the case of homogeneous systems, these formulas would give $\mathrm{d}U = nC_v\,\mathrm{d}T = mc_v\,\mathrm{d}T$ and $\mathrm{d}H = nC_p\,\mathrm{d}T = mc_p\,\mathrm{d}T$ (cf. Equations (39) and (40)). However, we are now interested in changes of phase. As we shall see later, only one independent variable is left for a system made out of a pure substance, when two phases are in equilibrium. Thus if we fix the pressure or the volume, the temperature at which the change of physical state may occur reversibly is also fixed, and the specific heats need not be considered in these processes.

The latent heats are defined for changes at constant pressure. Therefore, in general

$$L = \Delta H \tag{43}$$

or

$$l = \Delta h\,. \tag{43$'$}$$

In particular L may be L_f, L_v, L_s = molar heats of fusion, vaporization, sublimation. Similarly l can be any of the latent heats l_f, l_v, l_s.

It is of interest to know how L varies with temperature. We may write

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_\mathrm{p} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_\mathrm{T} \mathrm{d}p \tag{44}$$

for two states, a and b, such that $\Delta H = L = H_\mathrm{b} - H_\mathrm{a}$. Taking the difference of both exact differentials, we have

$$\mathrm{d}(\Delta H) = \left(\frac{\partial \Delta H}{\partial T}\right)_\mathrm{p} \mathrm{d}T + \left(\frac{\partial \Delta H}{\partial p}\right)_\mathrm{T} \mathrm{d}p\,. \tag{45}$$

If we now assume that p is maintained constant, only the first term on the right is left, and we have

$$\mathrm{d}(\Delta H)_\mathrm{p} = \mathrm{d}L = \left(\frac{\partial \Delta H}{\partial T}\right)_\mathrm{p} \mathrm{d}T = \left(\frac{\partial H_\mathrm{b}}{\partial T}\right)_\mathrm{p} \mathrm{d}T - \left(\frac{\partial H_\mathrm{a}}{\partial T}\right)_\mathrm{p} \mathrm{d}T = (C_{\mathrm{p_b}} - C_{\mathrm{p_a}})\,\mathrm{d}T$$

or

$$(\partial L/\partial T)_\mathrm{p} = \Delta C_\mathrm{p}\,. \tag{46}$$

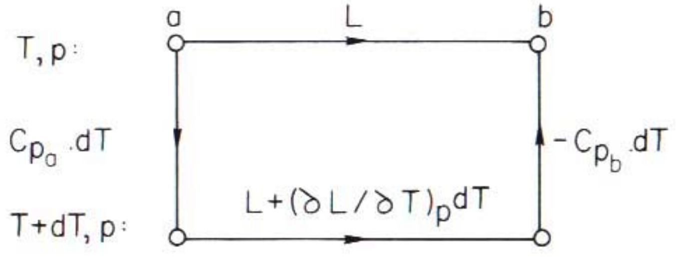
This is called Kirchhoff's equation. If the heat capacities are known as empirical functions of the temperature expressed as in Equation (33), L can be integrated in the same range as

$$\begin{aligned} L &= \int \Delta C_\mathrm{p}\,\mathrm{d}T \\ &= L_0 + \Delta\alpha T + \frac{\Delta\beta}{2} T^2 + \frac{\Delta\gamma}{3} T^3 + \ldots \end{aligned} \tag{47}$$

where L_0 is an integration constant, and the Δ are always taken as differences between phases a and b.

The physical sense of Kirchhoff's equation may perhaps become clearer by consideration of the cycle indicated below. By equating the change in enthalpy from a to b at the temperature T for the two paths indicated by the arrows, Equation (46) is again obtained.

It may be remarked that Kirchhoff's equation holds true also for reaction heats in thermochemistry, and that another similar equation may be derived for the change



in heat of reaction or of change of physical state with temperature at constant volume, where the internal energy U and the heat capacities at constant volume C_v play the same role as H and C_p in the above derivation:

$$\left(\frac{\partial \Delta U}{\partial T}\right)_v = \Delta C_v . \tag{48}$$

It should be remarked that the variation of L with T alone, i.e., while keeping p constant, cannot correspond to changes in which equilibrium conditions between the two phases are maintained. This would require a simultaneous variation of pressure, related to the temperature by the curve of equilibrium for the change of phase. To treat this problem requires the help of the Second Principle; this will be done in Chapter IV, Section 8, where the last term on the right in Equation (44) will be calculated. For vaporization and sublimation, however, it will be shown that this term is entirely negligible, while for fusion it should be taken into account, according to the formula

$$\frac{\mathrm{d}L_f}{\mathrm{d}T} = \Delta C_p + \frac{L_f}{T}\left[1 - \frac{T}{\Delta V}\left(\frac{\partial \Delta V}{\partial T}\right)_p\right] \tag{49}$$

where $\Delta V = V_{\text{liquid}} - V_{\text{solid}}$.

2.7. Adiabatic Processes in Ideal Gases. Potential Temperature

Considering Equations (39) and (40) we may write, for an adiabatic process in ideal gases:

$$\begin{aligned}\delta Q = 0 &= C_v\,\mathrm{d}T + p\,\mathrm{d}V = \\ &= C_p\,\mathrm{d}T - V\,\mathrm{d}p .\end{aligned} \tag{50}$$

Dividing by T and introducing the gas law we derive the two first following equations:

$$\begin{aligned}0 &= C_v\,\mathrm{d}\ln T + R^*\,\mathrm{d}\ln V \\ &= C_p\,\mathrm{d}\ln T - R^*\,\mathrm{d}\ln p \\ &= C_v\,\mathrm{d}\ln p + C_p\,\mathrm{d}\ln V .\end{aligned} \tag{51}$$

The third equation results from any of the other two by taking into account that $\mathrm{d}\ln p + \mathrm{d}\ln V = \mathrm{d}\ln T$ (by taking logarithms and differentiating the gas law) and

Equation (36). Integration of the three equations gives

$$\begin{aligned} T^{C_v}V^{R^*} &= \text{const.} \\ T^{C_p}p^{-R^*} &= \text{const.} \\ p^{C_v}V^{C_p} &= \text{const.} \end{aligned} \tag{52}$$

Or, introducing the ratios $\varkappa$ and η:

$$\begin{aligned} TV^{\eta-1} &= \text{const.} \\ Tp^{-\varkappa} &= \text{const.} \\ pV^{\eta} &= \text{const.} \end{aligned} \tag{53}$$

These are called Poisson's equations. They are equivalent, being related one to the other by the gas law. The third equation may be compared with Boyle's law for isotherms: $pV = \text{const.}$ In the p, V plane the *adiabats* (curves representing an adiabatic process) have larger slopes than the isotherms, due to the fact that $\eta > 1$. This is shown schematically in Figure II-3b. Figure II-3a shows the isotherms and adiabats on the three-dimensional surface representing the states of an ideal gas with coordinates p, V, T. Projections of the adiabats on the p, T and V, T planes are given in Figure II-3c and d, which also indicate the isochores and isobars.

If we apply the second Equation (53) between two states, we have:

$$\frac{T_0}{T} = \left(\frac{p_0}{p}\right)^{\varkappa}. \tag{54}$$

If we choose p_0 to be 1000 mb, T_0 becomes, by definition, the *potential temperature* θ:

$$\theta = T\left(\frac{1000\text{ mb}}{p}\right)^{\varkappa}. \tag{55}$$

The potential temperature of a gas is therefore the temperature that it would take if we compressed or expanded it adiabatically to the pressure of 1000 mb. We shall see that this parameter plays an important role in Meteorology.

The importance of potential temperature in meteorological studies is directly related to the fundamental role of adiabatic processes in the atmosphere. If we restrict our attention to dry air, we may assert that only radiative processes cause addition to or abstraction of heat from a system consisting of a unique sample of the atmosphere. In general, however, we must deal with bulk properties of the atmosphere, i.e., averaged properties, and in such an open system we recognize that three-dimensional mixing processes take place into and out of any system moving with the bulk flow. To this extent, then, we must add turbulent diffusion of heat to our non-adiabatic processes. Nevertheless, except in the lowest 100 mb of the atmosphere, these non-adiabatic processes are relatively unimportant and it is generally possible to treat changes of state as adiabatic, or at least as quasi-adiabatic.

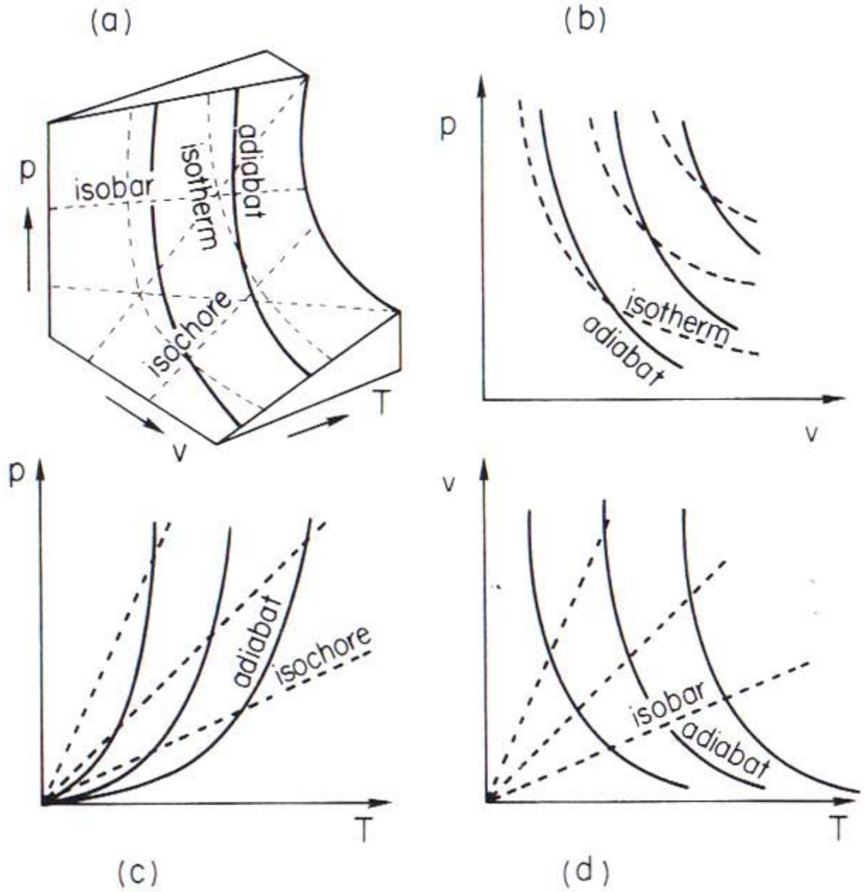


Fig. II-3. Thermodynamic surface for ideal gases and projections on p, v; p, T and v, T planes.

As can be seen from Equations (54) and (55), θ is a constant for an insulated gaseous system of fixed composition, i.e., for an adiabatic process. This constant may be used to help specify a particular system, such as a volume element of dry air. Its value does not change for any adiabatic process, and we say that potential temperature is conserved for adiabatic processes. Conservative processes are important in Meteorology since they enable us to trace the origin and subsequent history of air masses and air parcels, acting as tags (or tracers). If air moves along an isobaric surface (p constant), the temperature of the air sample will not change, if no external heat source exists. In general, air motion is very nearly along isobaric surfaces, but the small component through isobaric surfaces is of great importance. If the pressure of an air sample changes, then its temperature will change also, to maintain a constant value for the potential temperature. Changes of pressure and temperature will have the same signs; thus adiabatic compression is accompanied by warming and adiabatic expansion by cooling. Adiabatic compression, with pressure increasing along a trajectory, usually implies that the air is sinking or subsiding or descending (all these terms are employed in Meteorology), whereas adiabatic expansion, with the pressure on an air sample or element decreasing with time, usually implies ascent.

During adiabatic ascent, as the temperature falls the relative humidity rises (if the air contains any water vapor). Eventually a state of saturation is reached and further ascent causes condensation, releasing the latent heat of condensation which tends to warm the air and to change its potential temperature. Strictly speaking, this is still an adiabatic process, since the heat source is internal rather than external to the system. However, it is clear that our formulation of the first law for gases is no longer valid if phase changes occur. It is for this reason that the potential temperature is not conservative for processes of evaporation or condensation, regardless of whether the heat source (for the latent heat) is internal or external (for evaporation from a ground or water source, for example). We shall see later that the presence of unsaturated water vapor has no significant effect on the conservation of the (dry air) potential temperature.

For a non-adiabatic process, it is possible to evaluate the change in potential temperature to be expected, since by definition the potential temperature cannot be conserved during non-adiabatic processes. Let us take natural logarithms of Equation (55), and then differentiate:

$$\mathrm{d}\ln\theta = \mathrm{d}\ln T - \varkappa\,\mathrm{d}\ln p\,. \tag{56}$$

Using Equations (51) and (55), we obtain

$$\delta Q = C_{\mathrm{p}} T\,\mathrm{d}\ln\theta = C_{\mathrm{p}}\left(\frac{p}{p_0}\right)^{\varkappa}\mathrm{d}\theta\,. \tag{57}$$

These are, of course, merely additional formulations of the First Principle, for ideal gases.

2.8. Polytropic Processes

Although vertical motions can be generally considered to be adiabatic, there is a special type of situation where this approximation ceases to be valid. This is when very slow motions of horizontally-extended atmospheric layers are associated with some exchange of energy by radiation; the problem will be considered in Chapter VII, Section 11. Here we point out that such a process can be approximated by writing

$$\delta Q = C\,\mathrm{d}T \quad \text{or} \quad \delta q = c\,\mathrm{d}T \tag{58}$$

with a constant C or c, which can be called the polytropic molar or the polytropic specific heat capacity, respectively, associated with the process. By definition this is called a *polytropic process.*

Instead of (5), we must now write

$$C_{\mathrm{v}}\,\mathrm{d}T + p\,\mathrm{d}V = C_{\mathrm{p}}\,\mathrm{d}T - V\,\mathrm{d}p = C\,\mathrm{d}T \tag{59}$$

or

$$(C_{\mathrm{v}} - C)\,\mathrm{d}T + p\,\mathrm{d}V = (C_{\mathrm{p}} - C)\,\mathrm{d}T - V\,\mathrm{d}p = 0. \tag{60}$$

Repeating the derivation that led to (53), we find now:

$$\begin{aligned} TV^{n-1} &= \text{const.} \\ Tp^{-k} &= \text{const.} \\ pV^{n} &= \text{const.} \end{aligned} \tag{61}$$

where the 'polytropic exponent'

$$n = \frac{C_p - C}{C_v - C} = \frac{c_p - c}{c_v - c}$$

replaces η in the previous formulas and

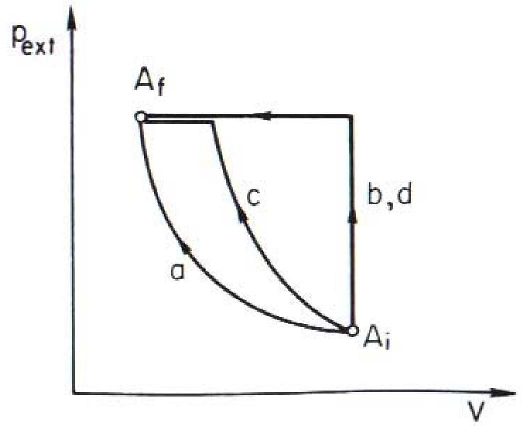
$$k = \frac{n-1}{n} = \frac{R^*}{C_p - C} = \frac{R}{c_p - c}$$

replaces κ in the previous formulas.

Any of the parameters c (or C), n and k can be used to characterize the polytropic process. We can easily see that, as particular cases, $C = C_p$ or $n = 0$ or $k = -\infty$ corresponds to an isobaric process; $C = \infty$ or $n = 1$ or $k = 0$ corresponds to an isothermal process; $C = 0$ or $n = \eta$ or $k = \varkappa$ corresponds to an adiabatic process; and $C = C_v$ or $n = \infty$ or $k = 1$ corresponds to an isochoric process.

PROBLEMS

1. Calculate A and Q for an isothermal compression (isothermal change, which may or may not be brought about by an isothermal process) of an ideal gas from A_i to A_f (see Figure) for each of the four following processes:



(a) isothermal reversible compression.

(b) sudden compression to $p_{\text{ext}} = p_{\text{f}}$ (e.g. dropping a weight on the piston of a cylinder containing the gas) and the subsequent contraction.

(c) adiabatic reversible compression to p_{f} followed by reversible isobaric cooling.

(d) reversible increase of the temperature at constant volume until $p = p_{\text{f}}$, followed by reversible decrease of temperature at constant pressure until $V = V_{\text{f}}$.

p_{ext} denotes the external pressure applied to the system.

2. A dry air mass ascends in the atmosphere from the 1000 mb level to that of 700 mb. Assuming that it does not mix and does not exchange heat with its surroundings, and that the initial temperature is 10 °C, calculate:

(a) Its initial specific volume.

(b) Its final temperature and specific volume.

(c) Its change in specific internal energy and in specific enthalpy (in J kg^{-1} and in cal g^{-1}).

(d) What is the work of expansion done by 1 km^3 of that air (volume taken at initial pressure)?

(e) What would the specific enthalpy change have been, for an isobaric cooling to the same final temperature, and for an isothermal expansion to the same final pressure?

(f) Compute (a), (b) and (c) for pure Ar, instead of dry air. (Atomic weight of Ar: 39.95.)

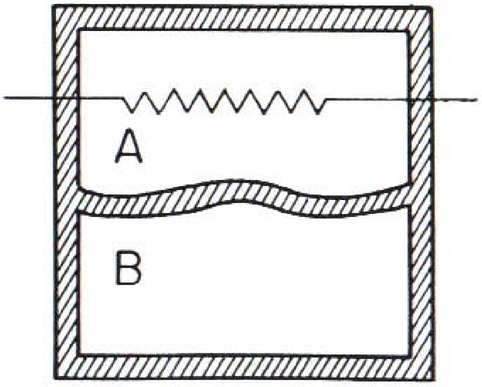
3. The figure represents an insulated box with two compartments A and B, each containing a monatomic ideal gas. They are separated by an insulating and perfectly flexible wall, so that the pressure is equal on both sides. Initially each compartment measures one liter and the gas is at 1 atm and 0 °C. Heat is then supplied to gas A (e.g. by means of an electrical resistance) until the pressure rises to 10 atm. Calculate:

(a) The final temperature T_{B}.

(b) The work performed on gas B.

(c) The final temperature T_{A}.

(d) The heat Q_{A} absorbed by gas A.



4. Consider one mole of air at 0°C and 1000 mb. Through a polytropic process, it acquires three times its initial volume at 250 mb. Calculate:
   (a) The value of n in $pV^n = \text{const}$.
   (b) The final temperature.
   (c) The change in internal energy.
   (d) The work received by the gas.
   (e) The heat absorbed by the gas.
   Consider that the air behaves as an ideal gas.
5. One gram of water is heated from 0 to 20°C, and then evaporated at constant temperature (at the vapour pressure of water corresponding to that temperature). Compute, in cal g^{-1} and cal g^{-1} K^{-1},
   (a) Δu
   (b) Δh
   (c) The mean value of c_{p_v} between 0 and 20°C, knowing that

$$l_{v, 0°C} = 597.3 \text{ cal g}^{-1}, \qquad l_{v, 20°C} = 586.0 \text{ cal g}^{-1}, \qquad c_w = 1.00 \text{ cal g}^{-1}\text{K}^{-1}$$

   (c_{p_v}: specific heat capacity of water vapor at constant pressure; c_w: specific heat capacity of liquid water).
   Note–Assume that any variation in pressure has a negligible effect and that water vapor behaves as an ideal gas.