CHAPTER IV

WATER-AIR SYSTEMS

4.1. Heterogeneous Systems

The fundamental equations seen in the previous chapter (Chapter III, Equation (26)) are valid for closed systems; no assumption regarding the internal structure of the system is implicit in them. Any of the four equivalent equations is a joint expression of the first and second principles, and therefore contains all that thermodynamics can say about closed systems, except as regards the third principle. Furthermore, while we deal with systems that, besides being closed, are homogeneous and of constant chemical composition*, it is not necessary to specify how the thermodynamic functions depend on the composition of the system, and in order to determine its state only two independent variables must be known (e.g., T and p); we do not need to take into account as another independent variable the total mass or the total number of moles, because this is assumed to be constant and, if we know the values of the extensive functions for the unit mass or the mole, generalization to any mass is done by simply multiplying by m or n (n: number of moles) (cf. Chapter I, Section 3).

However, in the study of heterogeneous systems, we are concerned with the conditions of internal equilibrium between the phases. And even if we consider a closed heterogeneous system, each one of its phases constitutes in its turn a homogeneous system (a 'subsystem'), which will be open, as we shall admit the possibility of exchange of components between phases. We must find therefore the form of the characteristic functions and of the fundamental equations, first for open homogeneous systems, and then for the total heterogeneous system.

The composition of an open homogeneous system is not constant in general; therefore, besides the two independent variables we used for closed systems (e.g., T and p) we have to consider the masses or concentrations of all the components, rather than a single mass m. In order to do so, we must specify precisely the notion of *number of components*; this is defined as the minimum number of chemical substances with which the composition of all phases can be expressed, separately for each one of them. In other words, the masses of the components can be considered as mathematical variables with which the composition of each phase can be expressed; the total number of such variables (chosen in such a way as to be a minimum) is defined as the number of components.

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* When we say 'chemical composition', we refer not only to the chemical species involved but also to their physical states.

We shall restrict ourselves to the specific case in which we are interested while introducing the new concepts and formulas. To develop the expressions for the most general case would require writing somewhat more complicated formulas, and this generality is unnecessary for the relatively simple systems that we have to study. In a later section (Section 4) we shall summarize the basic equations and the formulas will be written in their general way. Consideration of chemical reactions will of course be excluded, as unnecessary for our applications.

We are concerned with a system composed of moist air and water in either one of its two condensed states: liquid water or ice. The system composed of humid air, liquid water *and* ice is of considerable interest in cloud physics, but in that case it is not in general a system in equilibrium and it would therefore be a subject for the thermodynamics of irreversible processes; from the point of view of equilibrium conditions, its study would be restricted to that of the triple point of water in the presence of air.

Our system has two phases: one condensed and one gaseous phase. Obviously, water substance may be chosen as one of the components. If we should consider that the different gases do not dissolve in water in the same proportion as they are in air, each gas would be a different component; but the solubility of the air gases in water or ice is of no significance to our purposes, and we shall neglect it from the beginning. We may then count the constant mixture which we have called "dry air" as the second and last component of the system, and we shall consider that this component is restricted to the gas phase. On the other hand, the two phases can exchange water component: they constitute thus open systems.

The amounts of components will be expressed by their number of moles, n_d, n_v, n_c, n_g, n_w, n_i, where the subscripts *d*, *v*, *c*, *g*, *w*, *i* stand for dry air, water vapor, water in condensed phase, gaseous phase, liquid water and ice (n_c may be either n_w or n_i), respectively. Alternatively, they may be expressed by their masses m, with similar subindices.

Let Z be any extensive property (such as U, S, G, V, etc.). We shall call $Z_{g,tot}$, $Z_{c,tot}$ and Z_{tot} the total values of Z for the gas phase, the condensed phase and the total system, respectively, so that

$$Z_{tot} = Z_{g,tot} + Z_{c,tot} \tag{1}$$

Z_d, Z_v and Z_c, on the other hand, will be used as symbols of the molar values.

For each phase, the total value of Z is no longer a function of only two variables (e.g., p and T), because the mass of its components may also vary. The total differentials of Z for these two open systems can be expressed:

$$\mathrm{d}Z_{g,tot} = \left(\frac{\partial Z_{g,tot}}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial Z_{g,tot}}{\partial p}\right)_{T,n} \mathrm{d}p + \left(\frac{\partial Z_{g,tot}}{\partial n_d}\right)_{T,p,n} \mathrm{d}n_d + \left(\frac{\partial Z_{g,tot}}{\partial n_v}\right)_{T,p,n} \mathrm{d}n_v \tag{2}$$

$$\mathrm{d}Z_{\mathrm{c,tot}} = \left(\frac{\partial Z_{\mathrm{c,tot}}}{\partial T}\right)_{\mathrm{p,n}} \mathrm{d}T + \left(\frac{\partial Z_{\mathrm{c,tot}}}{\partial p}\right)_{\mathrm{T,n}} \mathrm{d}p + \left(\frac{\partial Z_{\mathrm{c,tot}}}{\partial n_{\mathrm{c}}}\right)_{\mathrm{T,p}} \mathrm{d}n_{\mathrm{c}} \tag{3}$$

where n as a subscript means 'at constant composition' (that is, keeping constant all values of n_{k} in the system, except the one that is being varied, in the last derivatives).

By a general definition,

$$\bar{Z}_{\mathrm{k}} = \left(\frac{\partial Z_{\mathrm{v,tot}}}{\partial n_{\mathrm{k}}}\right)_{\mathrm{T,p,n}} \tag{4}$$

is called the *partial molar property* Z of the component k in the phase considered (k stands for any component and v for any phase).

Similarly,

$$\bar{z}_{\mathrm{k}} = \left(\frac{\partial Z_{\mathrm{v,tot}}}{\partial m_{\mathrm{k}}}\right)_{\mathrm{T,p,m}} \tag{5}$$

is called the *partial specific property* Z, the mass subscript m having a similar meaning as n in the previous definition.

If in particular $Z = G$, the partial molar Gibbs function is written

$$\bar{G}_{\mathrm{k}} = \mu_{\mathrm{k}} \tag{6}$$

and is called the *chemical potential* of component k. It may be worth noting that partial molar properties are always referred to the independent variables T and p, as defined above, whatever the meaning of Z; G is in particular the function that is usually associated with T and p (cf. Chapter III, Section 5).

The interpretation of these quantities becomes clearer by considering for one phase a process at constant T and p; taking the gas phase, for example, we have

$$\mathrm{d}Z_{\mathrm{g,tot}} = \bar{Z}_{\mathrm{d}}\,\mathrm{d}n_{\mathrm{d}} + \bar{Z}_{\mathrm{v}}\,\mathrm{d}n_{\mathrm{v}}\,. \tag{7}$$

The partial molar properties are in general dependent on the composition of the phase. If we integrate this expression at constant composition, we obtain ($\bar{Z}_{\mathrm{d}}$ and $\bar{Z}_{\mathrm{v}}$ being then constants)

$$Z_{\mathrm{g,tot}} = n_{\mathrm{d}}\bar{Z}_{\mathrm{d}} + n_{\mathrm{v}}\bar{Z}_{\mathrm{v}}\,. \tag{8}$$

Physically, we may imagine this integration as the process of adding simultaneously both components in a constant proportion until the total mass of gaseous phase is obtained. The partial molar property $\bar{Z}_{\mathrm{k}}$ is therefore the amount contributed by one mole of component k when added while maintaining a constant proportion of all components. Equation (8) is of course of general validity, independent of the fact that it was derived from an argument based on a process at constant T, p and composition; it could not be otherwise, as $Z_{\mathrm{g,tot}}$ and the $\bar{Z}_{\mathrm{i}}$ are all state functions.

By differentiating Equation (8) and comparing with Equation (7), we find that

$$n_{\mathrm{d}}\,\mathrm{d}\bar{Z}_{\mathrm{d}} + n_{\mathrm{v}}\,\mathrm{d}\bar{Z}_{\mathrm{v}} = 0\,. \tag{9}$$

This is called the Gibbs-Duhem equation, valid for a system at constant T and p, as applied to our particular example.

The partial molar property $\bar{Z}_k$ will, in general, differ from the molar value Z_k for the pure component, but it can be taken as equal with very good approximation in our system. Therefore, we write

$$\bar{Z}_d \cong Z_d \quad \text{or} \quad \bar{z}_d \cong z_d \tag{10}$$

and

$$\bar{Z}_v \cong Z_v \quad \text{or} \quad \bar{z}_v \cong z_v .$$

For the condensed phase, as we have only one component, obviously $\bar{Z}_c \equiv Z_c$ (or $\bar{z}_c \equiv z_c$), and $Z_{c,\,tot} = n_c Z_c = m_c z_c$. In particular, we can write for the Gibbs function:

$$\mu_d \cong G_d, \qquad \mu_v \cong G_v, \qquad \mu_c \equiv G_c .$$

Introducing Equations (4), (8) and (10) into Equations (2) and (3), we may write

$$\begin{aligned} \mathrm{d}Z_{g,\,tot} &= \left(\frac{\partial Z_{g,\,tot}}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial Z_{g,\,tot}}{\partial p}\right)_{T,n} \mathrm{d}p + Z_d\, \mathrm{d}n_d + Z_v\, \mathrm{d}n_v \\ &= n_d\left(\frac{\partial Z_d}{\partial T}\right)_{p,n} \mathrm{d}T + n_v\left(\frac{\partial Z_v}{\partial T}\right)_{p,n} \mathrm{d}T + n_d\left(\frac{\partial Z_d}{\partial p}\right)_{T,n} \mathrm{d}p + \\ &\qquad + n_v\left(\frac{\partial Z_v}{\partial p}\right)_{T,n} \mathrm{d}p + Z_d\, \mathrm{d}n_d + Z_v\, \mathrm{d}n_v \end{aligned} \tag{11}$$

$$\begin{aligned} \mathrm{d}Z_{c,\,tot} &= \left(\frac{\partial Z_{c,\,tot}}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial Z_{c,\,tot}}{\partial p}\right)_{T,n} \mathrm{d}p + Z_c\, \mathrm{d}n_c \\ &= n_c\left(\frac{\partial Z_c}{\partial T}\right)_{p,n} \mathrm{d}T + n_c\left(\frac{\partial Z_c}{\partial p}\right)_{T,n} \mathrm{d}p + Z_c\, \mathrm{d}n_c . \end{aligned} \tag{12}$$

At this stage we may introduce the condition, which will always be assumed, that the total system is a closed one. This is expressed in our case by

$$\begin{aligned} n_d &= \text{const.} \\ n_v + n_c &= n_t = \text{const.} \end{aligned} \tag{13}$$

or by

$$\begin{aligned} \mathrm{d}n_d &= 0 \\ \mathrm{d}n_v &= -\,\mathrm{d}n_c . \end{aligned} \tag{14}$$

If we introduce these conditions in the previous expressions, and add them to obtain $\mathrm{d}Z_{tot}$ for the whole system, we have:

$$\mathrm{d}Z_{tot} = \left(\frac{\partial Z_{tot}}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial Z_{tot}}{\partial p}\right)_{T,n} \mathrm{d}p + (Z_v - Z_c)\, \mathrm{d}n_v \tag{15}$$

where

$$Z_{\text{tot}} = n_{\text{d}} Z_{\text{d}} + n_{\text{v}} Z_{\text{v}} + n_{\text{c}} Z_{\text{c}}$$

$$\left(\frac{\partial Z_{\text{tot}}}{\partial T}\right)_{\text{p,n}} = n_{\text{d}}\left(\frac{\partial Z_{\text{d}}}{\partial T}\right)_{\text{p,n}} + n_{\text{v}}\left(\frac{\partial Z_{\text{v}}}{\partial T}\right)_{\text{p,n}} + n_{\text{c}}\left(\frac{\partial Z_{\text{c}}}{\partial T}\right)_{\text{p,n}}$$

$$\left(\frac{\partial Z_{\text{tot}}}{\partial p}\right)_{\text{T,n}} = n_{\text{d}}\left(\frac{\partial Z_{\text{d}}}{\partial p}\right)_{\text{T,n}} + n_{\text{v}}\left(\frac{\partial Z_{\text{v}}}{\partial p}\right)_{\text{T,n}} + n_{\text{c}}\left(\frac{\partial Z_{\text{c}}}{\partial p}\right)_{\text{T,n}}.$$

If masses are used instead of numbers of moles, the expression will be written

$$\mathrm{d}Z_{\text{tot}} = \left(\frac{\partial Z_{\text{tot}}}{\partial T}\right)_{\text{p,m}} \mathrm{d}T + \left(\frac{\partial Z_{\text{tot}}}{\partial p}\right)_{\text{T,m}} \mathrm{d}p + (z_{\text{v}} - z_{\text{c}})\mathrm{d}m_{\text{v}} \tag{16}$$

with

$$Z_{\text{tot}} = m_{\text{d}} z_{\text{d}} + m_{\text{v}} z_{\text{v}} + m_{\text{c}} z_{\text{c}}$$

$$\left(\frac{\partial Z_{\text{tot}}}{\partial T}\right)_{\text{p,m}} = m_{\text{d}}\left(\frac{\partial z_{\text{d}}}{\partial T}\right)_{\text{p,m}} + m_{\text{v}}\left(\frac{\partial z_{\text{v}}}{\partial T}\right)_{\text{p,m}} + m_{\text{c}}\left(\frac{\partial z_{\text{c}}}{\partial T}\right)_{\text{p,m}}$$

$$\left(\frac{\partial Z_{\text{tot}}}{\partial p}\right)_{\text{T,m}} = m_{\text{d}}\left(\frac{\partial z_{\text{d}}}{\partial p}\right)_{\text{T,m}} + m_{\text{v}}\left(\frac{\partial z_{\text{v}}}{\partial p}\right)_{\text{T,m}} + m_{\text{c}}\left(\frac{\partial z_{\text{c}}}{\partial p}\right)_{\text{T,m}}$$

Z_{tot} can be written as mz, m being the total mass and z the average specific value of Z.

4.2. Fundamental Equations for Open Systems

Let us consider now the Gibbs function for the gas phase. Equation (2), with the definitions (4) and (6) and $Z = G$, gives

$$\mathrm{d}G_{\text{g, tot}} = \left(\frac{\partial G_{\text{g, tot}}}{\partial T}\right)_{\text{p,n}} \mathrm{d}T + \left(\frac{\partial G_{\text{g, tot}}}{\partial p}\right)_{\text{T,n}} \mathrm{d}p + \mu_{\text{d}}\,\mathrm{d}n_{\text{d}} + \mu_{\text{v}}\,\mathrm{d}n_{\text{v}} \tag{17}$$

where

$$G_{\text{g, tot}} = n_{\text{d}}\bar{G}_{\text{d}} + n_{\text{v}}\bar{G}_{\text{v}} = n_{\text{d}}\mu_{\text{d}} + n_{\text{v}}\mu_{\text{v}}. \tag{18}$$

We can consider a reversible process without exchange of mass (system acting as closed: $\mathrm{d}n_{\text{d}} = \mathrm{d}n_{\text{v}} = 0$) and compare Equation (17) with Chapter III, Equation (25):

$$\mathrm{d}G_{\text{g, tot}} = -\,S_{\text{g, tot}}\,\mathrm{d}T + V_{\text{g, tot}}\,\mathrm{d}p. \tag{19}$$

As T and p are independent variables, the coefficients of $\mathrm{d}T$ and $\mathrm{d}p$ must be identical in both expressions; i.e.:

$$\left(\frac{\partial G_{\text{g, tot}}}{\partial T}\right)_{\text{p,n}} = -\,S_{\text{g, tot}} \tag{20}$$

$$\left(\frac{\partial G_{\text{g, tot}}}{\partial p}\right)_{\text{T,n}} = V_{\text{g, tot}} \tag{21}$$

where

$$S_{\mathrm{g,tot}} = n_{\mathrm{d}}\bar{S}_{\mathrm{d}} + n_{\mathrm{v}}\bar{S}_{\mathrm{v}}$$

and $V_{\mathrm{g,tot}}$ is given by a similar expression.

These equalities will still be valid for processes with mass exchange (the two partial derivatives being state functions themselves, therefore independent of the process we choose to consider); therefore we introduce them into Equation (17) and obtain, for an open phase:

$$\mathrm{d}G_{\mathrm{g,tot}} = -S_{\mathrm{g,tot}}\,\mathrm{d}T + V_{\mathrm{g,tot}}\,\mathrm{d}p + \mu_{\mathrm{d}}\,\mathrm{d}n_{\mathrm{d}} + \mu_{\mathrm{v}}\,\mathrm{d}n_{\mathrm{v}}. \tag{22}$$

This is the generalization of the fundamental equation (Chapter III, Equation (25)) for our particular open system and for processes occurring reversibly with respect to mechanical and thermal equilibrium. This last condition is implicit in the equality sign; otherwise the Equation (25) of Chapter III should have been taken with the inequality sign.

Introducing the equalities $G=U+pV-TS=H-TS=F+pV$ (cf. Chapter III, Section 5), three other equations could be obtained, similar to Chapter III, Equation (25) except for the additive terms $\mu_{\mathrm{d}}\,\mathrm{d}n_{\mathrm{d}}+\mu_{\mathrm{v}}\,\mathrm{d}n_{\mathrm{v}}$ that will appear in all of them. Similar expressions could be written for the condensed phase; in particular, for the Gibbs function we have

$$\begin{aligned}\mathrm{d}G_{\mathrm{c,tot}} &= \left(\frac{\partial G_{\mathrm{c,tot}}}{\partial T}\right)_{\mathrm{p,n}}\mathrm{d}T + \left(\frac{\partial G_{\mathrm{c,tot}}}{\partial p}\right)_{\mathrm{T,n}}\mathrm{d}p + \mu_{\mathrm{c}}\,\mathrm{d}n_{\mathrm{c}}\\ &= -S_{\mathrm{c,tot}}\,\mathrm{d}T + V_{\mathrm{c,tot}}\,\mathrm{d}p + \mu_{\mathrm{c}}\,\mathrm{d}n_{\mathrm{c}}\end{aligned} \tag{23}$$

where

$$S_{\mathrm{c,tot}} = n_{\mathrm{c}}S_{\mathrm{c}};\quad V_{\mathrm{c,tot}} = n_{\mathrm{c}}V_{\mathrm{c}};\quad G_{\mathrm{c,tot}} = n_{\mathrm{c}}G_{\mathrm{c}} \equiv n_{\mathrm{c}}\mu_{\mathrm{c}}$$

4.3. Equations for the Heterogeneous System. Internal Equilibrium

We may assume now that we have both phases isolated and in equilibrium, both being at the same temperature and pressure. Let us bring them together. They shall continue to be in thermal and in mechanical equilibrium, because T and p are the same for both phases. But we do not know if they shall be in chemical equilibrium; for our particular system, this means that we do not know whether water (or ice, as the case may be) and vapor will remain in equilibrium, or whether condensation of vapor or evaporation of water (or sublimation of ice) will take place as a spontaneous process. The total value for $\mathrm{d}G$ is obtained by adding Equations (22) and (23):

$$\mathrm{d}G_{\mathrm{tot}} = -S_{\mathrm{tot}}\,\mathrm{d}T + V_{\mathrm{tot}}\,\mathrm{d}p + \mu_{\mathrm{d}}\,\mathrm{d}n_{\mathrm{d}} + \mu_{\mathrm{v}}\,\mathrm{d}n_{\mathrm{v}} + \mu_{\mathrm{c}}\,\mathrm{d}n_{\mathrm{c}}. \tag{24}$$

If we now introduce the condition that the total heterogeneous system is closed, i.e., condition (14), we obtain

$$\mathrm{d}G_{\mathrm{tot}} = -S_{\mathrm{tot}}\,\mathrm{d}T + V_{\mathrm{tot}}\,\mathrm{d}p + (\mu_{\mathrm{v}} - \mu_{\mathrm{c}})\,\mathrm{d}n_{\mathrm{v}}. \tag{25}$$

G_{tot}, S_{tot}, V_{tot} are the total values for the system; e.g.:

$$G_{\mathrm{tot}} = n_{\mathrm{d}}\mu_{\mathrm{d}} + n_{\mathrm{v}}\mu_{\mathrm{v}} + n_{\mathrm{c}}\mu_{\mathrm{c}}.$$

We consider now virtual displacements at constant T and p. The condition of equilibrium is (Chapter III, Section 6) $\mathrm{D}G \geqslant 0$ for any arbitrary $\mathrm{D}n_{\mathrm{v}}$. As $\mathrm{D}n_{\mathrm{v}}$ can be positive or negative, this condition requires that its coefficient vanish. Therefore, the condition of internal chemical equilibrium between the two phases is

$$\mu_{\mathrm{v}} = \mu_{\mathrm{c}} . \tag{26}$$

Again, introducing the relations between G and the other three characteristic functions U, H, F, a set of four equations of the type of Equation (24) (including (24)) could be obtained for the open heterogeneous system considered here, and another set of four equations like Equation (25) (including (25)) for the closed system.

4.4. Summary of Basic Formulas for Heterogeneous Systems *

The formulas considered so far have been developed for our particular system (water or ice + moist air). Their generalization to any heterogeneous system with c components and φ phases could be easily done without the need of any new concepts. The general expressions will now be written without derivation; the previous formulas will be easily recognized as particular cases.

The expression of the total differential of any extensive property Z is

$$\mathrm{d}Z = \left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p,n}} \mathrm{d}T + \left(\frac{\partial Z}{\partial p}\right)_{\mathrm{T,n}} \mathrm{d}p + \sum_{\mathrm{v}=1}^{\varphi} \sum_{\mathrm{i}=1}^{\mathrm{c}} \bar{Z}_{\mathrm{iv}} \, \mathrm{d}n_{\mathrm{iv}} . \tag{27}$$

We have now dropped the subscript 'tot'; Z refers to the total system. Subscripts i and ν refer to the component and the phase, respectively; thus $\bar{\mathrm{Z}}_{\mathrm{iv}}$ means the partial molar Z property of component i in phase ν.

For the particular case $Z = G$, we have

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{\mathrm{p,n}} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{\mathrm{T,n}} \mathrm{d}p + \sum_{\mathrm{v}=1}^{\varphi} \sum_{\mathrm{i}=1}^{\mathrm{c}} \mu_{\mathrm{iv}} \, \mathrm{d}n_{\mathrm{iv}} . \tag{28}$$

If the system is closed, the conditions

$$\sum_{\mathrm{v}=1}^{\varphi} \mathrm{d}n_{\mathrm{iv}} = 0 \quad (i = 1, 2, \ldots, c) \tag{29}$$

of conservation of components must hold, and Equation (28) becomes

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{\mathrm{p,n}} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{\mathrm{T,n}} \mathrm{d}p + \sum_{\mathrm{v}=2}^{\varphi} \sum_{\mathrm{i}=1}^{\mathrm{c}} (\mu_{\mathrm{iv}} - \mu_{\mathrm{i1}}) \, \mathrm{d}n_{\mathrm{iv}} . \tag{30}$$

The equivalent of Equation (30) for $Z = H$ would be:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{\mathrm{p,n}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{\mathrm{T,n}} \mathrm{d}p + \sum_{\mathrm{v}=2}^{\varphi} \sum_{\mathrm{i}=1}^{\mathrm{c}} (\bar{H}_{\mathrm{iv}} - \bar{H}_{\mathrm{i1}}) \, \mathrm{d}n_{\mathrm{iv}} . \tag{31}$$

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* This section is intended both as a summary and a presentation of the formulas in their general form. The reader may omit it without loss of continuity.

Here the terms $(\overline{H}_{\mathrm{i}\nu}-\overline{H}_{\mathrm{i}1})$ have the meaning of molar latent heats for the passage of component i from phase 1 (arbitrarily chosen) to phase ν.

The sum of Equations (11) and (12) would be a particular case of Equation (27). Equation (15) with $Z=G$ corresponds to Equation (30); Equation (17) corresponds to Equation (28).

Comparison with the fundamental equations (Chapter III, Equation (26)) and introduction of the other characteristic equations gives the following set of fundamental equations for processes in open heterogeneous systems occurring in conditions of thermal and mechanical reversibility:

$$\left.\begin{aligned} \mathrm{d}U &= T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{\nu=1}^{\varphi}\sum_{\mathrm{i}=1}^{\mathrm{c}} \mu_{\mathrm{i}\nu}\,\mathrm{d}n_{\mathrm{i}\nu} \\ \mathrm{d}H &= T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_{\nu=1}^{\varphi}\sum_{\mathrm{i}=1}^{\mathrm{c}} \mu_{\mathrm{i}\nu}\,\mathrm{d}n_{\mathrm{i}\nu} \\ \mathrm{d}F &= -\,S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_{\nu=1}^{\varphi}\sum_{\mathrm{i}=1}^{\mathrm{c}} \mu_{\mathrm{i}\nu}\,\mathrm{d}n_{\mathrm{i}\nu} \\ \mathrm{d}G &= -\,S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_{\nu=1}^{\varphi}\sum_{\mathrm{i}=1}^{\mathrm{c}} \mu_{\mathrm{i}\nu}\,\mathrm{d}n_{\mathrm{i}\nu}\,. \end{aligned}\right\} \qquad (32)$$

If the system is closed, the same formulas will hold with the substitution of

$$\sum_{\nu=2}^{\varphi}\sum_{\mathrm{i}=1}^{\mathrm{c}} (\mu_{\mathrm{i}\nu} - \mu_{\mathrm{i}1})\,\mathrm{d}n_{\mathrm{i}\nu} \qquad (33)$$

for the double sum in Equation (32); here phase 1 is any arbitrarily chosen phase.

Equation (24) will be recognized as a particular case of the fourth (32). Equation (25) is the same with the substitution of the expression (33).

It may be shown from formulas (32) with (33) that the conditions of internal chemical equilibrium are

$$\mu_{\mathrm{i}1} = \mu_{\mathrm{i}2} = \ldots = \mu_{\mathrm{i}\varphi} \quad (i = 1, 2, \ldots, c) \qquad (34)$$

i.e., that the chemical potential of each component, be the same for all phases. Equation (26) was the particular case of Equations (34) for our system. The magnitude of the double sum gives a measure of the deviation from chemical equilibrium – therefore, of the irreversibility of the process.

The set of Equation (32) shows that four alternative definitions can be given of the chemical potential:

$$\mu_{\mathrm{i}\nu} = \left(\frac{\partial U}{\partial n_{\mathrm{i}\nu}}\right)_{\mathrm{S,V,n}} = \left(\frac{\partial H}{\partial n_{\mathrm{i}\nu}}\right)_{\mathrm{S,p,n}} = \left(\frac{\partial F}{\partial n_{\mathrm{i}\nu}}\right)_{\mathrm{T,V,n}} = \left(\frac{\partial G}{\partial n_{\mathrm{i}\nu}}\right)_{\mathrm{T,p,n}}. \qquad (35)$$

The last one was the definition used to introduce it (cf. Equation (6)). It should be noticed that the other three derivatives are *not* the partial molar properties (which are all defined at constant T and p).

4.5. Number of Independent Variables

We have seen that for closed systems of constant composition the number of independent variables whose values have to be known, in order to specify the state of the system, is two; for instance, T and p. If we now have a heterogeneous system of one component and two phases (e.g., water and water vapor), we have four variables corresponding to the two phases: p, T, p', T'. But if we impose the condition of equilibrium between the two phases, the four variables must obey three conditions:

$$\begin{aligned} p &= p' \\ T &= T' \\ G &= G' \end{aligned} \tag{36}$$

which reduces to one the number of independent variables. $G=\mu$ is here the molar Gibbs function. $G=G(T,p)$ and $G'=G(T',p')$, so that the third equation implies a relation between T, p and T', p'. Therefore, if we fix the temperature at which both phases are in equilibrium, the value of the pressure also becomes fixed, and vice versa. This defines curves $p=f(T)$ along which an equilibrium can exist – the equilibrium curves for changes of state, which we shall discuss for water substance.

If the three phases (solid, liquid, gas) are present simultaneously, we have three pairs of variables (pressure and temperature), but also three pairs of conditions for equilibrium:

$$\begin{aligned} p &= p' = p'' \\ T &= T' = T'' \\ G &= G' = G''. \end{aligned} \tag{37}$$

Therefore, there is no independent variable; all values are fixed, and define what is called the *triple point*.

In our system of moist air plus one condensed phase of water, we may consider the same variables as for two phases of pure water (where the pressure of the gas phase would now become the partial pressure of water vapor), plus the partial pressure of dry air. As the number of conditions remain the same as before, we have now two independent variables, for instance T and p_d.

A general rule may be derived, which includes the previous systems as particular cases: the number of independent variables v that must be fixed in order to determine completely the equilibrium state of a heterogeneous system (its variance) is equal to the number of components c minus the number of phases φ plus two:

$$v = c - \varphi + 2. \tag{38}$$

This is the *phase rule*, derived by J. W. Gibbs. It is obtained immediately by a generalization of the previous argument (see Problem 12).

4.6. Phase-Transition Equilibria for Water

As we have seen above, phase-transition equilibria correspond to only one independent variable ($\nu = 1$) and may be represented by curves $p = f(T)$, as shown schematically in Figure IV-1. They define in the p, T plane the regions where the water is in solid, liquid or gaseous state.

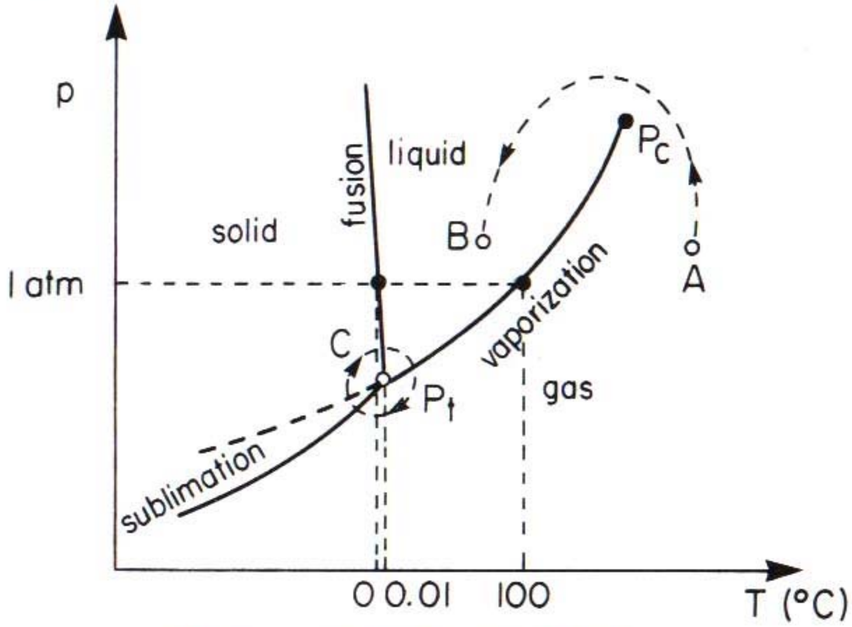

Fig. IV-1. Phase-transition equilibria for water.

The pressure of the vapor, when it is in equilibrium with the condensed phase at a certain temperature, is called the *vapor pressure* of the condensed phase at that temperature. The curves for sublimation and vaporization equilibria are thus the vapor pressure curves of ice and water. The curve for fusion corresponds to the equilibrium ice-water; its steep slope is negative, unlike what happens with similar curves for most other substances. The three curves meet at the triple point P_t, where the three phases coexist in equilibrium.

The extension of the vapor pressure curve of water at temperatures lower than the triple point, represented as a dashed curve, corresponds to supercooled water (metastable equilibrium).

The vapor pressure curve for water ends, for high temperatures, at the critical point P_c, beyond which there is no discontinuity between the liquid and gaseous phases. Thus, vapor represented by the point A could be transformed to water B without undergoing a two-phase condensation, if a path such as the one shown in Figure IV-1 is followed.

The pressure, temperature, and specific volumes for the three phases at the triple point are:

$$p_t = 610.7 \text{ Pa} = 6.107 \text{ mb}$$

$$T_t = 273.16\ \mathrm{K}$$

$$v_{i,t} = 1.091 \times 10^{-3}\ \mathrm{m^3\ kg^{-1}}; \qquad \text{ice density: } \varrho_{i,t} = 917\ \mathrm{kg\ m^{-3}}$$

$$v_{w,t} = 1.000 \times 10^{-3}\ \mathrm{m^3\ kg^{-1}}$$

$$v_{v,t} = 206\ \mathrm{m^3\ kg^{-1}}.$$

The latent heat for changes of state, at 0 °C, are:

$$l_v = 597.3\ \mathrm{cal\ g^{-1}} = 2.5008 \times 10^6\ \mathrm{J\ kg^{-1}}$$

$$l_s = 677.0\ \mathrm{cal\ g^{-1}} = 2.8345 \times 10^6\ \mathrm{J\ kg^{-1}}$$

$$l_f = \ \ 79.7\ \mathrm{cal\ g^{-1}} = 0.3337 \times 10^6\ \mathrm{J\ kg^{-1}}.$$

Within this approximation the same values hold for the triple point. It may be remarked that $l_s = l_f + l_v$. That this should be so is easily seen by considering a cycle around the triple point (C in Figure IV-1) performed by unit mass, and assuming that it tends to the point by becoming increasingly smaller. In the limit, the three transitions of state occur at constant temperature and pressure, so that for the cycle:

$$\Delta H = \Delta H_f + \Delta H_v - \Delta H_s = 0 \quad \text{at} \quad T_t,\ p_t,$$

or

$$l_f + l_v - l_s = 0.$$

The values for the critical point P_c (critical constants) are:

$$T_c = 647\ \mathrm{K}$$

$$p_c = 218.8\ \mathrm{atm} = 2.22 \times 10^7\ \mathrm{Pa}$$

$$v_c = 3.07 \times 10^{-3}\ \mathrm{m^3\ kg^{-1}}.$$

The changes in pressure and specific volume along isotherms are summarized schematically in the diagram of Amagat-Andrews, shown in Figure IV-2. The curves are isotherms. At high temperatures, they tend to become equilateral hyperbolae, corresponding to ideal gas behavior in the water vapor. At lower temperatures, they become first deformed, until reaching a point of zero slope: the critical point P_c. Below this temperature, the vapor and liquid regions are separated by a zone of discontinuity, where liquid water and vapor coexist. Thus, if vapor represented by the point A is isothermically compressed, if follows the isotherm until reaching B. At that point, condensation starts, giving liquid corresponding to point C. As condensation proceeds, the mean specific volume becomes smaller, while pressure, as well as temperature, remains constant; the representative point slides along the horizontal line, from B to C. It reaches C when all vapor has condensed into liquid, and from there on it follows the compression curve of the liquid, which shows a much larger slope (smaller compressibility) than for the vapor.

The same type of process could be described for the sublimation region, below the temperature T_t. The straight line (isotherm) TT corresponds to the triple point.

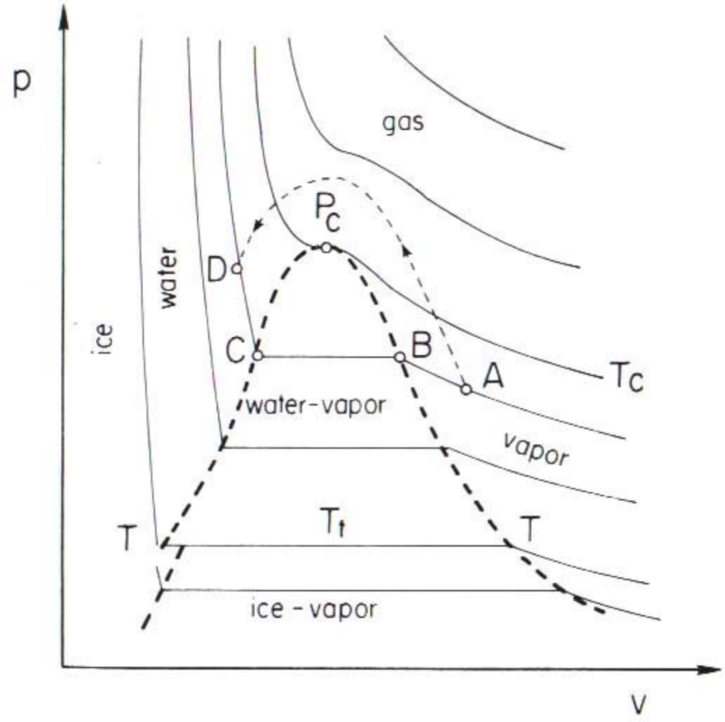

Fig. IV-2. Diagram of Amagat-Andrews.

Thus, several regions, corresponding to each of the three states, and to the changes of state, are defined in the diagram, as labelled in Figure IV-2. The region at temperatures higher than T_c is sometimes called the gas region as distinct from the vapor region (at the right, below T_c), to indicate that no two-phase discontinuity for condensation can occur in it.

As in Figure IV-1, a liquid state D can be reached from a vapor state A without discontinuity by a path such as shown by the dotted curve passing above P_c.

4.7. Thermodynamic Surface for Water Substance

Both diagrams p, T and p, v can be assembled into one tridimensional representation of the surface $f(p, v, T)=0$, the equation of state for water substance in its three states. This is called the *thermodynamic surface* for water substance, and can be seen (schematically only) in Figure IV-3. The different regions are labelled in it, and the isotherms are drawn as full lines. A projection of the figure on the p, T plane would reproduce Figure IV-1. This means that the two-phase surfaces are all perpendicular to the p, T plane, as they can be conceived as made out of straight lines representing changes of state at constant p and T; the projection of these curves thus determines curves in the p, T plane, and the projection of the T_t isotherm is the triple point P_t. Similarly, the projection of Figure IV-3 on the p, v plane would reproduce Figure IV-2.

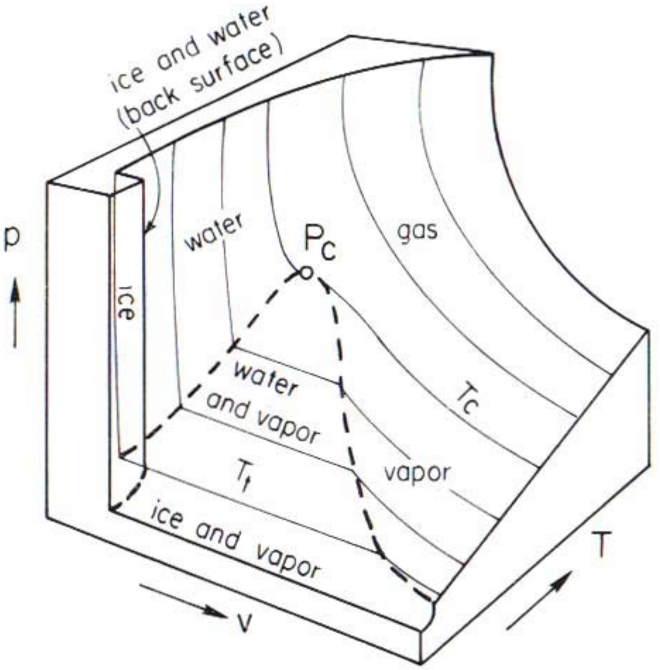

Fig. IV-3. Thermodynamic surface for water.

4.8. Clausius-Clapeyron Equation

We have seen that if we fix one of the two usual independent variables, let us say the pressure, and we heat a condensed phase, the temperature will increase until the equilibrium value is reached where two phases may coexist. The temperature then remains constant, as well as the pressure, until one of the phases has disappeared. For these changes we shall have

$$\Delta H = L \quad \text{or} \quad \Delta h = l \tag{39}$$

$$\Delta S = \frac{L}{T} \quad \text{or} \quad \Delta s = \frac{l}{T} \tag{40}$$

$$\Delta G = 0 \quad \text{or} \quad \Delta g = 0 \tag{41}$$

where L may be any of the three molar heats, and T the corresponding temperature of the change of phase.

We are now interested in calculating the relation between the changes in pressure and temperature when we change the conditions while preserving the equilibrium between the phases. At temperature T and the corresponding pressure p we have

$$G_a = G_b \tag{42}$$

a and b being the two phases. If we produce an infinitesimal change in the conditions, while preserving the equilibrium, we shall have, at $T+\mathrm{d}T$ and $p+\mathrm{d}p$,

$$G_a + \mathrm{d}G_a = G_b + \mathrm{d}G_b\,. \tag{43}$$

Therefore

$$\mathrm{d}G_a = \mathrm{d}G_b \tag{44}$$

or

$$-\,S_a\,\mathrm{d}T + V_a\,\mathrm{d}p = -\,S_b\,\mathrm{d}T + V_b\,\mathrm{d}p \tag{45}$$

and

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} = \frac{L}{T\Delta V}$$

or (46)

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{T\Delta v}\,.$$

Equation (46) gives us the ratio between the changes in the pressure and in the temperature along the equilibrium curves.

The physical meaning of Equation (46) may perhaps become clearer by considering a cycle for the particular case of vaporization. We shall have, in the p, v diagram, the cycle shown in Figure IV-4. We may go from water at T, p to vapor at $T+\mathrm{d}T$, $p+\mathrm{d}p$ by the two paths indicated in the diagram by the arrows. The changes in g in each step are also written in the diagram. Equating the variations in the specific Gibbs function for both equivalent processes (indicated in the figure for each of the steps), we obtain again Equation (46).

If we now apply Equation (46) to the melting of water, we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -\,1.344 \times 10^5\ \mathrm{mb\,K^{-1}}\,. \tag{47}$$

This shows that great increases in pressure correspond to small decreases in melting

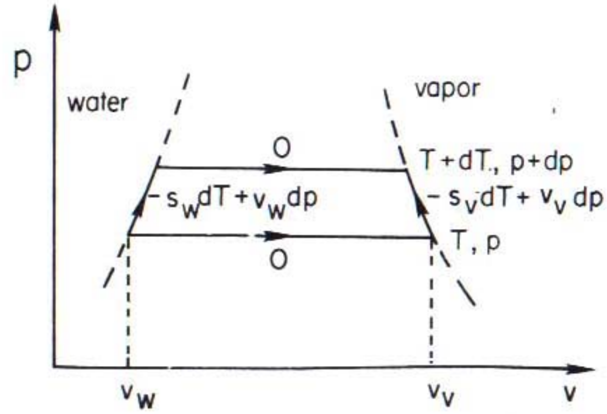

Fig. IV-4. Cycle related to the Clausius-Clapeyron equation.

temperature. The sign of the variation, peculiar to water and few other substances, corresponds to the fact that the solid contracts, instead of expanding, as it melts.

In the case of sublimation and vaporization, Equation (46) can be transformed and simplified by neglecting in Δv (or ΔV) the specific (or molar) volume of the condensed phase against that of the vapor ($\Delta v \cong v_v$), and by introducing the gas law to eliminate v_v:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{lp}{R_v T^2} \tag{47}$$

or

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{l}{R_v T^2} = \frac{L}{R^* T^2}. \tag{48}$$

This is the equation of Clausius-Clapeyron, where T is the sublimation or the boiling temperature, as the case may be. Its integration gives

$$\ln p = \frac{1}{R_v}\int l\,\frac{\mathrm{d}T}{T^2} + \text{const.} = \frac{1}{R^*}\int L\,\frac{\mathrm{d}T}{T^2} + \text{const.}$$

As a first approximation (particularly for small variations of T) l may be considered as constant, and

$$\ln p = -\frac{l}{R_v T} + \text{const.} = -\frac{L}{R^* T} + \text{const.} \tag{49}$$

or

$$\ln\frac{p_2}{p_1} = \frac{l}{R_v}\,\frac{\Delta T}{T_1 T_2} = \frac{L}{R^*}\,\frac{\Delta T}{T_1 T_2}. \tag{50}$$

l/R_v is thus given by the slope of the straight line $\ln p = f(1/T)$.

If a better approximation is desired, the expression in Chapter II, Equation (47) can be used for L. The integration gives then:

$$\ln p = \frac{1}{R^*}\left[-\frac{L_0}{T} + \Delta\alpha \ln T + \frac{\Delta\beta}{2}T + \frac{\Delta\gamma}{6}T^2 + \ldots\right] + \text{const.} \tag{51}$$

where the integration constant may be determined by an experimental pair of values T, p.

Let us consider vaporization. The first approximation (49), with the value of l_v above mentioned (Section 6), gives

$$\log p = 9.4041 - \frac{2354}{T} \tag{52}$$

where *log* is decimal logarithm, and p is given in mb.

The second approximation would be to consider the heat capacities as constant, so that l becomes a linear function of T. With this approximation there may be obtained:

$$\log p = -\frac{2937.4}{T} - 4.9283 \log T + 23.5470 \tag{53}$$

(p in mb). This is sometimes called Magnus' formula; it corresponds to taking two terms within the bracket in Equation (51).

Table IV-1 compares some experimental values with the formulas (52) and (53). 0 ° C has been taken as reference temperature, to fix the integration constant.

TABLE IV-1

Vapor pressure of water

t(°C)		− 10	0	10	20	30
p from (52)	(mb)	2.875	6.11	12.32	23.7	43.6
p from (53)	(mb)	2.865	6.11	12.27	23.35	42.37
p observed	(mb)	2.863	6.11	12.27	23.37	42.43

For sublimation, the first approximation gives

$$\log p = 10.550 - \frac{2667}{T} \tag{54}$$

(p in mb). The second approximation might be obtained by using a constant value for the specific heat capacity of ice:

$$c_i = 2060 \text{ J kg}^{-1}\text{K}^{-1}$$

(as for water, no specification of constant pressure is necessary for ice). Due to the actual variation of c_i with temperature, however, it turns out that there is no advantage in using the second approximation*.

The table of physical constants at the end of the book contains a skeleton tabulation of thermodynamic properties of condensed water, in its solid and liquid phases.

4.9. Variation of Latent Heat Along the Equilibrium Curve

In Chapter II, Section 6, we studied the influence of temperature on enthalpy changes associated with changes of phase (i.e., on the latent heats of change of state). The influence of pressure was mentioned to be small for sublimation and vaporization, but appreciable for fusion. We are now in a position to easily calculate this term, and shall do so for the pressure change necessary to keep the two-phase system in equilibrium when the temperature is altered; that is, we shall find the variation in latent heat *along*

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* More exact formulas for the thermodynamic properties of water substance can be found in the World Meteorological Organization tables, the Smithsonian Meteorological Tables and other references given in the Bibliography.

the equilibrium curve. The thermodynamic equation of state III-(42), applied to a change of phase, gives (taking the difference between the two phases):

$$\left(\frac{\partial \Delta H}{\partial p}\right)_{\mathrm{T}} = \Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_{\mathrm{p}} = \Delta V - T\Delta(V\alpha_{\mathrm{p}}) \tag{55}$$

where α_{p} is the isobaric coefficient of expansion and Δ refers to the difference of values between the two phases. We take (46) in the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T\Delta V} \tag{56}$$

so that

$$\left(\frac{\partial \Delta H}{\partial p}\right)_{\mathrm{T}} \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H}{T}\left[1 - \frac{T}{\Delta V}\left(\frac{\partial \Delta V}{\partial T}\right)_{\mathrm{p}}\right] = $$
$$= \frac{\Delta H}{T}\left[1 - \frac{T\Delta(V\alpha_{\mathrm{p}})}{\Delta V}\right] \tag{57}$$

and (cf. II-45):

$$\frac{\mathrm{d}\Delta H}{\mathrm{d}T} = \left(\frac{\partial \Delta H}{\partial T}\right)_{\mathrm{p}} + \left(\frac{\partial \Delta H}{\partial p}\right)_{\mathrm{T}} \frac{\mathrm{d}p}{\mathrm{d}T} = $$
$$= \Delta C_{\mathrm{p}} + \frac{\Delta H}{T}\left[1 - \frac{T}{\Delta V}\left(\frac{\partial \Delta V}{\partial T}\right)_{\mathrm{p}}\right] = \Delta C_{\mathrm{p}} + \frac{\Delta H}{T}\left[1 - \frac{T\Delta(V\alpha_{\mathrm{p}})}{\Delta V}\right] \tag{58}$$

For vaporization ($\Delta H = L_{\mathrm{v}}$) and sublimation ($\Delta H = L_{\mathrm{s}}$) we can make the approximation

$$\Delta V \cong V_{\mathrm{v}} = \frac{R^*T}{p} \tag{59}$$

which makes the last term of (58) zero. In the case of fusion ($\Delta H = L_{\mathrm{f}}$) this term is generally not negligible.

4.10. Water Vapor and Moist Air

We shall now consider more carefully the type of gaseous phase with which we shall be concerned: a mixture of dry air and water vapor. In what follows we shall represent the water vapor pressure by e, and the partial pressure of dry air by p_{d}, leaving the symbol p for the total pressure. Subscripts w and i on the water vapor pressure will indicate saturation values with respect to liquid water and ice, respectively; subscript c will stand for any of the two condensed phases ($e_{\mathrm{c}} = e_{\mathrm{w}}$ or e_{i}, as the case may be).

Let us first consider pure water vapor. We have seen in Chapter I, Section 12 that dry air can be treated with good approximation as an ideal gas. The same is true for water vapor in the range of temperatures and partial pressures of meteorological interest. For each temperature water vapor will depart most from ideal behavior when it approaches saturation. Table IV-2 shows these maximal departures for several temperatures.

TABLE IV-2

$t(^\circ\mathrm{C})$	$e_\mathrm{w}V/R^*T$
−50	1.0000
0	0.9995
25	0.9980
50	0.9961

As these data indicate, the departure from ideal behavior reaches only a few tenths per cent at the most. Thus in virtually all cases we can assume, with fairly good approximation:

$$ev_\mathrm{v} = R_\mathrm{v}T \tag{60}$$

where v_v is the specific volume and $R_\mathrm{v} = R^*/M_\mathrm{v}$ is the specific constant for water vapor: $M_\mathrm{v} = 18.015$ is the molecular weight of water. This gives for the gas constant:

$$R_\mathrm{v} = 461.5\ \mathrm{J\ kg^{-1}\ K^{-1}}\,.$$

It is customary to express R_v as a function of the dry air constant R_d. As $R^* = M_\mathrm{d}R_\mathrm{d} = M_\mathrm{v}R_\mathrm{v}$ (cf. Chapter I, Section 11),

$$R_\mathrm{v} = \frac{M_\mathrm{d}}{M_\mathrm{v}}R_\mathrm{d} = \frac{1}{\varepsilon}R_\mathrm{d}\,; \qquad \varepsilon = 0.622 \cong \frac{5}{8}. \tag{61}$$

Equation (60) becomes with this notation:

$$ev_\mathrm{v} = \frac{1}{\varepsilon}R_\mathrm{d}T\,. \tag{62}$$

For accurate computations, however, the departure from ideal conditions should be taken into account. Besides, we are interested in moist air, rather than pure water vapor. Two further effects occur with the addition of dry air, which modify appreciably the values of the saturation vapor pressures over water and ice. In the first place, we have to consider the displacement of the equilibrium caused by the increase in the total pressure. This can be computed by using Chapter III, Equation (25), which, written for unit mass, is

$$\mathrm{d}g = -\,s\,\mathrm{d}T + v\,\mathrm{d}p\,. \tag{63}$$

The increase in specific Gibbs function of the condensed phase due to the increase in pressure at constant temperature will be:

$$\Delta g_\mathrm{c} = \int_{e_\mathrm{c}}^{p=e_\mathrm{c}+p_\mathrm{d}} v_\mathrm{c}\,\mathrm{d}p \cong v_\mathrm{c}\,\Delta p \tag{64}$$

where $\Delta p = p_d \cong p$. Similarly, for the water vapor:

$$\Delta g_v = \int_{e_c}^{e_c + \Delta e_c} v_v \, de \cong v_v \, \Delta e_c \tag{65}$$

where the approximation can be made because Δe_c turns out to be very small.

Preservation of equilibrium implies that the chemical potentials of water in condensed phase and vapor must remain equal to each other. With adequate approximation this means equality in the Gibbs function (cf. Equation (10)). Therefore

$$\Delta g_c = \Delta g_v \tag{66}$$

and introducing Equations (64) and (65):

$$\Delta e_c = \frac{v_c}{v_v} \Delta p = \frac{v_c}{v_v} p_d \,. \tag{67}$$

For instance, at 0 °C and $p_d \cong p = 1$ atm, $\Delta e_w = 0.005$ mb.

The second effect that air has on the water vapor equilibrium with the condensed phase arises from the small, but not entirely negligible, solubility of the gas in water; the solubility in ice is smaller and may be neglected. According to Raoult's law, this produces a decrease of the vapor pressure proportional to the molar fraction of dissolved gas.

Thus, we have three types of departure from the ideal case of pure water or ice in the presence of vapor behaving as an ideal gas: (1) total pressure is not the sum of the partial pressures of two ideal gases (Dalton's law of mixture of ideal gases: Chapter I, Section 11) as neither water vapor nor dry air are strictly ideal gases; (2) the condensed phase is under a total pressure augmented by the presence of the dry air; and (3) the condensed phase is not pure water substance, but contains dissolved gas. The three effects can be taken into account by an empirical correction factor f_c, which will be a function of both temperature and pressure. We can then write

$$e'_c(T, p) = f_c(T, p) \, e_c(T) \tag{68}$$

where $e_c(T)$ represents the vapor pressure of the pure condensed phase in absence of air, and is a function of the temperature alone, and $e'_c(T, p)$ is the corrected value

TABLE IV-3

Typical values of Empirical Correction factors

t(°C) \ p(mb)	f_i 30	f_i 100	f_i 1100	t(°C) \ p(mb)	f_w 30	f_w 100	f_w 1100
−80	1.0002	1.0008	1.0089	−40	1.0002	1.0006	1.0060
−40	1.0002	1.0006	1.0061	0	1.0005	1.0008	1.0047
0	1.0005	1.0008	1.0048	40		1.0019	1.0054

when air is present. Table IV-3 gives some values of f_i and f_w. We see from this table that even by assuming f_i and f_w to be unity we can ensure that the error is always less than 1%.

We can illustrate the effects of the presence of air on the saturation vapor pressures (second and third effects mentioned above) by considering how the triple point becomes modified. This is shown in Figure IV-5. P_t is the triple point of pure water substance characterized by the temperature and pressure mentioned in Section 6. The effect of dissolved air is to lower the whole curve of water-vapor equilibrium; in the figure, the full curve becomes the lower dashed curve. The solubility of air gases in ice is truly negligible; therefore, if solubility was the only effect, the equilibrium ice-water-vapor would be now at the intersection of the dashed curve with the ice-vapor equilibrium curve, i.e. in P'_t. However, we must also consider the effect of pressure which will be different for the two condensed phases; according to Equation (66):

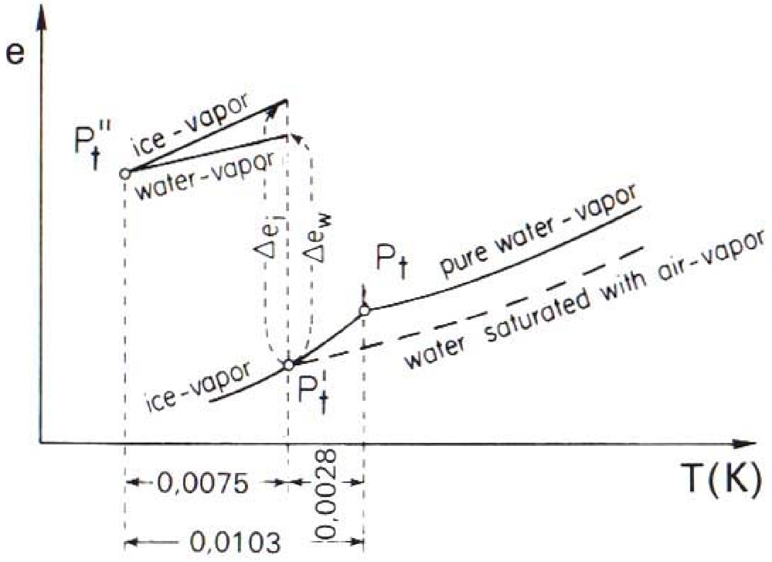

Fig. IV-5. Influence of air solubility and pressure on the triple-point equilibrium.

$$\Delta e_i = \frac{v_i}{v_v}\, p_d$$

$$\Delta e_w = \frac{v_w}{v_v}\, p_d\,.$$

These two increments must be added to the pressure corresponding to P'_t in order to obtain the new saturated vapor pressures over ice and over water; the former will be higher than the latter, because $v_i > v_w$ and therefore $\Delta e_i > \Delta e_w$. Through each of the two new points obtained, the corresponding equilibrium curves (ice-vapor and water-vapor, respectively) must pass; their slopes must be given by the two Clausius-Clapeyron equations (for ice and for water). With these slopes we extend the two curves until they intersect, at point P_t''. This is the new triple point, where ice, water saturated with air and water vapor will be in equilibrium, under a total pressure of $p = p_d + e_t''$ (the second term being the vapor pressure at P_t''). The changes in temperature indicated in the figure correspond to a total pressure of one atmosphere ($\sim 10^5$ Pa); solubility displaces the triple point by ~ 0.0028 K, and pressure by 0.0075 K, the total effect thus being a decrease in temperature of 0.010 K.

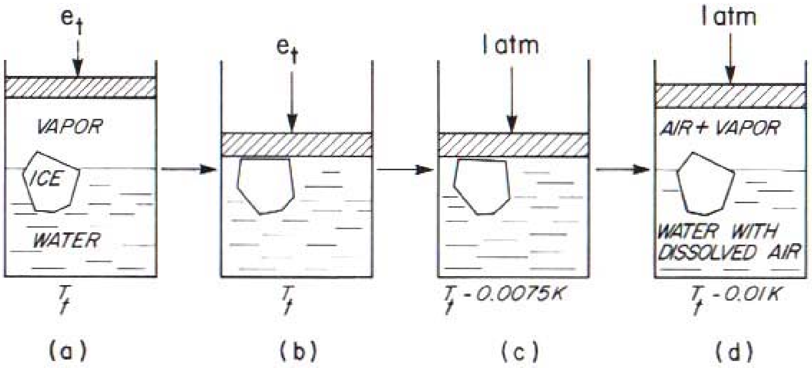

Fig. IV-6. Influence of air solubility and pressure on the triple-point equilibrium.

These relations may become clearer by performing an equivalent calculation with the help of an imaginary experiment. Figure IV-6 indicates schematically that in (a) we have a triple point equilibrium, with water substance only; e_t and T_t are the corresponding pressure and temperature. Now we condense all the vapor quasi-statically, at constant e_t and T_t (b). The pressure is then increased to $p = 1$ atm, while keeping equilibrium conditions; the system slides upwards on the fusion curve of Figure IV-1 (notice that the vertical axis variable is here the total pressure p, rather than the vapor pressure e, as in Figure IV-5). According to (47), the variation in temperature corresponding to the increase in pressure must be -0.0075 K; the system is in the situation (c). Finally, the piston is lifted while letting dry air come in, so as to preserve a total pressure of 1 atm (d). The liquid is under the same pressure as in (c), but air dissolves in the water, causing a new reduction in temperature of ~ -0.0028 K. The final temperature is $T_t - 0.01 = 273.15$ K. It will be noticed that (d) corresponds to the zero point chosen in the original definition of the Celsius scale (Chapter I, Section 5).

4.11. Humidity Variables

The water vapor content of moist air can be expressed through a number of different variables, several of which are of common use in meteorology. We shall first define the *specific humidity* q as the ratio of the mass of water vapor m_v to the total mass m:

$$q = m_v/m\,. \qquad (69)$$

The specific gas constant for moist air will be:

$$R = \frac{m_d R_d + m_v R_v}{m} = (1 - q)R_d + qR_v$$
$$= \left[1 + q\left(\frac{1}{\varepsilon} - 1\right)\right] R_d = (1 + 0.608\,q)R_d. \tag{70}$$

The equation of state becomes:

$$pv = (1 + 0.61\,q)R_d T = R_d T_v \tag{71}$$

by which we have defined the *virtual temperature* T_v

$$T_v = (1 + 0.61\,q)T \tag{72}$$

as the temperature of dry air having the same values of p and v as the moist air considered.

Another humidity variable is often used: the *mixing ratio* r, defined by

$$r = \frac{m_v}{m_d}. \tag{73}$$

Let us derive the relations between these two variables. From $m = m_d + m_v$ and the definitions of q and r, we obtain immediately

$$q = \frac{r}{1 + r}; \qquad r = \frac{q}{1 - q}. \tag{74}$$

Both r and q are always smaller than 0.04. We may thus write, without great error,

$$q \cong r. \tag{75}$$

If we write both partial pressure equations for a given mass of moist air, and divide them side by side, we obtain:

$$p_d V = m_d R_d T$$

$$eV = \frac{1}{\varepsilon} m_v R_d T$$

$$\frac{e}{p_d} = \frac{r}{\varepsilon}.$$

That is:

$$r = \frac{\varepsilon e}{p - e}; \qquad e = \frac{pr}{\varepsilon + r} \tag{76}$$

or approximately

$$r \cong \frac{\varepsilon}{p} e . \tag{77}$$

From $e = N_v p$ (cf. Chapter 1, Equation (21)) where N_v is the molar fraction of water vapor, comparing with Equation (76) (or directly from the definition of N_v) we see that

$$N_v = \frac{r}{\varepsilon + r} . \tag{78}$$

If the air is saturated with respect to water,

$$r_w = \frac{\varepsilon e_w}{p - e_w} ; \qquad e_w = \frac{p r_w}{\varepsilon + r_w} \tag{79}$$

and with respect to ice:

$$r_i = \frac{\varepsilon e_i}{p - e_i} ; \qquad e_i = \frac{p r_i}{\varepsilon + r_i} . \tag{80}$$

In the atmosphere, almost invariably

$$e_w < 60 \text{ mb} ; \qquad r_w < 0.04$$

so that we may write as an approximation

$$e \cong \frac{p}{\varepsilon} r \tag{81}$$

$$e_w \cong \frac{p}{\varepsilon} r_w ; \qquad e_i \cong \frac{p}{\varepsilon} r_i . \tag{82}$$

We shall also define another humidity variable, the *relative humidity*, as the ratio of the molar fraction of water vapor to the molar fraction corresponding to saturation with respect to water N_{vw} or with respect to ice N_{vi}. The corresponding relative humidities will be represented by U_w and U_i, respectively. Because we consider vapor and air as ideal gases, we can write

$$U_w = \frac{N_v}{N_{vw}} = \frac{p N_v}{p N_{vw}} = \frac{e}{e_w} \tag{83}$$

and similarly

$$U_i = \frac{e}{e_i} . \tag{84}$$

Within the usual ideal gas approximation, (83) and (84) can be taken as the definition of relative humidity.

To derive r as a function of U_w and r_w, we take the expression of r given by Equation (76), and we replace $e = U_w e_w$, and e_w by the second Equation (79). We obtain

$$r = \frac{U_w r_w}{1 + \frac{(1 - U_w) r_w}{\varepsilon}} \cong \tag{85}$$

$$\cong U_w r_w . \tag{86}$$

And similarly for U_i and r_i.

Usually U_w is obtained experimentally. p and T are also known. r_w is obtained from T through a table or a graph. q and r may then be calculated from the formulas above mentioned.

U_w and U_i are commonly given in percentage, q and r in units per mille (as grammes per kilogramme).

It should be noted that it is customary, for meteorological purposes, to express relative humidity at temperatures less than 0 °C with respect to water. The advantages of this procedure are as follows:

(a) Most hygrometers which are essentially responsive to the relative humidity indicate relative humidity with respect to water at all temperatures.

(b) The majority of clouds (between 0 °C and at least −20 °C) consist, in whole or in part, of supercooled water. Only below −40 °C are clouds always entirely glaciated.

(c) As a corollary to the above, supersaturation with respect to ice can frequently occur; this is not true with respect to water, so that it is convenient to require only two digits in coded messages for relative humidity.

4.12. Heat Capacities of Moist Air

In Chapter II, Section 5 we have seen the values for the heat capacities and ratios $\varkappa$ and η for diatomic gases, which may be applied to dry air.

The water vapor molecule is a triatomic non-linear molecule, whose position may be described by 3 translational and 3 rotational coordinates, giving 6 quadratic terms in the expression of its kinetic energy. Correspondingly, the equipartition theorem would give

$$c_{v_v} = \tfrac{6}{2} R_v = 3R_v = 0.331 \text{ cal g}^{-1} \text{ K}^{-1}$$

and

$$c_{p_v} = 4R_v = 0.441 \text{ cal g}^{-1} \text{K}^{-1}$$

on the assumption that the vibrational energy does not contribute to the specific heat capacity (all molecules in ground state). However, spectra of atmospheric radiation show vibration-rotation bands produced by water vapor at atmospheric temperatures (particularly a strong vibration band centered at 6.27 μm). Larger experimental

TABLE IV-5

Specific heat capacities of ice (c_i), water (c_w) and water vapor at constant pressure (c_{p_v}) (IT cal g^{-1} K^{-1}).

t(°C)	c_i	c_w	c_{p_v} (pressure = e_i)	c_{p_v} (pressure = e_w)
− 60	0.397	–	–	–
− 40	0.433	1.14	0.4429	0.4430
− 30	0.450	1.08	0.4434	0.4436
− 20	0.468	1.04	0.4441	0.4443
− 10	0.485	1.02	0.4451	0.4452
0	0.503	1.0074	0.4465	0.4465
10	–	1.0013	–	0.4482
20	–	0.9988	–	0.4503
30	–	0.9980	–	0.4530
40	–	0.9980	–	0.4552

values are therefore obtained, somewhat dependent on temperature and pressure. Table IV-5 gives some values for c_p, as well as for c_w and c_i.

If we take the specific heat capacities c_{v_v} and c_{p_v}, as well as those of dry air, as approximately independent of temperature, we may write to a good approximation

$$c_{p_v} = 0.447 \text{ cal g}^{-1}\text{K}^{-1} = 1870 \text{ J kg}^{-1}\text{K}^{-1}$$

$$c_{v_v} = 0.337 \text{ cal g}^{-1}\text{K}^{-1} = 1410 \text{ J kg}^{-1}\text{K}^{-1}.$$

If we now consider unit mass of moist air, the heat δQ absorbed at constant pressure for an increase $\mathrm{d}T$ in the temperature will be:

$$\delta Q = m_d \delta q_d + m_v \delta q_v = (1 - q)\delta q_d + q\delta q_v$$

where δq_d and δq_v are the heats absorbed by unit mass of dry air and of water vapor, respectively, and q is the specific humidity. Dividing by $\mathrm{d}T$:

$$c_p = (1 - q)c_{p_d} + qc_{p_v} = c_{p_d}\left[1 + \left(\frac{c_{p_v}}{c_{p_d}} - 1\right)q\right]$$

$$= c_{p_d}(1 + 0.87q) \cong c_{p_d}(1 + 0.37r). \tag{87}$$

Similarly we can obtain

$$c_v = c_{v_d}(1 + 0.97q) \cong c_{v_d}(1 + 0.97r) \tag{88}$$

$$\varkappa = \frac{R}{c_p} = \frac{(1 + 0.61q)R_d}{(1 + 0.87q)c_{p_d}} = \frac{1 + 0.61q}{1 + 0.87q}\varkappa_d$$

$$\cong \varkappa_d(1 - 0.26q) \cong \varkappa_d(1 - 0.26r) \tag{89}$$

$$\eta \cong \eta_\mathrm{d}(1 - 0.10\,q) \cong \eta_\mathrm{d}(1 - 0.10\,r) \tag{90}$$

where account has been taken of the fact that $q \ll 1$.

4.13. Moist Air Adiabats

According to Poissons's equations (Chapter II, Equation (53)), for an adiabatic expansion or compression from p, T to p', T', we must have

$$T' = T\left(\frac{p'}{p}\right)^{\varkappa}. \tag{91}$$

As $\varkappa$ varies with q for moist air, the adiabats passing through a point p, T will be different for different values of q. In particular $\varkappa = \varkappa_\mathrm{d}$ for dry air, and as $\varkappa \leqslant \varkappa_\mathrm{d}$, the adiabats in a diagram T, p will be slightly less steep (T will vary slightly more slowly) for moist air than for dry air.

The potential temperature of unsaturated moist air, θ_m, will be from Chapter II, Equation (55), and (89),

$$\theta_\mathrm{m} \cong T\left(\frac{1000}{p}\right)^{\varkappa_\mathrm{d}(1-0.26q)} \cong \theta\left(\frac{1000}{p}\right)^{-0.07q} \tag{92}$$

(p in mb). Differentiation yields

$$\frac{\partial \theta_\mathrm{m}}{\partial q} \cong -\,0.07\,\theta \ln\left(\frac{1000}{p}\right). \tag{93}$$

Calculation with Equation (93) shows that the difference $(\theta_\mathrm{m} - \theta)$ generally is less than 0.1 °C, so that one can treat unsaturated ascent or descent of air as if it were dry.

If in the definition of potential temperature

$$\theta = T\left(\frac{1000}{p}\right)^{\varkappa}$$

we put $\varkappa \cong \varkappa_\mathrm{d}$ and substitute the virtual temperature T_v for T, the new expression defines the *virtual potential temperature* θ_v.

4.14. Enthalpy, Internal Energy and Entropy of Moist Air and of a Cloud

When we consider moist air as a closed system, and within the accepted approximations of ideal behavior, the values of the internal energy, enthalpy or entropy will be given by the expressions derived in Chapter II, Equations (37) and (38) and Chapter III, Equation (52). Referring to unit mass:

$$u = c_\mathrm{v}T + \text{const.} \tag{94}$$

$$h = c_\mathrm{p}T + \text{const.} \tag{95}$$

$$s = c_\mathrm{p} \ln T - R \ln p + \text{const.} \tag{96}$$

where R, c_p and c_v are given by Equations (70), (87) and (88).

But we are also interested in the study of clouds of water droplets or of ice crystals. We shall treat them as closed heterogeneous systems; each phase, as seen in Section 1, is an open subsystem. We may then apply Equation (16) to the enthalpy. It will be, assuming that the condensed phase is water:

$$\begin{aligned} \mathrm{d}H &= \left(\frac{\partial H}{\partial T}\right)_{\mathrm{p,m}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{\mathrm{T,m}} \mathrm{d}p + (h_\mathrm{v} - h_\mathrm{w})\,\mathrm{d}m_\mathrm{v} \\ &= \left(\frac{\partial H}{\partial T}\right)_{\mathrm{p,m}} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{\mathrm{T,m}} \mathrm{d}p + l_\mathrm{v}\,\mathrm{d}m_\mathrm{v}. \end{aligned} \tag{97}$$

The enthalpy of the system will be the sum of the enthalpies of the two components in the two phases:

$$\begin{aligned} H &= m_\mathrm{d} h_\mathrm{d} + m_\mathrm{v} h_\mathrm{v} + m_\mathrm{w} h_\mathrm{w} \\ &= m_\mathrm{d} h_\mathrm{d} + m_\mathrm{v}(h_\mathrm{v} - h_\mathrm{w}) + m_\mathrm{t} h_\mathrm{w} \\ &= m_\mathrm{d} h_\mathrm{d} + m_\mathrm{v} l_\mathrm{v} + m_\mathrm{t} h_\mathrm{w}\,. \end{aligned} \tag{98}$$

Here the partial specific enthalpies $\bar{h}_\mathrm{k}$ have been taken as the specific enthalpies h_k, as indicated in Section 1, and $m_\mathrm{t} = m_\mathrm{v} + m_\mathrm{w}$ is the total mass of the water substance component. The conditions of a closed total system (implicit in Equation (97) are expressed by

$$m_\mathrm{d} = \text{const.}$$

$$m_\mathrm{t} = m_\mathrm{v} + m_\mathrm{w} = \text{const.}$$

According to Equation (98), the partial derivatives in Equation (97) are really sums of the partial derivatives for the two components in the two phases, multiplied by the respective masses. Of these derivatives, we know that, within the ideal gas approximation,

$$\left(\frac{\partial h_\mathrm{d}}{\partial T}\right)_{\mathrm{p,m}} = c_{\mathrm{p_d}}\,, \qquad \left(\frac{\partial h_\mathrm{v}}{\partial T}\right)_{\mathrm{p,m}} = c_{\mathrm{p_v}}\,, \qquad \left(\frac{\partial h_\mathrm{d}}{\partial p}\right)_{\mathrm{T,m}} = \left(\frac{\partial h_\mathrm{v}}{\partial p}\right)_{\mathrm{T,m}} = 0\,.$$

For water,

$$\left(\frac{\partial h_\mathrm{w}}{\partial T}\right)_{\mathrm{p,m}} = c_\mathrm{w}$$

where we do not need to specify "at constant pressure" in the specific heat, because c_p and c_v differ very little for water and ice (cf. Chapter III, Section 11). It may also be shown that

$$\left(\frac{\partial h_\mathrm{w}}{\partial p}\right)_{\mathrm{T,m}}$$

which may be computed from Equation (42) in Chapter III, Section 8, is a negligible quantity*.

Introducing these values into Equation (97), we obtain

$$\begin{aligned} \mathrm{d}H &= (m_\mathrm{d}c_{\mathrm{p_d}} + m_\mathrm{v}c_{\mathrm{p_v}} + m_\mathrm{w}c_\mathrm{w})\,\mathrm{d}T + l_\mathrm{v}\,\mathrm{d}m_\mathrm{v} \\ &= mc_\mathrm{p}\,\mathrm{d}T + l_\mathrm{v}\,\mathrm{d}m_\mathrm{v} \end{aligned} \tag{99}$$

where c_p is the mean specific heat, given by

$$mc_\mathrm{p} = m_\mathrm{d}c_{\mathrm{p_d}} + m_\mathrm{v}c_{\mathrm{p_v}} + m_\mathrm{w}c_\mathrm{w}. \tag{100}$$

If we now want to integrate the expression (99), to find the enthalpy of any given state, we must choose a reference state by specifying a certain value of the temperature and of the mass of water vapor m_v; the pressure does not need to be specified, because the expression (99) does not depend on it. The integration constant is then fixed by assigning the value $H = 0$ to the reference state. We shall choose a state at a temperature T_0 and with all the water in the liquid state.

We have to consider a process by which the system changes its temperature to T and a mass m_v of water goes into the gas phase. We may choose, among others, the two paths indicated below: a) first evaporating m_v grammes of water at a constant temperature T_0 and pressure, and then heating the whole system to T, or b) first heating the dry air and the water to T and then evaporating m_v grammes of water at T.

$$\begin{tikzcd}
 & \left\{\begin{matrix} T_0 \\ m_\mathrm{d} \\ m_\mathrm{v} \\ m_\mathrm{w} \end{matrix}\right. \arrow[dr] & \\
\left.\begin{matrix} \text{Temperature:} & T_0 \\ \text{Mass of dry air:} & m_\mathrm{d} \\ \text{Mass of water vapor:} & 0 \\ \text{Mass of liquid water:} & m_\mathrm{t} \end{matrix}\right] \arrow[ur, "a"] \arrow[dr, "b"'] & & \left\{\begin{matrix} T \\ m_\mathrm{d} \\ m_\mathrm{v} \\ m_\mathrm{w} \end{matrix}\right. \\
 & \left\{\begin{matrix} T \\ m_\mathrm{d} \\ 0 \\ m_\mathrm{t} \end{matrix}\right. \arrow[ur] &
\end{tikzcd}$$

If we now integrate Equation (99) along both paths (inserting in each step the appropriate values of the temperature, or of the masses of vapor and water, and considering the specific heats as independent of the temperature), we obtain:

---

* $\left(\dfrac{\partial h_\mathrm{w}}{\partial p}\right)_{T,m} = v_\mathrm{w}(1 - \alpha_\mathrm{p}T) \cong v_\mathrm{w} \quad (\alpha_\mathrm{p} = -6 \times 10^{-5}\ \mathrm{K}^{-1})$

This will contribute in (97) a term $m_\mathrm{w}v_\mathrm{w}\,\mathrm{d}p$, which may be compared with the contribution $m_\mathrm{w}c_\mathrm{w}\,\mathrm{d}T$ from the temperature derivative. We see by comparing these two terms that a change of as much as 1 atm in the pressure is equivalent to a temperature change as small as 1/40 K.

(a)
$$H = H_0 + (m_d c_{p_d} + m_v c_{p_v} + m_w c_w)(T - T_0) + l_v(T_0) m_v$$
$$= H_0 + m c_p (T - T_0) + l_v(T_0) m_v \tag{101}$$

(b)
$$H = H_0 + (m_d c_{p_d} + m_t c_w)(T - T_0) + l_v(T) m_v \tag{102}$$

where H_0 is the value of H in the reference state. Both expressions, which are equivalent, are related by Kirchhoff's theorem Chapter II, Section 6 which may be written here (in integrated form):

$$l_v(T) - l_v(T_0) = (c_{p_v} - c_w)(T - T_0). \tag{103}$$

It should be noticed that the coefficient of $(T - T_0)$ in Equation (101) varies with m_v, and $l_v(T_0)$ is a constant, while in Equation (102) the coefficient is a constant, and $l_v(T)$ is a function of T(l_v decreases about 0.1% for each degree of increase in temperature). In Equation (102) the terms with T_0 and H_0 can thus be written as an integration constant:

$$H = (m_d c_{p_d} + m_t c_w) T + l_v(T) m_v + \text{const.} \tag{104}$$

If the formula is referred to the unit mass of dry air, i.e., if the system contains the unit mass of dry air, its enthalpy can be written

$$H_1 = (c_{p_d} + r_t c_w) T + l_v(T) r + \text{const.} \tag{105}$$

where $r_t = m_t/m_d$ and the subscript of H indicates that its value is referred to unit mass of dry air.

If the heat capacities of the vapor and the water are considered as small quantities, m_t is assumed negligible as compared with m_d and l_v is taken as approximately independent of the temperature, we may write the formulas:

$$H_1 = h \cong c_p T + l_v q + \text{const.}$$
$$\cong c_p T + l_v r + \text{const.} \tag{106}$$

where h is the enthalpy of the unit mass of the total system (including both components), as approximate expressions for either Equations (101) or (102). Here the expressions (87) for moist air can be written for c_p.

The advantage of having an integrated expression like Equation (101), (102) or (104) lies in that we can calculate the difference ΔH between any two states of a closed system by simple difference, the integration having been done once and for all. Differentiation of these formulas will of course give back Equation (99) or an equivalent expression.

If we want to derive an expression for the internal energy, we start with

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_{p,m} \mathrm{d}T + \left(\frac{\partial U}{\partial p}\right)_{T,m} \mathrm{d}p + (\mathrm{u}_v - \mathrm{u}_w)\,\mathrm{d}m_v \tag{107}$$

instead of Equation (97). We may then notice that the derivatives with respect to p vanish as before, that the derivatives with respect to T give specific heats at constant volume (instead of at constant pressure; the one for liquid water being practically the same), and that

$$\mathrm{u}_{\mathrm{w}} = h_{\mathrm{w}} - pv_{\mathrm{w}}$$

$$\mathrm{u}_{\mathrm{v}} = h_{\mathrm{v}} - ev_{\mathrm{v}} = h_{\mathrm{v}} - R_{\mathrm{v}}T\,.$$

Following then the same integration as before, we obtain through the path b

$$U = (m_{\mathrm{d}}c_{\mathrm{v_d}} + m_{\mathrm{t}}c_{\mathrm{w}})T + [l_{\mathrm{v}}(T) - R_{\mathrm{v}}T]m_{\mathrm{v}} + \text{const.} \tag{108}$$

which could also be derived from Equation (104), with the appropriate substitutions ($h_{\mathrm{d}} = \mathrm{u}_{\mathrm{d}} + R_{\mathrm{d}}T; h_{\mathrm{v}} = \mathrm{u}_{\mathrm{v}} + R_{\mathrm{v}}T; h_{\mathrm{w}} \cong \mathrm{u}_{\mathrm{w}}; c_{\mathrm{p_d}} = c_{\mathrm{v_d}} + R_{\mathrm{d}}$); using (98) and a similar expression for U).

For a system with unit mass of dry air:

$$U_1 = (c_{\mathrm{v_d}} + r_{\mathrm{t}}c_{\mathrm{w}})T + [l_{\mathrm{v}}(T) - R_{\mathrm{v}}T]r + \text{const.} \tag{109}$$

and with simplifications similar to the ones applied to the enthalpy, Equation (108) becomes

$$U_1 \cong \mathrm{u} \cong c_{\mathrm{v}}T + (l_{\mathrm{v}} - R_{\mathrm{v}}T)q + \text{const.} = c_{\mathrm{v}}T + (l_{\mathrm{v}} - R_{\mathrm{v}}T)r + \text{const.} \tag{110}$$

$$\cong c_{\mathrm{v}}T + l_{\mathrm{v}}q + \text{const.} \cong c_{\mathrm{v}}T + l_{\mathrm{v}}r + \text{const.} \tag{111}$$

where U_1 and u have similar meanings to those of H_1 and h. In (111) the term $R_{\mathrm{v}}T$ has been neglected against the latent heat, considering that it only amounts to about 5 or 6% of l_{v}.

A similar derivation can be performed for the entropy, but now we can no longer disregard the effect of pressure, and the reference state must be specified with both the temperature and the pressure. We shall define it as two phases, isolated from each other, one consisting of m_{d} grams of dry air at temperature T_0 and pressure p_0, and the other consisting of m_{t} grams of liquid water at the same temperature (and pressure, although this parameter is immaterial for the condensed phase).

We shall now apply the total differential expression of the entropy separately for the two components in the two phases:

$$\mathrm{d}S_{\mathrm{i}} = \left(\frac{\partial S_{\mathrm{i}}}{\partial T}\right)_{\mathrm{p,m}} \mathrm{d}T + \left(\frac{\partial S_{\mathrm{i}}}{\partial p}\right)_{\mathrm{T,m}} \mathrm{d}p + s_{\mathrm{i}}\,\mathrm{d}m_{\mathrm{i}} \tag{112}$$

i stands for *d*, *v* or *w*, and $S_{\mathrm{i}} = m_{\mathrm{i}}s_{\mathrm{i}}$. We may notice that p is here the pressure of the particular component for the two gases, p_{d} and e, while for water it is the total pressure p exerted upon it. As before,

$$S = S_{\mathrm{d}} + S_{\mathrm{v}} + S_{\mathrm{w}} = m_{\mathrm{d}}s_{\mathrm{d}} + m_{\mathrm{v}}s_{\mathrm{v}} + m_{\mathrm{w}}s_{\mathrm{w}}\,. \tag{113}$$

In applying Equation (112) to the dry air we notice that $\mathrm{d}m_{\mathrm{d}} = 0$, and that (cf. Chapter III, Section 7)

$$\left(\frac{\partial s_{\mathrm{d}}}{\partial T}\right)_{\mathrm{p,m}} = \frac{c_{\mathrm{p_d}}}{T}; \quad \left(\frac{\partial s_{\mathrm{d}}}{\partial p}\right)_{\mathrm{T,m}} = -\left(\frac{\partial v}{\partial T}\right)_{\mathrm{p,m}} = -\frac{R_{\mathrm{d}}}{p_{\mathrm{d}}}\,.$$

Therefore:

$$dS_d = m_d ds_d = m_d c_{p_d}\, d \ln T - m_d R_d\, d \ln p_d\,. \tag{114}$$

We also notice that

$$\left(\frac{\partial s_v}{\partial T}\right)_{p,m} = \frac{c_{p_v}}{T}; \qquad \left(\frac{\partial s_w}{\partial T}\right)_{p,m} = \frac{c_w}{T}$$

$$\left(\frac{\partial s_v}{\partial p}\right)_{T,m} = -\frac{R_v}{e}; \qquad \left(\frac{\partial s_w}{\partial p}\right)_{T,m} = -\left(\frac{\partial v_w}{\partial T}\right)_{p,m} \cong 0\,,$$

so that

$$dS_v = m_v c_{p_v}\, d \ln T - m_v R_v\, d \ln e + s_v\, dm_v \tag{115}$$

$$dS_w = m_w c_w\, d \ln T + s_w\, dm_w\,. \tag{116}$$

We now make the sum $dS = dS_d + dS_v + dS_w$, taking into account that $dm_w = -dm_v$ and that

$$s_v - s_w = \frac{l_v}{T}.$$

We obtain

$$dS = (m_d c_{p_d} + m_v c_{p_v} + m_w c_w)\, d \ln T - m_d R_d\, d \ln p_d - - m_v R_v\, d \ln e + \frac{l_v}{T}\, dm_v\,. \tag{117}$$

In order to integrate this expression, we consider now that the air undergoes the reversible processes

$$T_0,\ p_0 \to T,\ p_0 \to T,\ p_d$$

and the water substance the reversible processes

$$\left\{\begin{array}{ll}\text{mass of vapor:} & 0\\ \text{mass of water:} & m_t\\ \text{temperature:} & T_0\\ \text{pressure:} & p_0\end{array}\right. \to \left\{\begin{array}{l}0\\ m_t\\ T\\ p_0\end{array}\right. \to \left\{\begin{array}{l}0\\ m_t\\ T\\ e_w(T)\end{array}\right. \to \left\{\begin{array}{l}m_v\\ m_w\\ T\\ e_w(T)\,.\end{array}\right.$$

We integrate Equation (117) over the total change, and obtain

$$S = S_0 + (m_d c_{p_d} + m_t c_w) \ln \frac{T}{T_0} - m_d R_d \ln \frac{p_d}{p_0} + \frac{l_v(T) m_v}{T} \tag{118}$$

where S_0 is the entropy at the reference state*.

We have now two separate subsystems, one consisting of dry air at T, p_d and the other consisting of water in presence of its saturated vapor. The two gaseous phases occupy the same volume v, by hypothesis (within the ideal behavior assumption), and they can be mixed by an ideal process using semipermeable membranes, as described in Chapter III, Section 10, without change in entropy.

Provision should also be made in this ideal process, to perform the increase in pressure over the water from e_w to $p = p_d + e_w$, but this can be disregarded because the effect on the entropy is negligible.

We have thus finally the heterogeneous system in which we are interested: m_w grammes of liquid water in presence of a mixture of dry air and saturated vapor at the partial pressures p_d and e_w. Its entropy (referred to the reference state as defined) is given by Equation (118).

As we did for the enthalpy (Equation (104)), we can consider the terms with T_0, p_0 and s_0 as an undetermined integration constant, and write

$$S = (m_d c_{p_d} + m_t c_w) \ln T - m_d R_d \ln p_d + \frac{l_v(T)\, m_v}{T} + \text{const.} \tag{119}$$

The entropy S_1 of a system with unit mass of dry air can be written

$$S_1 = (c_{p_d} + r_t c_w) \ln T - R_d \ln p_d + \frac{l_v(T) r}{T} + \text{const.} \tag{120}$$

Making the same simplifications as before (Equation (106)) and considering that $p_d \cong p$, we obtain the approximate expressions

$$S_1 \cong s \cong c_p \ln T - R_d \ln p + \frac{l_v q}{T} + \text{const.} =$$

$$= c_p \ln T - R_d \ln p + \frac{l_v r}{T} + \text{const.} \tag{121}$$

where s is the entropy of unit mass of cloud.

We have derived the expression for a system with the vapor pressure saturated at the given temperature, because it is the case in which we shall be interested. By separating the water phase and adding an appropriate expansion of the vapor in the series of steps imagined for the water substance in the derivation, it could be easily seen that a term $-m_v R_v \ln (e/e_w)$ should be added to Equation (119) if the vapor pressure of the system is e rather than e_w; obviously, such a system could not be in equilibrium.

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* We may notice that by differentiation of this expression, one obtains

$$\mathrm{d}s = (m_d c_{p_d} + m_t c_w)\, \mathrm{d} \ln T - m_d R_d\, \mathrm{d} \ln p_d + \frac{l_v(T)}{T} \mathrm{d}m_v - \frac{l_v(T) m_v}{T^2} \mathrm{d}T + \frac{m_v}{T} \mathrm{d}l_v(T).$$

This is an alternative formula for Equation (117) and can be seen to coincide with it by taking into account the Clausius-Clapeyron equation $\mathrm{d} \ln e/\mathrm{d}T = l_v(T)/R_v T^2$ and Kirchhoff's law $\mathrm{d}l_v = (c_{p_v} - c_w)\,\mathrm{d}T$.

PROBLEMS

1. The average value of the heat of vaporization of water in the temperature interval 90–100 °C is 542 cal g^{-1}. Derive the value of the water vapor pressure at 90 °C.
2. From the equation

$$\log_{10} e = -\frac{2937.4}{T} - 4.9283 \log_{10} T + 23.5471$$

for the saturation vapor pressure of water (where e is given in mb), derive its latent heat of vaporization at 10 °C.

3. The specific volume of liquid water is 1.000 cm^3 g^{-1}, and that of ice, 1.091 cm^3 g^{-1}, at 0 °C. What is the rate of change of the melting point of ice with pressure in K atm^{-1}?
4. (*a*) The formula

$$\log_{10} e = 9.4041 - \frac{2354}{T}$$

gives the water vapor pressure (e in mb) as a function of the temperature. Using this expression, whose constants have been adjusted to give the experimental value $e = 6.11$ mb for 0 °C, and the value of R^* from tables, derive the change in entropy when 1 mol of water evaporates in conditions close to equilibrium, at 0 °C. Give the result in cal K^{-1} mol^{-1}.

(b) How much should be added to ΔS if the process takes place at 25 °C?

Use the value $e_{25\,^\circ\mathrm{C}} = 31.67$ mb. Assume that l_v is unknown.

5. The melting point of ice is depressed by 0.075 degrees when the pressure is increased by 10 atm. From this information derive the value of the latent heat of freezing. The density of ice is 0.917 g cm^{-3}.
6. An air mass has a temperature of 30 °C and a relative humidity of 50% at a pressure of 1000 mb. Derive the values of: water vapor pressure, mixing ratio, specific humidity, specific heat capacity at constant pressure, virtual temperature, and the coefficient $\varkappa$. What would be the values of its potential temperature and its virtual potential temperature after expanding the air adiabatically to 900 mb.
7. A mass of moist air is at a pressure of 900 mb and a temperature of 2.1 °C. The mixing ratio is $r = 3 \times 10^{-3}$. Compute T_v, R, c_p and $\varkappa$.
8. The saturation vapor pressure at 25 °C is 31.67 mb.
   (a) What is the partial vapor pressure of a parcel of air at that temperature, if its dew point is 5 °C? (The dew point is the temperature at which the air becomes saturated, when cooled isobarically). Use neither diagrams nor the vapor pressure table.
   (b) What is the value of the mixing ratio r, if the pressure is 1000 mb?
   (c) What will be the values of the vapor pressure and the mixing ratio, if the parcel expands to 800 mb?

9. Knowing that saturated air at 30 °C and 1000 mb has a mixing ratio $r_w = 27.7\ \mathrm{g\ kg^{-1}}$, and that the average value of the latent heat of vaporization between 30 °C and 0 °C is 588.4 cal $\mathrm{g^{-1}}$, calculate the saturation mixing ratio at this last temperature and 500 mb.
10. Using the value of the latent heat of fusion from tables, calculate the ratio e_w/e_i at -10 °C (e_w = saturation vapor pressure with respect to water; e_i = *id.* with respect to ice).
11. 1 g of dry air is saturated with water vapor at 20 °C.

    (1) What is the specific change in enthalpy and in entropy of the moist air, when cooled at 1 atm of total pressure from 20 °C to 0 °C, condensation taking place?

    (2) What are the relative errors in Δh and Δs made in the following approximations:

    (*a*) Assuming $l_v = \text{const.} = 590\ \mathrm{cal\ g^{-1}}$:

    (*b*) Neglecting the heat capacity of water?

    (*c*) Taking $m = m_d$? (m: total mass; m_d: mass of dry air).
12. Derive Gibbs' phase rule (Equation (38)).