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**PART ONE** 

## **TWO-PHASE FLOW**

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## 1 Thermodynamic and Single-Phase Flow Fundamentals

## 1.1 States of Matter and Phase Diagrams for Pure Substances

## 1.1.1 Equilibrium States

Recall from thermodynamics that for a system containing a pure and isotropic substance that is at equilibrium, without any chemical reaction, and not affected by any external force field (also referred to as a P-v-T system), an equation of state of the following form exists:

$$f(P, v, T) = 0. (1.1)$$

This equation, plotted in the appropriate Cartesian coordinate system, leads to a surface similar to Fig. 1.1, the segments of which define the parameter ranges for the solid, liquid, and gas *phases*. The substance can exist in a stable equilibrium state only on points located on this surface. Using the three-dimensional plot is awkward, and we often use the *phase diagrams* that are the projections of the aforementioned surface on P-v (Fig. 1.2) and T-v (Fig. 1.3) planes. Figures 1.2 and 1.3 also show where *vapor* and *gas* occur. The projection of the aforementioned surface on the P-T diagram (Fig. 1.4) indicates that P and T are interdependent when two phases coexist under equilibrium conditions. All three phases can coexist at the *triple point*.

To derive the relation between *P* and *T* when two phases coexist at equilibrium, we note that equilibrium between any two phases  $\alpha$  and  $\beta$  requires that

$$g_{\alpha} = g_{\beta}, \tag{1.2}$$

where g = u + Pv - Ts is the specific Gibbs free energy. For small changes simultaneously in both *P* and *T* while the mixture remains at equilibrium, this equation gives

$$dg_{\alpha} = dg_{\beta}.\tag{1.3}$$

From the definition of g one can write

$$dg = d\mathbf{u} + Pdv + vdP - Tds - sdT.$$
(1.4)

However, from the Gibbs' equation (also referred to as the first Tds relation) we have

$$T\,ds = d\,\boldsymbol{u} + P\,dv. \tag{1.5}$$

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Figure 1.1. The P-v-T surface for a substance that contracts upon freezing.





We can now combine Eqs. (1.3) and (1.4) and write for the two phases

$$dg_{\alpha} = -s_{\alpha}dT + v_{\alpha}dP \tag{1.6}$$

and

$$dg_{\beta} = -s_{\beta}dT + v_{\beta}dP. \tag{1.7}$$

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# $P = P_{cr}$ $T_{cr}$ $T_{cr}$ $T_{sat}(P_1)$ Liquid $P_1$ $P_1$ $P_2 < P_1$ Vapor Vapor Vapor Vapor Triple point Sublimation T

## 1.1 States of Matter and Phase Diagrams for Pure Substances





Substitution from Eqs. (1.6) and (1.7) into Eq. (1.3) gives

$$\frac{dP}{dT} = \frac{s_{\beta} - s_{\alpha}}{v_{\beta} - v_{\alpha}}.$$
(1.8)

Now, for the reversible process of phase change of a unit mass at constant temperature, one has  $q = T(s_{\beta} - s_{\alpha}) = (h_{\beta} - h_{\alpha})$ , where q is the heat needed for the process. Combining this with Eq. (1.8), the well-known *Clapeyron's relations* are obtained:

evaporation:

$$\frac{dP}{dT} = \left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{\text{fg}}}{T_{\text{sat}}(v_{\text{g}} - v_{\text{f}})},\tag{1.9}$$

sublimation:

$$\left(\frac{dP}{dT}\right)_{\text{sublim}} = \frac{h_{\text{sg}}}{T_{\text{sublim}}(v_{\text{g}} - v_{\text{s}})},\tag{1.10}$$

melting:

$$\left(\frac{dP}{dT}\right)_{\text{melt}} = \frac{h_{\text{sf}}}{T_{\text{melt}}(v_{\text{f}} - v_{\text{s}})}.$$
(1.11)

## 1.1.2 Metastable States

The surface in Fig. 1.1 defines the stable equilibrium conditions for a pure substance. Experience shows, however, that it is possible for a pure and unagitated substance to remain at equilibrium in superheated liquid ( $T_{\rm L} > T_{\rm sat}$ ) or subcooled (supercooled) vapor ( $T_{\rm G} < T_{\rm sat}$ ) states. Very slight deviations from the stable equilibrium diagrams are in fact common during some phase-change processes. Any significant deviation from the equilibrium states renders the system highly unstable and can lead to rapid and violent phase change in response to a minor agitation.

In the absence of agitation or impurity, spontaneous phase change in a metastable fluid (homogeneous nucleation) must occur because of the random molecular fluctuations. Statistical thermodynamics predicts that in a superheated liquid, for example, pockets of vapor covering a range of sizes are generated continuously while surface tension attempts to bring about their collapse. The probability of the formation of 5

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Figure 1.5. Metastable states and the spinodal lines.

vapor embryos increases with increasing temperature and decreases with increasing embryo size. Spontaneous phase change (homogeneous boiling) will occur only when vapor microbubbles that are large enough to resist surface tension and would become energetically more stable upon growth are generated at sufficiently high rates.

One can also argue based on classical thermodynamics that a metastable state is in principle possible only as long as (Lienhard and Karimi, 1981)

$$\left(\frac{\partial v}{\partial P}\right)_T \le 0. \tag{1.12}$$

This condition implies that fluctuations in pressure are not followed by positive feedback, where a slight increase in pressure would cause volumetric expansion of the fluid, itself causing a further increase in pressure. When the constant-*T* lines on the *P*-v diagram are modified to permit unstable states, a figure similar to Fig. 1.5 results. The *spinodal lines* represent the loci of points where Eq. (1.12) with equal sign is satisfied. Lines AB and FG are constant-temperature lines for stable equilibrium states. Line BC represents metastable, superheated liquid. Metastable subcooled vapor occurs on line EF, and line CDE represents impossible (unstable) states.

Using the spinodal line as a criterion for nucleation does not appear to agree well with experimental data for homogeneous boiling. For pure water, the required liquid temperature for spontaneous boiling can be found from the following empirical correlation (Lienhard, 1976):

$$\frac{T_{\rm L}}{T_{\rm cr}} = 0.905 + 0.095 \left(\frac{T_{\rm sat}}{T_{\rm cr}}\right)^8,$$
(1.13)

where

 $T_{\rm cr}$  = critical temperature of water (647.15 K),  $T_{\rm L}$  = local liquid temperature (K),  $T_{\rm sat} = T_{\rm sat}(P_{\infty})$  (K), and  $P_{\infty}$  = pressure of water.

**EXAMPLE 1.1.** Calculate the superheat needed for spontaneous boiling in pure atmospheric water.

## 1.2 Transport Equations and Closure Relations

Table 1.1. Summary of parameters for Eq. (1.14).

Conservation/transport law	ψ	<i>φ</i>	J**
Mass	1	0	0_
Momentum	$ec{U}$	$\vec{g}$	$Par{I} - ar{ar{ au}}$
Energy	$u + \frac{U^2}{2}$	$ec{g}\cdotec{U}+\dot{q}_v/ ho$	$ec q' + (P ar {ar t} - ar {ar  au}) \cdot ec U$
Thermal energy in terms of enthalpy	h	$rac{1}{ ho}\Big(\dot{q}_{\mathrm{v}}+rac{DP}{Dt}+ar{ar{ au}}: ablaec{U}\Big)$	$ec{q}'$
Thermal energy in terms of internal energy	u	$rac{1}{ ho} \Big( \dot{q}_{ ext{v}} + P  abla \cdot ec{U} + ar{ar{ au}} :  abla ec{U} \Big)$	$ec{q}'$
Species <i>l</i> , mass-flux-based	$m_l$	$\frac{\dot{r}_l}{\rho}$	ji
Species <i>l</i> , molar-flux-based*	$X_l$	$\frac{R_l}{C}$	$ec{J_l}$

\* In Eq. (1.14),  $\rho$  must be replaced with **C**.

**SOLUTION.** We have  $P_{\infty} = 1.013$  bar; therefore  $T_{\text{sat}} = 373.15$  K. The solution of Eq. (1.13) then leads to  $T_{\text{L}} = 586.4$  K. The superheat needed is thus  $T_{\text{L}} - T_{\text{sat}} = 213.3$  K.

Example 1.1 shows that extremely large superheats are needed for homogeneous nucleation to occur in pure and unagitated water. The same is true for other common liquids. Much lower superheats are typically needed in practice, owing to heterogeneous nucleation. Subcooled (supercooled) vapors in particular undergo fast nucleation (fogging) with a supersaturation (defined as  $\frac{P_{\text{sat}}(T_{\text{G}})-P}{P_{\text{sat}}(T_{\text{G}})}$ ) of 1% or so (Friedlander, 2000).

## **1.2 Transport Equations and Closure Relations**

The local instantaneous conservation equations for a fluid can be presented in the following shorthand form (Delhaye, 1969):

$$\frac{\partial \rho \psi}{\partial t} + \nabla \cdot (\vec{U} \rho \psi) = -\nabla \cdot J^{**} + \rho \varphi, \qquad (1.14)$$

where  $\rho$  is the fluid density, U is the local instantaneous velocity, f represents the transported property, y is the source term for f, and  $J^{**}$  is the flux of f. Table 1.1 summarizes the definitions of these parameters for various conservation laws. All these parameters represent the mass-averaged mixture properties when the fluid is multicomponent. Other parameters used in the table are defined as follows:

- $\vec{g}$  = acceleration due to all external body forces,
- $\dot{q}_{\rm v}$  = volumetric energy generation rate,
- $\dot{r}_l = mass$  generation rate of species l in unit volume,
- $\dot{R}_l$  = mole generation rate of species *l* in unit volume,

$$\vec{a}'' = \text{heat flux},$$

- $\mathbf{u} =$ specific internal energy,
- h = specific enthalpy, and
- $m_l, X_l = \text{mass and mole fractions of species } l.$

Angular momentum conservation only requires that the tensor  $(P\bar{I} - \bar{\tau})$  remain unchanged when it is transposed. The thermal energy equation, represented by either 7

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the fourth or fifth row in Table 1.1, is derived simply by first applying  $\vec{U}$  (i.e., the dot product of the velocity vector) on both sides of the momentum conservation equation, and then subtracting the resulting equation from the energy conservation equation represented by the third row of Table 1.1. The energy conservation represented by the third row and the thermal energy equation are thus not independent from one another.

The equation set that is obtained by substituting from Table 1.1 into Eq. (1.14) of course contains too many unknowns and is not solvable without *closure relations*. The closure relations for single-phase fluids are either *constitutive relations*, meaning that they deal with constitutive laws such as the equation of state and thermophysical properties, or *transfer relations*, meaning that they represent some transfer rate law. The most obvious constitutive relations are, for a pure substance,

$$\rho = \rho(\mathbf{u}, P) \tag{1.15}$$

or

$$\rho = \rho(h, P). \tag{1.16}$$

For a multicomponent mixture these equations should be recast as

$$\rho = \rho(\mathbf{u}, P, m_1, m_2, \dots, m_{n-1}) \tag{1.17}$$

or

$$\rho = \rho(h, P, m_1, m_2, \dots, m_{n-1}), \tag{1.18}$$

where n is the total number of species. For a single-phase fluid, the constitutive relations providing for fluid temperature can be

$$T = T(\mathbf{u}, P) \tag{1.19}$$

$$T = T(h, P);$$

for a multicomponent mixture,

$$T = T(\mathbf{u}, P, m_1, m_2, \dots, m_{n-1})$$
(1.21)

or

$$T = T(h, P, m_1, m_2, \dots, m_{n-1}).$$
(1.22)

In Eqs. (1.17) through (1.22), the mass fractions  $m_1, m_2, ..., m_{n-1}$  can be replaced with mole fractions  $X_1, X_2, ..., X_{n-1}$ .

Let us assume that the fluid is Newtonian, and it obeys Fourier's law for heat diffusion and Fick's law for the diffusion of mass. The transfer relations for the fluid will then be

$$\bar{\bar{\tau}} = \tau_{ij} \mathbf{e}_i \mathbf{e}_j; \ \tau_{i,j} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \delta_{ij} \nabla \cdot \vec{U},$$
(1.23)

$$\vec{q}^{\prime\prime\prime} = -k\nabla \mathbf{T} + \sum_{l} \vec{j}_{l} h_{l}, \qquad (1.24)$$

$$\vec{j_l} = -\rho \boldsymbol{D}_{lm} \nabla m_l, \tag{1.25}$$

$$\vec{J_l} = -\mathbf{C}\boldsymbol{D}_{lm}\nabla X_l, \tag{1.26}$$

(1.20)

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## 1.2 Transport Equations and Closure Relations

where  $\mathbf{e}_i$  and  $\mathbf{e}_j$  are unit vectors for *i* and *j* coordinates, respectively, and  $\mathbf{D}_{lm}$  represents the *mass diffusivity* of species *l* with respect to the mixture.

Mass-flux- and molar-flux-based diffusion will be briefly discussed in the next section. The second term on the right side of Eq. (1.24) accounts for energy transport from the diffusion of all of the species in the mixture. For a binary mixture, one can use subscripts 1 and 2 for the two species, and the mass diffusivity will be  $D_{12}$ . The diffusive mass transfer is typically a slow process in comparison with the diffusion of heat, and certainly in comparison with even relatively slow convective transport rates. As a result, in most nonreacting flows the second term on the right side of Eq. (1.24) is negligibly small.

The last two rows of Table 1.1 are equivalent and represent the transport of species *l*. The difference between them is that the sixth row is in terms of mass flux and its rate equation is Eq. (1.25), whereas the last row is in terms of molar flux and its rate equation is Eq. (1.26). A brief discussion of the relationships among mass-fraction-based and mole-fraction-based parameters will be given in the next section. A detailed and precise discussion can be found in Mills (2001). The choice between the two formulations is primarily a matter of convenience. The precise definition of the average mixture velocity in the mass-flux-based formulation is consistent with the way the mixture momentum conservation is formulated, however. The mass-flux-based formulation is therefore more convenient for problems where the momentum conservation equation is also solved. However, when constant-pressure or constant-temperature processes are dealt with, the molar-flux-based formulation is more convenient.

In this formulation, and everywhere in this book, we consider only one type of mass diffusion, namely the *ordinary diffusion* that is caused by a concentration gradient. We do this because in problems of interest to us concentration gradient-induced diffusion overwhelms other types of diffusion. Strictly speaking, however, diffusion of a species in a mixture can be caused by the cumulative effects of at least four different mechanisms, whereby (Bird *et al.*, 2002)

$$\vec{j}_l = \vec{j}_{l,d} + \vec{j}_{l,p} + \vec{j}_{l,g} + \vec{j}_{l,T}.$$
(1.27)

The first term on the right side is the concentration gradient-induced diffusion flux, the second term is caused by the pressure gradient in the flow field, the third term is caused by the external body forces that may act unequally on various chemical species, and the last term represents the diffusion caused by a temperature gradient, also called the *Soret effect*. A useful discussion of these diffusion terms and their rate laws can be found in Bird *et al.* (2002).

The conservation equations for a Newtonian fluid, after implementing these transfer rate laws in them, can be written as follows.

Mass conservation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0 \tag{1.28}$$

or

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \vec{U} = 0. \tag{1.29}$$

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Momentum conservation, when the fluid is incompressible and viscosity is constant:

$$\rho \frac{D\vec{U}}{Dt} = \frac{D(\rho \vec{U})}{Dt} = -\nabla P + \rho \vec{g} + \mu \nabla^2 \vec{U}.$$
(1.30)

Thermal energy equation for a pure substance, in terms of specific internal energy:

$$\rho \frac{D\mathbf{u}}{Dt} = \nabla \cdot k \nabla T - P \nabla \cdot \vec{U} + \mu \Phi.$$
(1.31)

Thermal energy equation for a pure substance, in terms of specific enthalpy:

$$\rho \frac{Dh}{Dt} = \nabla \cdot (k \nabla T) + \frac{DP}{Dt} + \mu \Phi, \qquad (1.32)$$

where the parameter  $\Phi$  is the dissipation function (and where  $\mu\Phi$  represents the viscous dissipation per unit volume). For a multicomponent mixture, the energy transport caused by diffusion is sometimes significant and needs to be accounted for in the mixture energy conservation. In terms of specific enthalpy, the thermal energy equation can be written as

$$\rho \frac{Dh}{Dt} = \nabla \cdot (k \nabla T) + \frac{DP}{Dt} + \mu \Phi - \nabla \cdot \sum_{l=1}^{n} \vec{j}_{l} h_{l}.$$
 (1.33)

Chemical species mass conservation, in terms of partial density and mass flux:

$$\frac{\partial \rho_l}{\partial t} + \nabla \cdot (\rho_l \vec{U}) = \nabla \cdot (\rho \boldsymbol{D}_{12} \nabla m_l) + \dot{r}_l.$$
(1.34)

Chemical species mass conservation in terms of mass fraction and mass flux:

$$\rho \left[ \frac{\partial m_l}{\partial t} + \nabla \cdot (m_l \vec{U}) \right] = \nabla \cdot (\rho \boldsymbol{D}_{12} \nabla m_l) + \dot{r}_l.$$
(1.35)

Chemical species mass conservation, in terms of concentration and molar flux:

$$\frac{\partial \mathbf{C}_l}{\partial t} + \nabla \cdot (\mathbf{C}_l \vec{\tilde{U}}) = \nabla \cdot (\mathbf{C} \mathbf{D}_{12} \nabla X_l) + \dot{R}_l.$$
(1.36)

Chemical species mass conservation, in terms of mole fraction and molar flux:

$$\mathbf{C}\left[\frac{\partial X_l}{\partial t} + \vec{\tilde{U}} \cdot \nabla X_l\right] = \nabla \cdot (\mathbf{C} \mathbf{D}_{12} \nabla X_l) + \dot{R}_l - X_l \sum_{j=1}^n \dot{R}_j.$$
(1.37)

## 1.3 Single-Phase Multicomponent Mixtures

By mixture in this chapter we mean a mixture of two or more chemical species in the same phase. Ordinary dry air, for example, is a mixture of  $O_2$ ,  $N_2$ , and several noble gases in small concentrations. Water vapor and  $CO_2$  are also present in air most of the time.

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### **1.3 Single-Phase Multicomponent Mixtures**

The *partial density* of species  $l, \rho_l$ , is simply the in situ mass of that species in a unit mixture volume. The mixture density  $\rho$  is related to the partial densities according to

$$\rho = \sum_{l=1}^{n} \rho_l \tag{1.38}$$

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with the summation here and elsewhere performed on all the chemical species in the mixture. The mass fraction of species l is defined as

$$m_l = \frac{\rho_l}{\rho}.\tag{1.39}$$

The *molar concentration* of chemical species i,  $\rho_l$ , is defined as the number of moles of that species in a unit mixture volume. The forthcoming definitions for the mixture molar concentration and the *mole fraction* of species l will then follow:

$$\mathbf{C} = \sum_{l=1}^{n} \mathbf{C}_{l} \tag{1.40}$$

and

$$X_l = \frac{\mathbf{C}_l}{\mathbf{C}}.\tag{1.41}$$

Clearly,

$$\sum_{l=1}^{n} m_l = \sum_{l=1}^{n} X_l = 1.$$
(1.42)

The following relations among mass-fraction-based and mole-fraction-based parameters can be easily shown:

$$\rho_l = M_l \mathbf{C}_l, \tag{1.43}$$

$$m_{l} = \frac{X_{l}M_{l}}{\sum_{j=1}^{n} X_{j}M_{j}} = \frac{X_{l}M_{l}}{M},$$
(1.44)

$$X_{l} = \frac{m_{l}/M_{l}}{\sum_{j=1}^{n} \frac{m_{j}}{M_{j}}} = \frac{m_{l}M}{M_{l}},$$
(1.45)

where M and  $M_i$  represent the mixture and chemical specific i molar masses, respectively, with M defined according to

$$M = \sum_{j=1}^{n} X_{j} M_{j}$$
 (1.46a)

or

$$\frac{1}{M} = \sum_{j=1}^{n} \frac{m_j}{M_j}.$$
 (1.46b)

When one component, say component *j*, constitutes the bulk of a mixture, then

$$M \approx M_j \tag{1.47}$$