

# **Thermodynamics and Physical Kinetics**

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# Contents

<b>1 The basis for thermodynamic reasoning</b>	<b>8</b>
1.1 Definitions and Postulates . . . . .	8
1.1.1 System boundaries . . . . .	9
1.1.2 Equilibrium states . . . . .	11
1.1.3 Thermodynamic properties of systems . . . . .	12
1.2 Postulates . . . . .	13
1.2.1 The Energy Postulate . . . . .	13
1.2.2 Definition of temperature, pressure, and chemical potentials . . . . .	15
1.2.3 The Entropy Postulate . . . . .	16
1.3 The Euler and Gibbs-Duhem Relations . . . . .	17
1.3.1 First-order homogeneous functions . . . . .	17
1.3.2 Intensive properties . . . . .	19
1.3.3 Derivation of the Euler relation . . . . .	20
1.3.4 Derivation of the Gibbs-Duhem relation . . . . .	21
1.3.5 Change of the independent variables . . . . .	22
1.3.6 The Helmholtz and Gibbs functions . . . . .	24
1.4 The number of independent intensive variables for a single component simple-material system . . . . .	26
1.4.1 $T$ and $P$ as independent intensive properties for a single component system . . . . .	26

1.4.2	Single component, simple-material system with $s$ and $v$ as the independent variables . . . . .	28
1.5	The second derivatives for single component, simple-material systems . . . . .	30
1.5.1	Maxwell relations and relations between partial derivatives . . . . .	30
1.5.2	The $Tds$ equations and number of independent second partials . . . . .	32
1.6	Equations of state from physical arguments . . . . .	33
1.6.1	Ideal gas . . . . .	34
1.6.2	Ideal gas mixture . . . . .	34
1.6.3	Compressible liquid . . . . .	35
1.6.4	Weak liquid solution . . . . .	37
1.6.5	Example C1.7-1 . . . . .	44
1.7	Phases of a single component system . . . . .	50
1.8	Equilibrium between a liquid and its vapor . . . . .	50
1.8.1	The saturation-vapor pressure . . . . .	53
1.8.2	Saturation-vapor temperature . . . . .	55
1.8.3	Equilibrium between a liquid and its vapor when $T$ and $v$ are the independent variables . . . . .	57
1.8.4	Slope of the phase boundary between the liquid and its vapor: the Clausius-Clapeyron equation . . . . .	58
1.9	Equilibrium between the solid and liquid phases of a single component substance	60
1.9.1	Energy required to change the phase of a substance . . . . .	62
1.10	Triple point of a substance . . . . .	65
1.11	Thermodynamic potentials and phase stability . . . . .	67
1.11.1	Interaction between a composite system with a reservoir . . . . .	69
1.11.2	The Helmholtz function as the criterion for equilibrium . . . . .	73
1.11.3	The Gibbs interaction between a composite system and reservoir . . . . .	75
1.12	Phase transitions and phase stability . . . . .	76
1.13	Phase stability predicted from an equation of state . . . . .	80

1.13.1 The absent mechanism for a liquid-vapor phase transition . . . . .	83
1.14 Chapter 1 Problems . . . . .	84
	<b>96</b>

# List of Figures

1.1	A simple-material system may be viewed as a composite system in which each subsystem consists of the same substance. . . . .	18
1.2	The liquid is initially pure, and the walls of the piston-cylinder relation are impermeable. . . . .	38
1.3	Schematic of a composite system, with subsystem A and B, that interacts with a reservoir. System A is a liquid solution and system B is pure solute. Initially the temperature of the system and the reservoir are different. . . . .	41
1.4	An ideal mixture that consists of $\text{H}_2\text{O}$ vapor and $\text{N}_2$ is in contact weak $\text{H}_2\text{O}$ at 25 °C and 101.325 kPa . . . . .	46
1.5	A phase diagram is shown for a substance that contracts on freezing. . . . .	51
1.6	Fluid phases of a component enclosed in a constant volume system. . . . .	52
1.7	In an isothermal two phase system, the chemical potentials of the liquid and vapor phases can be equal at only one pressure. . . . .	54
1.8	Possible relations between $P_s(T)$ and T. . . . .	55
1.9	For a given pressure, the relation between the chemical potential functions of a liquid and its vapor is shown. . . . .	57
1.10	The fluid phases the system shown Fig. ?? could adopt are shown schematically.	59
1.11	A liquid phase in equilibrium with a solid phase in the absence of surface effects and gravity . . . . .	60

1.12 In A. the chemical potential of a solid which contract on solidifying is plotted, and on the right the chemical potential of a solid that expands on solidifying is shown. . . . .	62
1.13 When the solid phase has a larger specific volume than the liquid phase, the slope of $P_{ls}(T)$ is negative, but if the specific volume of the solid is smaller than that of the liquid, the slope is positive as seen Fig 1.5 . . . . .	63
1.14 The solid and liquid phases of a single component system are initially in equilibrium are then heated to produce more liquid. . . . .	64
1.15 An isolated system containing three phases of a pure substance. . . . .	66
1.16 For a given temperature, since the solid, liquid and vapor phases have different values of their specific volumes, the chemical potentials cannot be equal in more than one thermodynamic state. . . . .	68
1.17 Non-quasistatic work is done on a composite system. The system is initially in equilibrium and finally returns to equilibrium with the reservoir, but between the two equilibrium configurations, disequilibrium can exist. . . . .	70
1.18 A composite system is indicated that is in equilibrium with a surrounding reservoir when a constraint is in place. The constraint is then removed and the system is allowed to evolve for a short period of time. The constraint is replaced, and the system allowed to come to a new equilibrium state. . . . .	72
1.19 Each time the constraint is released on the system shown in Fig. 1.18, the function that acts as the thermodynamic potential spontaneously decreases. Then when the constraint is replaced the system comes to equilibrium again. The solid dots indicate these states. The function that acts as a thermodynamic potential depends on the constraints. . . . .	74
1.20 Schematic of a system interacting with a surrounding reservoir. The interactions allow the reservoir to impose its temperature and pressure on the system, but no molecular exchange between the system and the reservoir are allowed.	75

1.21 Calculated van der Waals isotherm for CO <sub>2</sub> . The upper one is for a temperature and a pressure above the critical values (304.2 K and 7.39 MPa), and the lower one is 275.16 K. . . . .	78
1.22 A fluid in a piston-cylinder arrangement that is maintained isothermal and at constant pressure is predicted to have three possible configurations. . . . .	79
1.23 Calculated isotherm for CO <sub>2</sub> at 2 °C. . . . .	81
1.24 Calculated isotherm for CO <sub>2</sub> at 2 °C. . . . .	83
1.25 . . . . .	90
1.26 . . . . .	91
1.27 Two phase system. . . . .	92
1.28 Two phase system. . . . .	94

# List of Tables

1.1	Properties at the critical point [1]. . . . .	77
1.2	Calculated values of van der Waals constants . . . . .	80
1.3	Thermodynamic stability of the different branches of a van der Waals isotherm. . . . .	82
1.4	Properties of water at the triple point [1]. . . . .	88

# Chapter 1

## The basis for thermodynamic reasoning

In this chapter, we set down the thermodynamic postulates and define the thermodynamic properties such as temperature, pressure and chemical potentials. From the postulates, we investigate the physical characteristics of these definitions. All thermodynamic predictions are based on these postulates. We compare the theoretical definitions of these properties with empirical observations, but we do not try to investigate the postulates themselves. We accept the postulates and examine the predictions that follow.

### 1.1 Definitions and Postulates

The boundary of a system determines how the system interacts with its surroundings. Once the boundary of a system is defined, thermodynamics can be applied to make extraordinarily general predictions about the **equilibrium** or final macroscopic state of the system. Many of these predictions are independent of the molecular composition of the system, but concern properties that all macroscopic systems share in an equilibrium state. We begin by consid-

ering a system that is limited to only certain possible **mechanisms of energy storage**. When other modes of energy storage become important, the description of the system is generalized.

### 1.1.1 System boundaries

A **system** is a region of space enclosed by a boundary, possibly containing a material. We consider two types of systems: one is a **simple-material system**, and the other, a **composite system**.

We suppose that an energy can be associated with a simple-material system, and that this energy arises from the molecular motion and interactions of the constituent molecules, atoms, electrons and nuclei in the system. For a simple-material system, this energy is denoted  $U$ , and called the internal energy. It is not the exact energy of the system, but it is the average energy of a large collection of systems that each satisfies a certain set of constraints. At present, we will not try to define how the average is obtained, but will save that discussion for Statistical Thermodynamics (Chapter 5). For now, we treat  $U$  as the mean of the system energy, and suppose the mean is very well defined, i.e., the standard deviation about the mean is very small compared to the mean.

If a simple-material system is in an equilibrium state, it is homogeneous in composition, isotropic, and there are no chemical reactions or effects that arise from electrical charges, surfaces or fields. A system that consists of a neutral fluid (a liquid or a vapor) can be approximated as a simple-material system. A solid system can also be approximated as a simple-material system provided energy storage in shearing strains can be neglected. This eliminates bending in a simple-material system.

A simple-material system can consist of an arbitrary number of chemical species. The amount of any one species is indicated by the number of moles of that species. For chemical species  $i$ , the number of moles is denoted  $N_i$ . The composition of the system is indicated by the

number of moles of each chemical component:  $N_1, N_2 \dots N_r$  where there are a total of  $r$  components present in the simple-material system. We will generalize later to more general types of systems, but we will start with a simple-material system.

The boundaries of a simple-material system can be diathermal or adiabatic; its walls can be rigid but immovable, or rigid and freely moving; and the walls may be molecularly impermeable or semi-permeable or completely permeable. The boundaries of a system determine how the energy of the system can be changed.

An **isolated**, simple-material system is one that has adiabatic, immovable, and impermeable boundaries. Its energy,  $U$ , cannot be changed and its properties are independent of its surroundings.

An **isolated composite system** consists of a number of constituent subsystems that are each simple-material systems. There can be exchanges of energy, moles or expansion of the constituent subsystems within an isolated composite system, but no exchanges between the composite system and its surroundings. So the total energy, total volume and total number of moles of an isolated composite system are each constants, and these constants act as constraints on the composite system.

The concept of thermodynamic work is the same as that in mechanics: if a force acts on the boundary of a system to change the volume of the system (a force moves through a distance), then work is done on the system. Thus, one method of changing the energy of a simple-material system is by changing its volume, i.e., by doing work at the system boundary.

If the boundary of a simple-material system is **immovable, permeable, but adiabatic**, the system can undergo a change in energy as a result of exchanging molecules with its surroundings, but the system cannot be heated by the surroundings nor can the surroundings do work on the system. Thus, a second mode of changing the energy of a simple-material system is by molecular transport through its boundaries.

If the boundary of a simple-material system is **freely moving, permeable, and diathermal**, the system can undergo a change in energy by work being done at the boundary, by changing the number of moles of any component, and by heating the system. Thus, there are only  $r+2$  mechanisms by which the energy of a simple-material system may be changed. Our postulates will reflect this limitation.

### 1.1.2 Equilibrium states

There are special states that a simple-material system can occupy, called **equilibrium** states, and there are three different types of these states that we consider.

The one most commonly considered is the **stable equilibrium state**. Once a system arrives in a stable equilibrium state, **spontaneous macroscopic** changes are no longer possible. In other words, the system remains **indefinitely** in the same thermodynamic state. At all times, there are, of course, spontaneous changes at the microscopic or molecular scale, due to molecular or atomic motion, but if the system is in a stable equilibrium state, these **microscopic changes** do not cause **macroscopic** changes in the system. A stable equilibrium state satisfies both the necessary and sufficient conditions for equilibrium. These conditions will be defined by the postulates.

Another type of equilibrium state that is often encountered is the **metastable** equilibrium state. Such a state satisfies the necessary conditions for equilibrium, but not the sufficient conditions. In other words, if a sufficiently large spontaneous, microscopic change takes place in such a system, the system would be displaced from the metastable state. It is often argued that if one waits long enough, sufficiently large microscopic changes do take place in a simple-material system so that a metastable system cannot stay indefinitely in a metastable state.

The third type of equilibrium state is an **unstable** equilibrium state. These states are not thought to exist in simple-material systems, but they can exist in composite systems, as

will be seen in Chapter 3. A composite system can remain in an unstable equilibrium state only for an infinitesimal time. Microscopic or molecular motion is sufficient to cause an unstable system to make a spontaneous transition out of an unstable equilibrium state. For a system to be in an unstable equilibrium state, it must satisfy the necessary conditions for an equilibrium state, but cannot satisfy the sufficient conditions. We will encounter all three types of equilibrium states.

In order for a **composite system** to be in a stable equilibrium state, all of the constituent subsystems must be in stable equilibrium states. A composite system may be isolated, if its **outer boundary is adiabatic, impermeable, rigid and immovable**, while the boundary between its constituent subsystems are unrestricted. Thus, the internal system boundaries can be diathermal, permeable, semi-permeable, rigid and moveable or any combination of these, but the composite system itself remains isolated.

### 1.1.3 Thermodynamic properties of systems

For a quantity to be an equilibrium thermodynamic property, the quantity must be independent of the history of the system, and every time a system is put in a particular equilibrium state the quantity must have the same value. Thus, there can be no hysteresis in the value of a thermodynamic equilibrium property. Below we discuss what properties must be known to **fully characterize** a simple-material system in an equilibrium state.

A thermodynamic property is either extensive or intensive. The **extensive properties** of a system are those that define the size of a system. For example, the volume, the number of moles of each component, the total **internal energy** are extensive properties of a simple material system. These properties are denoted  $V, N_1, N_2, \dots, N_r$  and  $U$  respectively.

**Intensive properties** are only defined for simple material systems. They can be measured at a point in a simple-material system, and have the same value at every point, once the system has arrived in an equilibrium state.

## 1.2 Postulates

Since we are neglecting fields, surfaces, and chemical reactions, a simple-material system that has  $r$  chemical species present has  $r + 2$  energy storage modes.

### 1.2.1 The Energy Postulate

- A simple-material system has a property internal energy, denoted  $U$ , and a property **entropy**, denoted  $S$ . When a simple-material system is in an equilibrium state, it is characterized **completely** at the **macroscopic** level by  $r + 2$  extensive properties:  $S, V, N_1, N_2, \dots, N_r$ , and these properties act as the **independent variables** for the internal-energy function. Mathematically, then

$$U = U(S, V, N_1, \dots, N_r). \quad (1.1)$$

- The principle of conservation-of-energy is valid and can be applied to describe changes in energy of a simple-material system or a composite system.
- For a simple-material system in an equilibrium state, the internal energy function may be differentiated with respect to each of its independent variables:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N_1 \dots N_r} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N_1 \dots N_r} dV + \sum_{i=1}^r \left(\frac{\partial U}{\partial N_i}\right)_{S, V, \dots, N_j \dots} dN_i. \quad (1.2)$$

- The internal energy function is sufficiently well behaved mathematically so that it may be inverted to write

$$S = S(U, V, N_1 \dots N_r). \quad (1.3)$$

This requires

$$\left(\frac{\partial U}{\partial S}\right)_{V, N_1, \dots, N_r} \neq 0.$$

Equation (1.3) is the second form of a fundamental relation for a simple-material system. It contains all of the information that Eq. (1.1) contains, but it has a different set of independent variables. We emphasize that only certain functions can act as a fundamental relation. The postulates of thermodynamics are also discussed by Callen [2] who gives a slightly different version.

Each of the independent variables in the internal-energy function corresponds to a mode of energy storage. When we wish to generalize the thermodynamic description to systems other than simple-material systems, one of the first issues will be to identify the modes of energy storage of the new system.

As will be seen, if the function  $U(S, V, N_1, \dots, N_r)$  for a particular simple-material system is given in the form indicated in Eq. 1.1, then a complete description of the system at the macroscopic level is being given. The values of all of its macroscopic properties can be calculated from this function if the values of its independent variables are known. Such a relation is called a **fundamental relation** in the internal energy formulation, and it acts as the **definition of the simple material** at a macroscopic level. If a system is to be described at the molecular level, then the molecules constituting the system must be described, but a simple-material system is defined completely at the macroscopic level by  $U(S, V, N_1, \dots, N_r)$ . All of its macroscopic properties can be determined from this function.

In thermodynamics, we do not try to construct the fundamental relation—that is a task for statistical thermodynamics—but we make predictions about a system’s behavior knowing only that such a relation exists. As will be seen, this function can be transformed so other variables become the independent variables of the system without losing any information about the system. Thus, a simple material can be **defined** by more than one fundamental relation. The idea of using Eq. 1.1 as the definition of a substance at the macroscopic level was introduced by Gibbs [3] who formulated thermodynamics on a firm mathematical basis.

### 1.2.2 Definition of temperature, pressure, and chemical potentials

There is no definition of an intensive property for a composite system. The intensive properties are defined only for a simple-material system.

The **thermodynamic definition of temperature** is

$$T \equiv \left( \frac{\partial U}{\partial S} \right)_{V, N_1 \dots N_r}. \quad (1.4)$$

For a simple-material system, we will suppose  $T$  is positive. When we consider systems subjected to fields—in particular, magnetic fields—we will find that the temperature as defined by Eq. 1.4 can be negative, but to understand this result we must examine temperature from a quantum mechanical point of view. We postpone this generalization of the temperature concept until we consider statistical thermodynamics.

The **thermodynamic definition of pressure** is

$$P \equiv - \left( \frac{\partial U}{\partial V} \right)_{S, N_i \dots N_r}. \quad (1.5)$$

Note that there is no consideration of a force or a stress balance. The thermodynamic definition is based on the dependence of the internal energy on volume. A “pressure” is also defined in continuum mechanics that is based on a force balance. We will show that these two definitions of pressures are the same, **only if** the boundary on which the pressure acts is impermeable to molecular transport.

The **thermodynamic definition of the chemical potential** of component  $i$  in a simple-material system,  $\mu_i$ , is

$$\mu_i \equiv \left( \frac{\partial U}{\partial N_i} \right)_{S, V, \dots N_j \dots}. \quad (1.6)$$

When these definitions of the intensive properties are combined with Eq. (1.2), one obtains

an expression for the total differential of the internal energy

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dN_i \quad (1.7)$$

Since the postulates indicate the internal energy function  $U = U(S, V, N_1, \dots, N_r)$  may be inverted to obtain  $S = S(U, V, N_1, \dots, N_r)$ , we may invert Eq. (1.7) to obtain

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^r \frac{\mu_i}{T}dN_i. \quad (1.8)$$

Equations 1.7 and 1.8 are used repeatedly in thermodynamic analysis. Note their sources are the energy postulate and the definitions of  $T, P$  and  $\mu_1, \mu_2, \dots, \mu_r$ .

### 1.2.3 The Entropy Postulate

- The entropy of a simple-material system cannot be negative:

$$S = S(U, V, N_1 \dots N_r) \geq 0. \quad (1.9)$$

- If any simple-material substance is in a state for which

$$\left( \frac{\partial U}{\partial S} \right)_{V, N_1 \dots N_r} = 0, \quad (1.10)$$

then the entropy vanishes in this state.

- When an **isolated composite system** is in equilibrium, its entropy,  $S_c$ , is the sum of the entropies of each of its constituent subsystems. Thus, if there are  $\alpha$  subsystems in a particular isolated composite system

$$S_c = \sum_{i=1}^{\alpha} S^i(U^i, V^i, N_1^i, \dots, N_r^i). \quad (1.11)$$

- Similarly, the internal energy of an isolated composite system,  $U_c$ , is given by

$$U_c = \sum_{i=1}^{\alpha} U^i(S^i, V^i, N_1^i, \dots, N_r^i). \quad (1.12)$$

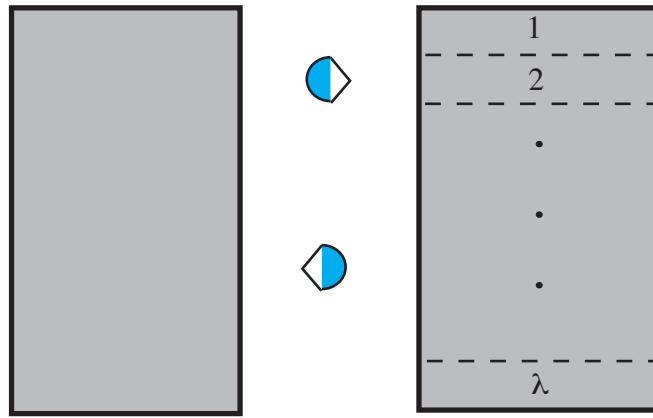
- If an isolated-composite system is not initially in a stable equilibrium state, it spontaneously evolves to a new state. Of the many configurations that satisfy the constraints on the composite system, the state finally adopted corresponds to a maximum of the total entropy of the composite system. This is the stable equilibrium state of the composite system.

## 1.3 The Euler and Gibbs-Duhem Relations

In general, there is **not** a fundamental relation for a **composite** system. Only a simple-material system has a fundamental relation. However, an important special case arises when a simple-material system is **viewed** as a **composite** system with each of the subsystems consisting of the **same substance**. Since a substance is defined by its fundamental relation, when a simple-material system is viewed in this way every subsystem has the same fundamental relation. The other way a simple material may be viewed is as a single system with properties  $S, V, N_1 \dots N_r$ . In order for these two ways of viewing a simple-material system to be thermodynamically consistent, a relation must exist between the extensive and intensive properties of a simple-material system. This relation is the Euler equation for simple material systems.

### 1.3.1 First-order homogeneous functions

As indicated in Fig. 1.1 any simple-material system may be **viewed** as a composite system with each subsystem consisting of the same substance. We show that this requires the



**Figure 1.1:** A simple-material system may be viewed as a composite system in which each subsystem consists of the same substance.

fundamental relation of a simple material system to be a first-order homogeneous function.

<sup>1</sup>

According to the Entropy Postulate, the total internal energy of a composite system,  $U_c$ , for which each of its  $\lambda$  subsystems has an internal energy  $U(S, V, N_1 \dots N_r)$  is given by

$$U_c = \lambda U(S, V, N_1 \dots N_r). \quad (1.13)$$

However, as indicated in Fig. 1.1, we have only imagined that the simple-material system to be divided into  $\lambda$  subsystems. Thus, in this special case, the composite system has the same fundamental relation as any one of its subsystems, but only different values of the independent variables:

$$U(S_c, V_c, N_{1c} \dots N_{rc}) = \lambda U(S, V, N_1 \dots N_r). \quad (1.14)$$

---

<sup>1</sup> **Definition:** A function  $f(x_1, x_2 \dots x_r)$  is a first-order homogeneous function if

$$f(\lambda x_1, \lambda x_2 \dots \lambda x_r) = \lambda f(x_1, x_2 \dots x_r).$$

where  $\lambda$  is a constant.

The independent variables of the composite system are each extensive; thus

$$S_c = \lambda S, \quad (1.15)$$

$$V_c = \lambda V, \quad (1.16)$$

and

$$N_{ic} = \lambda N_i \text{ for } 1 \leq i \leq r. \quad (1.17)$$

and Eq. 1.14 gives

$$U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r) = \lambda U(S, V, N_1 \dots N_r). \quad (1.18)$$

Thus, the fundamental relation of a simple-material system is a first-order homogeneous function. No function that is not a first-order homogeneous function can be claimed to be a fundamental relation.

### 1.3.2 Intensive properties

Now we show that since fundamental relations must be first-order homogeneous functions, the temperature, pressure, and chemical potentials must be intensive properties of a simple-material system, or in other words they must zero-order homogeneous functions.

Since a simple-material system may be viewed as a composite system with each of the constituent subsystems consisting of the same substance

$$U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r) = \lambda U(S, V, N_1 \dots N_r). \quad (1.19)$$

The partial differential of the left-side of Eq. (1.19) with respect to  $S$  gives

$$\begin{aligned} \left( \frac{\partial U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)}{\partial S} \right)_{\lambda V, \lambda N_1 \dots \lambda N_r} &= \left( \frac{\partial U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)}{\partial \lambda S} \right) \left( \frac{\partial \lambda S}{\partial S} \right) \\ &= \lambda T((\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)). \end{aligned} \quad (1.20)$$

From the right side of Eq. (1.19)

$$\lambda \left( \frac{\partial U(S, V, N_1 \dots N_r)}{\partial S} \right) = \lambda T(S, V, N_1 \dots N_r). \quad (1.21)$$

Thus,

$$T(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r) = T(S, V, N_1 \dots N_r). \quad (1.22)$$

A function that satisfies this condition is a zero-order homogeneous function.

Also, this equation says the temperature is independent of the size of a simple-material system. If the size of the system is expanded homogeneously—by increasing the value of each of the independent variables by a factor  $\lambda$ —the value of the temperature does not change. Thus, the definition of the temperature that is given in Eq. 1.4 defines an intensive property.

One may follow a similar procedure to show, the pressure and chemical potentials are also zero-order homogeneous functions, or intensive properties.

### 1.3.3 Derivation of the Euler relation

We return to Eq. 1.14, but this time we differentiate with respect to  $\lambda$  giving

$$\begin{aligned} & \frac{\partial U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)}{\partial \lambda S} \frac{\partial \lambda S}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)}{\partial \lambda V} \frac{\partial \lambda V}{\partial \lambda} \\ & + \sum_{i=1}^{\lambda} \frac{\partial U(\lambda S, \lambda V, \lambda N_1 \dots \lambda N_r)}{\partial \lambda N_i} \frac{\partial \lambda N_i}{\partial \lambda} = U(S, V, N_1 \dots N_r), \end{aligned} \quad (1.23)$$

and after making use of the definitions of the intensive properties, this equation may be written

$$TS - PV + \sum_{i=1}^r N_i \mu_i = U. \quad (1.24)$$

This relation expresses the internal energy of a simple material system in terms of the other thermodynamic properties. The Euler relation is part of the foundation of thermodynamics.

### 1.3.4 Derivation of the Gibbs-Duhem relation

If the Euler relation is differentiated, one finds

$$dU = TdS + SdT - PdV - VdP + \sum_{i=1}^r (\mu_i dN_i + N_i d\mu_i). \quad (1.25)$$

From the energy postulate and the definition of the intensive variables, Eq. 1.7 has been established:

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dN_i.$$

When the two expressions for  $dU$  are equated, one finds the Gibbs-Duhem equation

$$\sum_{i=1}^r N_i \mu_i = -SdT + VdP. \quad (1.26)$$

The Gibbs-Duhem equation will be applied repeatedly, but to see how strongly it affects the structure of thermodynamics, consider an important special case. Suppose a simple material system consists of  $N$  moles of a single component. Then the general Gibbs-Duhem relation for a single component system reduces to

$$d\mu = -sdT + vdP. \quad (1.27)$$

where  $s$  is the specific molar entropy and  $v$  is the specific molar volume. From the form of this equation, we may conclude that the independent variables of  $\mu$  are  $T$  and  $P$ . Then from Eq. (1.27), we may show that the independent, intensive variables of  $s$  and  $v$  are also  $T$  and  $P$ .

For example

$$\begin{aligned}s &= -\left(\frac{\partial \mu}{\partial T}\right), \\ v &= \left(\frac{\partial \mu}{\partial P}\right).\end{aligned}\quad (1.28)$$

Since  $\mu$  has been shown to have  $T$  and  $P$  as their independent intensive properties, Eq. (1.28) indicates that  $s$  and  $v$  have the same independent, intensive variables,  $T$  and  $P$ .

If the Euler relation is written on a per mole basis, then for a single component system

$$u = Ts - Pv + \mu \quad (1.29)$$

and since  $\mu$ ,  $s$  and  $v$  all have  $T$  and  $P$  as their independent, intensive variables so does  $u$ .

Thus, for a single-component, simple material system,  $T$  and  $P$  may be assigned independently. The other intensive properties may also be expressed in terms of  $T$  and  $P$ .

### 1.3.5 Change of the independent variables

The total differential of the internal energy of a simple-material system that has  $r$ -components present has been shown to be of the form

$$dU = TdS - PdV + \sum_{i=1}^r \mu_i dN_i. \quad (1.30)$$

The independent variables can be read from the expression for the total differential of a function; thus, as we know, the independent variables of  $U$  are  $S, V, N_1 \dots N_r$ . We define the extensive **Helmholtz function** as a **Legendre transform** of  $U$ , the internal energy.

A general procedure may be applied to make this transformation. The total differential of a function, say  $f = f(x_1, x_2, \dots, x_k)$ , can be expressed

$$df = \sum_{i=1}^k \left( \frac{\partial f}{\partial x_i} dx_i \right). \quad (1.31)$$

A Legendre transform of

$$f = f(x_1, x_2, \dots, x_k)$$

that has as its objective the introduction of

$$\left( \frac{\partial f}{\partial x_1} \right)$$

as an independent variable while eliminating  $x_1$  as an independent variable is done by defining a new function,  $g$ :

$$g \equiv f - x_1 \left( \frac{\partial f}{\partial x_1} \right). \quad (1.32)$$

To show that  $g$  has the desired set of independent variables, we form the total differential:

$$dg = df - x_1 d \left( \frac{\partial f}{\partial x_1} \right) - \left( \frac{\partial f}{\partial x_1} \right) dx_1, \quad (1.33)$$

and after combining Eqs. (1.31) and (1.33)

$$dg = -x_1 d \left( \frac{\partial f}{\partial x_1} \right) + \sum_{i=2}^k \left( \frac{\partial f}{\partial x_i} dx_i \right). \quad (1.34)$$

Hence, the independent variables of  $g$  are

$$\left( \frac{\partial f}{\partial x_1} \right), x_2, x_3, \dots, x_k,$$

and the Legendre transform has defined a function that has the desired properties.

If the function from which  $g$  was obtained were a first-order homogeneous function, the function  $g$  is also a first-order homogeneous function as may be seen by considering the following: So suppose  $f(x_1, x_2, \dots, x_r)$  is a first-order homogeneous function:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_r) = \lambda f(x_1, x_2, \dots, x_r). \quad (1.35)$$

If Eq. (1.35) is differentiated with respect to  $x_1$ , one obtains

$$\left( \frac{\partial f(\lambda x_1, \lambda x_2, \dots, \lambda x_r)}{\partial(\lambda x_1)} \right) \lambda = \lambda \left( \frac{\partial f(x_1, x_2, \dots, x_r)}{\partial x_1} \right),$$

or

$$\left( \frac{\partial f(\lambda x_1, \lambda x_2, \dots, \lambda x_r)}{\partial(\lambda x_1)} \right) = \left( \frac{\partial f(x_1, x_2, \dots, x_r)}{\partial x_1} \right). \quad (1.36)$$

From Eqs. (1.32) and (1.36)

$$\begin{aligned} g(\lambda x_1, \lambda x_2, \dots, \lambda x_r) &= f(\lambda x_1, \lambda x_2, \dots, \lambda x_r) - \lambda x_1 \left( \frac{\partial f(\lambda x_1, \lambda x_2, \dots, \lambda x_r)}{\partial(\lambda x_1)} \right), \\ g(\lambda x_1, \lambda x_2, \dots, \lambda x_r) &= \lambda \left( f(x_1, x_2, \dots, x_r) - x_1 \left( \frac{\partial f(x_1, x_2, \dots, x_r)}{\partial x_1} \right) \right), \\ g(\lambda x_1, \lambda x_2, \dots, \lambda x_r) &= \lambda g(x_1, x_2, \dots, x_r). \end{aligned} \quad (1.37)$$

Thus,  $g(x_1, x_2, \dots, x_r)$  is a first-order homogeneous function. And we conclude that when a Legendre transform is applied to change from one set of independent variables to another, the first-order homogeneous property of the original function is preserved.

### 1.3.6 The Helmholtz and Gibbs functions

We now define the Legendre transform of the internal energy that eliminates  $S$  as an independent variable. The new function is the Helmholtz function,  $F$ :

$$F \equiv U - TS. \quad (1.38)$$

After differentiating Eq. (1.38) and combining with Eq. 1.30, one finds

$$dF = -SdT - PdV + \sum_{i=1}^r \mu_i dN_i. \quad (1.39)$$

Thus,

$$F = F(T, V, N_1 \dots N_r).$$

and

$$\begin{aligned} S &= S(T, V, N_1 \dots N_r), \\ P &= P(T, V, N_1 \dots N_r), \\ \mu_i &= \mu(T, V, N_1 \dots N_r). \end{aligned} \quad (1.40)$$

These expressions for  $S$ ,  $P$  and  $\mu$  are equations of state in the Helmholtz formulation. Thus, all of the extensive variables may be expressed in terms of the new set of independent variables:  $T, V, N_1 \dots N_r$ ,

For a composite system that has  $\zeta$  subsystems

$$F_c = \sum_{\alpha=1}^{\zeta} F^{\alpha}. \quad (1.41)$$

A function also may be defined as the Legendre transform of the Helmholtz function that has as its independent variables  $T, P, N_1 \dots N_r$ . This function is the Gibbs function,  $G$ :

$$G \equiv U - TS + PV. \quad (1.42)$$

When the definition of the Gibbs function is combined with the Euler relation, Eq. (1.24), one finds the Gibbs function can be expressed

$$G = \sum_i^r N_i \mu_i. \quad (1.43)$$

The total differential of  $G$  is given by

$$dG = -SdT + VdP + \sum_{i=1}^r \mu_i dN_i. \quad (1.44)$$

The equations of state in the Gibbs formulation are

$$\begin{aligned} S &= S(T, P, N_1 \dots N_r), \\ V &= V(T, P, N_1 \dots N_r), \\ \mu_i &= \mu(T, P, N_1 \dots N_r). \end{aligned} \quad (1.45)$$

Note the change in the independent variables, compared to the Helmholtz function.

Since  $F$  and  $G$  were obtained from the Legendre transforms of  $U$  both are first-order homogeneous functions. Also, both are extensive functions. Below we show that each has other important properties. In particular, under different constraints, each provides a criterion for equilibrium for a composite system that satisfies different constraints.

## 1.4 The number of independent intensive variables for a single component simple-material system

An important issue in the thermodynamic analysis is always the number of independent intensive variables. We first consider this issue for a single component, simple-material system. As will be seen, there are two independent intensive variables if the right pair of intensive variables is chosen.

### 1.4.1 $T$ and $P$ as independent intensive properties for a single component system

If the residual strains and shear stresses may be neglected, a single component, single phase system may be described as a simple-material system. Thus, a single phase fluid may always be treated as a simple-material system. In general for such a system, the Euler equation, 1.24 reduces to

$$U = TS - PV + \mu N. \quad (1.46)$$

After dividing by the number of moles, one finds a relation between the intensive properties

$$u = Ts - Pv + \mu, \quad (1.47)$$

where  $u$ ,  $s$ ,  $v$  are the specific internal energy, entropy, and volume respectively. The Gibbs-Duhem equation, Eq. (??), simplifies to

$$d\mu = -sdT + vdP, \quad (1.48)$$

and from this equation, we may conclude that the independent variables of the chemical potential are  $T, P$ :

$$\mu = \mu(T, P). \quad (1.49)$$

Also, from Eq. (1.48)

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_P \quad (1.50)$$

$$= s(T, P), \quad (1.51)$$

and

$$v = \left(\frac{\partial \mu}{\partial P}\right)_T \quad (1.52)$$

$$= v(T, P). \quad (1.53)$$

Thus, the specific entropy and the specific volume have  $T$  and  $P$  as their independent variables.

Also, Eq. (1.47) may be written

$$\begin{aligned} u &= Ts(T, P) - Pv(T, P) + \mu(T, P) \\ u &= u(T, P). \end{aligned} \quad (1.54)$$

Thus, the intensive internal energy has  $T$  and  $P$  as its independent variables, as well. This allows other properties to be defined that are often used to describe a substance. For example, from Eq. 1.51, the constant pressure specific heat,  $c_p$ , is defined

$$c_p \equiv T \left(\frac{\partial s}{\partial T}\right)_P; \quad (1.55)$$

From Eq. 1.76 the isothermal compressibility,  $\kappa_T$ , is given by

$$\kappa_T \equiv -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T, \quad (1.56)$$

and the thermal expansivity,  $\alpha$ , is defined

$$\alpha \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P. \quad (1.57)$$

Thus, we conclude  $T$  and  $P$  may be chosen as the independent intensive variables for a single component simple-material system. Of the six intensive variables that we have defined so far, only two,  $T$  and  $P$ , may be assigned independently, but  $T$  and  $P$  are not unique in this regard.

### 1.4.2 Single component, simple-material system with $s$ and $v$ as the independent variables

The specific entropy and specific volume,  $s$  and  $v$ , may be chosen as be the independent intensive variables. The procedure for formulating the description of the system in terms of these variables begins with the internal energy expression for the fundamental relation. This relation,  $U(S, V, N)$ , must be a first-order homogeneous function (see Eq. (1.18)). Thus,

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N).$$

We may choose the parameter  $\lambda$  at our convenience. Suppose we choose it to be  $1/N$ , then the latter relation gives

$$U\left(\frac{S}{N}, \frac{V}{N}\right) = \frac{U(S, V, N)}{N},$$

or

$$u = u(s, v). \quad (1.58)$$

Thus,

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv. \quad (1.59)$$

By definition of the temperature

$$\begin{aligned} T &\equiv \left(\frac{\partial U}{\partial S}\right)_{N,V} \\ &= \left(\frac{\partial(U/N)}{\partial(S/N)}\right)_v \\ &= \left(\frac{\partial u}{\partial s}\right)_v \end{aligned} \quad (1.60)$$

The pressure may be similarly introduced:

$$\begin{aligned} P &\equiv -\left(\frac{\partial U}{\partial V}\right)_{N,S} \\ &= -\left(\frac{\partial(U/N)}{\partial(V/N)}\right)_s \\ &= -\left(\frac{\partial u}{\partial v}\right)_s, \end{aligned} \quad (1.61)$$

and Eq. 1.59 may be written

$$du = Tds - Pdv. \quad (1.62)$$

The Euler equation, Eq. 1.47, indicates that

$$\begin{aligned} \mu &= u - sT(s, v) + vP(s, v), \\ \mu &= \mu(s, v) \end{aligned} \quad (1.63)$$

Hence, all the intensive variables could be determined from knowledge of  $u(s, v)$  and the value of its independent variables.

Note that from Eq. (1.62), we may write

$$ds = \frac{1}{T}du + \frac{P}{T}dv \quad (1.64)$$

and from this equation

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{1}{T} \left(\frac{\partial u}{\partial T}\right)_v \quad (1.65)$$

We have already defined the constant pressure specific heat,  $c_p [\equiv T(\partial s/\partial T)_P]$ . We may now define the constant volume specific heat,  $c_v$ :

$$c_v \equiv \left(\frac{\partial s}{\partial T}\right)_v \quad (1.66)$$

From Eq. (1.65), one finds  $c_v$  may also be written

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v. \quad (1.67)$$

Note then that if the function  $u(s, v)$  were known along with the value of its independent properties, the value of the temperature and pressure could be determined. From Eq. 1.62, we may define the constant volume specific heat,  $c_v$

$$c_v \equiv T \left(\frac{\partial s}{\partial T}\right)_v \quad (1.68)$$

$$= \left(\frac{\partial u}{\partial T}\right)_v. \quad (1.69)$$

This last equation suggest that  $T$  and  $v$  may also be chosen as independent intensive properties .

## 1.5 The second derivatives for single component, simple-material systems

The “language” of thermodynamics is multivariable calculus, and we can make use of this language to establish important relations between the intensive variables of single component systems. Our second postulate says that the extensive internal energy,  $U$  has as its independent variables  $S, V$ , and  $N$ . From this relation, the intensive variables  $T, P, \mu$  have been defined and shown to have the expected physical interpretations.

Also, it has been seen that certain pairs of the intensive variables may be assigned independently. From these intensive variables, the “second order partials”,  $c_v, c_P, \kappa_T$  and  $\alpha$ . have also been defined. The second order partial differentials define material properties of a substance. For a single component system, there are many possible material properties that can be defined, but, as will be seen, only three of them can be independent.

### 1.5.1 Maxwell relations and relations between partial derivatives

We wish to determine how many of these second derivatives may be chosen independently. From Eq. (1.62)

$$du - Tds = -Pdv \quad (1.70)$$

$$d(u - Tds) = -sdT - Pdv. \quad (1.71)$$

The intensive Helmholtz function is defined  $f \equiv u - Ts$ . Thus

$$df = -sdT - Pdv. \quad (1.72)$$

Hence the independent variables of  $f$  are  $T$  and  $v$ . As will be seen, the Helmholtz function has a number of important thermodynamic applications. Here we use it to establish a **Maxwell relation**.

Since the postulates tell us that the thermodynamic functions are sufficiently continuous so that they may be differentiated

$$\left( \frac{\partial^2 f}{\partial T \partial v} \right) = - \left( \frac{\partial s}{\partial v} \right)_T, \quad (1.73)$$

and

$$\left( \frac{\partial^2 f}{\partial v \partial T} \right) = - \left( \frac{\partial P}{\partial T} \right)_v. \quad (1.74)$$

For a continuous function, the order of the differentiation does not affect the value, we obtain a Maxwell relation

$$\left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial P}{\partial T} \right)_v. \quad (1.75)$$

Note that once an equation such as Eq. (1.72) is established, a Maxwell relation may also be obtained. Thus, there are many Maxwell relations in thermodynamics, and the procedure used to establish this one may be used to establish others.

Since there are only two independent, intensive properties, there must be relations between the partial derivatives. We establish one of the relations that arises when  $T$  and  $P$  are chosen to act as the independent variables. The specific volume may be expressed in terms of these variables

$$v = v(T, P), \quad (1.76)$$

and thus,

$$dv = \left( \frac{\partial v}{\partial T} \right)_P dT + \left( \frac{\partial v}{\partial P} \right)_T dP. \quad (1.77)$$

If we divide Eq. (1.77) through by  $dT$  and then hold  $v$  constant, we find

$$0 = \left( \frac{\partial v}{\partial T} \right)_P + \left( \frac{\partial v}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_v, \quad (1.78)$$

or

$$\left( \frac{\partial P}{\partial T} \right)_v = - \frac{\left( \frac{\partial v}{\partial T} \right)_P}{\left( \frac{\partial v}{\partial P} \right)_T}. \quad (1.79)$$

Thus, the partial derivative

$$\left(\frac{\partial P}{\partial T}\right)_v$$

may be expressed in terms of partial differentials of  $v$ . And from Eqs. (1.56) and (1.57)

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\alpha}{\kappa_T}. \quad (1.80)$$

The procedure used to obtain Eq. (1.80) is often used in thermodynamics to rewrite a partial differential in terms of a desired set of independent variables. Note that it results from  $v$  only having two independent variables,  $T$  and  $P$ .

### 1.5.2 The $Tds$ equations and number of independent second partials

Since the intensive entropy may be expressed  $s = s(T, P)$  or  $s = s(T, v)$ , we may obtain two expressions for  $Tds$ . First suppose  $s = s(T, P)$ :

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP, \quad (1.81)$$

and from Eq. (1.48) we may obtain a Maxwell relation and then make use of the definition of  $\alpha$

$$\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P \quad (1.82)$$

$$= -v\alpha. \quad (1.83)$$

After making use of the definition of  $c_p$  and Eq. 1.83, Eq. (1.81) may be written

$$Tds = c_p dT - T\alpha v dP. \quad (1.84)$$

By considering  $s(T, v)$  and following a similar procedure, one finds the second  $Tds$  equation

$$Tds = c_v dT + T \frac{\alpha}{\kappa_T} dv \quad (1.85)$$

If we now divide Eq. (1.84) by  $dT$  and then hold  $v$  constant, we obtain

$$T \left( \frac{\partial s}{\partial T} \right)_v = c_p - T\alpha v \left( \frac{\partial P}{\partial T} \right)_v, \quad (1.86)$$

and after making use of Eqs. (1.55) and (1.80)

$$c_v = c_p - T v \frac{\alpha^2}{\kappa_T}. \quad (1.87)$$

Thus, for a simple-material system only three of the second partials may be assigned independently.

## 1.6 Equations of state from physical arguments

Thermodynamics defines a substance using a fundamental relation, but it does not provide a method for constructing a fundamental relation. Rather, it makes statements such as those indicated by Eq. 1.45, e.g., the volume of **any** simple material system may be expressed in terms of a certain set of independent variables

$$V = V(T, P, N_1 \dots N_r),$$

or Eq. 1.40, that indicates the pressure of any simple-material system may be expressed

$$P = P(T, V, N_1 \dots N_r).$$

The theorems of thermodynamics may be used to determine the independent variables of the equations of state in any of the possible formulations of thermodynamics.

One can proceed by proposing an equations of state on a physical basis, as long as the proposed equations of state are consistent with thermodynamics. We consider three particular simple materials: an ideal gas, an ideal gas mixture, and a slightly compressible liquid.

### 1.6.1 Ideal gas

We define an ideal gas as a substance that has a chemical potential function that may be represented

$$\mu(T, P) = \mu(T, P_r) + \bar{R}T \ln \frac{P}{P_r}. \quad (1.88)$$

where  $\bar{R}$  is the molar gas constant (8.31447 Joule per mole per K) and  $P_r$  is a parameter that must be defined in the circumstance where the relation is to be applied. The Gibbs-Duhem relation indicates

$$v = \left( \frac{\partial \mu}{\partial P} \right)_T, \quad (1.89)$$

$$= \frac{\bar{R}T}{P}. \quad (1.90)$$

or

$$Pv = \bar{R}T. \quad (1.91)$$

Thus, the relation that is sometimes used as the definition of an ideal gas is obtained as a theorem from the definition.

### 1.6.2 Ideal gas mixture

We define an ideal gas mixture as a simple material that satisfies

$$\mu_i = \mu_i^0(T, P) + \bar{R}T \ln x_i, \quad (1.92)$$

where  $\mu_i^0$  is the chemical potential of pure, ideal-gas component  $i$ , and  $x_i$  is the mole fraction:

$$x_i \equiv \frac{N_i}{\sum_{i=1}^r (N_i)}.$$

Note that there is no limit on the concentration of any particular component in the mixture.

The mole fraction of any component can only have any value in the range:

$$0 \leq x_i \leq 1.$$

Below we consider solutions (as opposed to mixtures). In these multicomponent, simple materials, at least one component can only have a limited mole fraction.

The Gibbs-Duhem equation, Eq. 1.26, gives

$$\sum_{i=1}^r N_i \mu_i = -SdT + VdP,$$

and then from the definition of an ideal gas mixture

$$\sum_{i=1}^r N_i \left( \frac{\partial \mu_i}{\partial P} \right) = V,$$

or

$$PV = \bar{R}T \sum_{i=1}^r N_i. \quad (1.93)$$

The partial pressure of a component,  $P_i$ , is defined

$$P_i = x_i P. \quad (1.94)$$

Then from Eq. 1.93

$$P_i V = N_i \bar{R} T. \quad (1.95)$$

In other words, each component of an ideal gas mixture behaves as though it occupied the volume alone, i.e., the interaction between components in an ideal gas mixture is neglected.

### 1.6.3 Compressible liquid

The characteristic that distinguishes a liquid from a gas or vapor is its relatively small compressibility, and smaller specific volume than the other fluid phase at the same temperature and pressure. The isothermal compressibility,  $\kappa_T$ , for a single component fluid is defined

$$\kappa_T \equiv -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T. \quad (1.96)$$

If the liquid were incompressible,  $\kappa_T$  would vanish.

If Eq. (1.97) is integrated at a constant temperature, then

$$\kappa_T P = -\ln v + f(T), \quad (1.97)$$

where  $f(T)$  is an arbitrary function of  $T$ .

For a single component system, the Gibbs-Duhem relation indicates the molar specific volume is only a function of  $T$  and  $P$

$$\begin{aligned} v &= \left( \frac{\partial \mu(T, P)}{\partial P} \right)_T, \\ &= v(T, P). \end{aligned} \quad (1.98)$$

We introduce a reference state in which the pressure and temperature are  $P_r, T$ . Then specific molar volume would have a particular value, denoted  $v_r$ , and  $f(T)$  may be written in terms of these properties evaluated in the reference state:

$$f(T) = \kappa_T P_r + \ln v(T, P_r), \quad (1.99)$$

and when this relation is combined with Eq. (1.97), one finds

$$\begin{aligned} \kappa_T (P - P_r) &= \ln \left( \frac{v(T, P_r)}{v} \right), \\ v &= v_r \exp[\kappa_T (P_r - P)]. \end{aligned} \quad (1.100)$$

The expression for the chemical potential of the slightly compressible liquid may now be obtained from the Gibbs-Duhem relation:

$$\begin{aligned} \left( \frac{\partial \mu(T, P)}{\partial P} \right)_T &= v(T, P_r) \exp[\kappa_T (P_r - P)], \\ \mu(T, P) &= \frac{-v(T, P_r)}{\kappa_T} \exp[\kappa_T (P_r - P)] + f_1(T), \end{aligned}$$

then

$$\mu(T, P) - \mu(T, P_r) = \frac{v(T, P_r)}{\kappa_T} (1 - \exp[\kappa_T(P_r - P)]). \quad (1.101)$$

If

$$|\kappa_T(P_r - P)| \ll 1,$$

then Eq. (1.101) simplifies to

$$\mu(T, P) - \mu(T, P_r) = v_r(P - P_r). \quad (1.102)$$

The latter indicates the chemical potential increases as the pressure of the fluid increases. This is an important characteristic of pressure that will be examined further below.

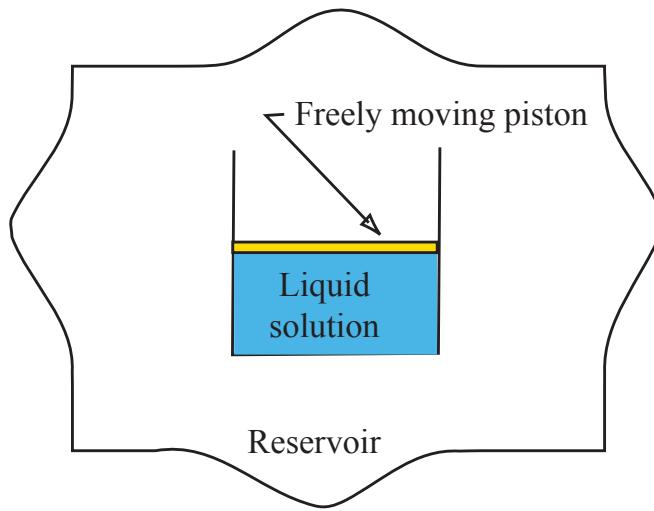
#### 1.6.4 Weak liquid solution

For a ideal-gas mixture the mole fraction of a component,  $x_i$ , can have any value in the range  $0 \leq x_i \leq 1$  and the system remain as a single phase system. This behaviour is in contrast to that of a **solution**. If a liquid solution is to remain a single phase system while maintained at a given temperature and a pressure, there is a limited concentration for which one component can be dissolved. This component is referred to as the **solute** and the component of larger mole fraction as the **solvent**. This limiting mole fraction is the **solubility** of the solute in the solvent. It defines a characteristic of a solute-solvent combination.

For example, if a water-oxygen solution is to remain a single-phase system, there is a limiting mole fraction of the oxygen that can be dissolved in the water. When the limiting mole fraction is exceeded, the liquid phase becomes metastable and can break into two phases. For a solution to be in a stable equilibrium state, the mole fraction of the solute,  $x_j$ , must be in the range

$$0 \leq x_j \leq x_s,$$

where  $x_s$  is the mole fraction of component  $j$  in a saturated solution.



**Figure 1.2:** The liquid is initially pure, and the walls of the piston-cylinder relation are impermeable.

We now want to construct the Gibbs function for a special type of solution. At the molecular level, in general, there are interactions between solvent molecules, between solute and solvent molecules and between solute molecules. A **weak solution** is a solution in which the interaction between solute molecules, even at the saturation concentration, can be neglected.

We now want to use the definition of the Gibbs function to determine the expression for the chemical potential of the solvent and of the solute in a weak solution. Ultimately, a complete expression for the Gibbs function cannot be obtained without the introduction of a result from statistical thermodynamics, but here we will simply state the relation, and show that it is valid when we consider statistical thermodynamics.

Suppose that initially the liquid consists of only component 1, the solvent, Fig. 1.2. In this case, from Eq. (1.43),

$$G(T, P, N_1) = N_1 \mu_1^0(T, P), \quad (1.103)$$

where the superscript zero indicates the chemical potential is that of a pure component. Now suppose that one molecule of the solute is added to the liquid phase. As a result, there would be some change in the Gibbs function of the liquid phase:

$$G(T, P, N_1, 1) = N_1 \mu_1^0(T, P) + \alpha(T, P, N_1). \quad (1.104)$$

The solute molecule would only be surrounded by solvent molecules; thus,  $\alpha(T, P, N_1)$  is the amount by which the Gibbs function is changed by a solute molecule when the solute molecules only interacts with solvent molecules. **If we suppose** we can count molecules, we could add  $N_2$  solute molecules, and maintain  $N_2 \ll N_1$ . There would not be any significant solute-solute molecule interactions with the  $N_2$  molecules present. The Gibbs function would be given by

$$G(T, P, N_1, N_2) = N_1 \mu_1^0(T, P) + N_2 \alpha(T, P, N_1). \quad (1.105)$$

However, Eq. (1.105) was obtained by assuming the molecules could each be identified. (We counted them as they were added.) This assumption is known to be invalid. When molecules are treated in this way, it has been found that thermodynamics is not logically consistent. There are paradoxes. The most famous is perhaps is the Gibbs paradox.

We have learned from statistical thermodynamics that this assumption can be corrected by adding  $k_b T \ln N_2!$  where  $k_b$  is the Boltzmann constant:

$$G(T, P, N_1, N_2) = N_1 \mu_1^0(T, P) + N_2 \alpha(T, P, N_1) + k_b T \ln N_2!. \quad (1.106)$$

Since the number of molecules being considered is very large compared to unity,  $N_2 \gg 1$ , we may use the Sterling approximation:

$$\ln N_2! \simeq N_2 \ln N_2 - N_2. \quad (1.107)$$

With this approximation

$$G(T, P, N_1, N_2) = N_1 \mu_1^0(T, P) + N_2 \alpha(T, P, N_1) + k_B T (N_2 \ln N_2 - N_2). \quad (1.108)$$

$$= N_1 \mu_1^0(T, P) + N_2 k_B T \ln \left[ N_2 \frac{\exp(\frac{\alpha(T, P, N_1)}{k_B T})}{e} \right]. \quad (1.109)$$

The Gibbs function was obtained from a Legendre transform of the internal energy and thus must be a first-order homogeneous function:

$$G(T, P, \lambda N_1, \lambda N_2) = \lambda G(T, P, N_1, N_2).$$

An inspection of Eq. (1.109), indicates  $\alpha(T, P, N_1)$  must be of the form

$$\alpha(T, P, N_1) = \ln \left( \frac{f(T, P)}{N_1} \right), \quad (1.110)$$

where  $f$  is an arbitrary function of  $T$  and  $P$ . The expression for the Gibbs function is then

$$G(T, P, N_1, N_2) = N_1 \mu_1^0(T, P) + N_2 k_b T \ln \left( \frac{N_2 f(T, P)}{N_1} \right). \quad (1.111)$$

Note that  $f(T, P)$  is related to  $\alpha(T, P, N_1)$  and must be evaluated empirically.

The expressions for the chemical potentials may be obtained from Eq. (1.111). For the solvent one finds:

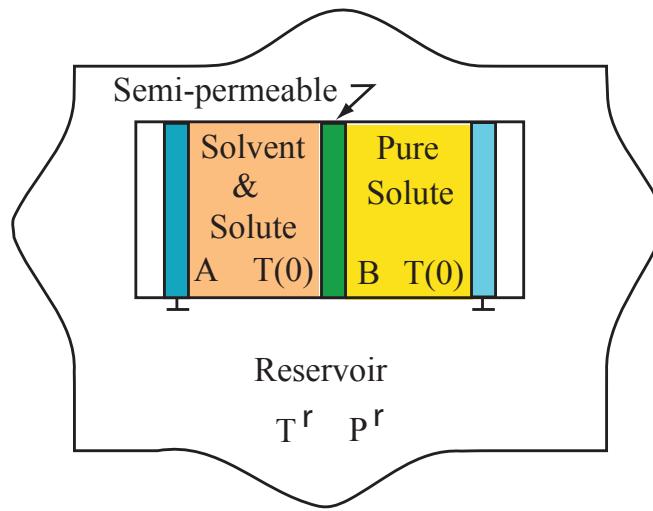
$$\begin{aligned} \mu_1 &= \left( \frac{\partial G}{\partial N_1} \right)_{T, P, N_2}, \\ &= \mu_1^0(T, P) - k_b T \left( \frac{N_2}{N_1} \right). \end{aligned} \quad (1.112)$$

The chemical potential for the solute

$$\mu_2(T, P, x_1, x_2) = \left( \frac{\partial G}{\partial N_2} \right)_{T, P, N_1}, \quad (1.113)$$

$$= k_b T [1 + \ln f(T, P)] + k_b T \ln \left( \frac{x_2}{x_1} \right). \quad (1.114)$$

Note that the expression for the chemical potential of the solvent does not depend on the unknown function  $f(T, P)$ . This permits a number of predictions to be made that act as tests of the method by which the expressions for the chemical potentials were derived. Nonetheless, for some calculation,  $f(T, P)$  is needed. We consider methods by which it could, in principle, be measured.



**Figure 1.3:** Schematic of a composite system, with subsystem A and B, that interacts with a reservoir. System A is a liquid solution and system B is pure solute. Initially the temperature of the system and the reservoir are different.

### Saturation concentration or solubility

A saturated solution is one in which the concentration of the solute,  $x_s$ , is such that equilibrium exists between the **pure** solute and the solution when both phases are at the same temperature and pressure.

We suppose the two-phase system interacts with a **reservoir**, i.e. a system that is large its intensive properties are changed negligibly as a result of any change in the properties of the smaller system.

A system such as that shown in Fig. 1.10 can, in principle, be used to determine  $f(T, P)$ .

Suppose the membrane separating the systems A and B in Fig. 1.3 is diathermal but permeable only to the solute. The other pistons are rigid, impermeable and diathermal. When the constraints are released—the outside pistons are unpinned—we assume the system comes to equilibrium. We may adopt the entropy postulate to determine the conditions for

equilibrium; thus we consider virtual displacements about the equilibrium state

$$S_c = S^A + S^B + S^r. \quad (1.115)$$

The constraints are

$$\begin{aligned} U_c &= U^A + U^B + U^r, \\ V_c &= V^A + V^B + V^r, \end{aligned}$$

and

$$\begin{aligned} N_{c1} &= N_1^A \\ N_{c2} &= N_2^A + N_2^B \end{aligned} \quad (1.116)$$

where  $U_c$ ,  $V_c$ , and  $N_{c1}$  and  $N_{c2}$  are each constant. After differentiating  $S_c$  and the constraints, and combining the results one finds:

$$dS_c = \left(\frac{1}{T^A} - \frac{1}{T^r}\right)dU^A + \left(\frac{1}{T^B} - \frac{1}{T^r}\right)dU^B + \left(\frac{P^A}{T^A} - \frac{P^r}{T^r}\right)dV^L + \left(\frac{P^B}{T^B} - \frac{P^r}{T^r}\right)dV^V - \left(\frac{\mu_2^A}{T^A} - \frac{\mu_2^B}{T^B}\right)dN^B. \quad (1.117)$$

where  $T^A$  and  $T^B$  are the equilibrium temperatures in the system, but note that the temperature of the reservoir does not change from its initial value.

The necessary condition for equilibrium is that  $dS_c$  vanishes for all virtual displacements about the equilibrium state, then

$$\begin{aligned} T^r &= T^A, \\ &= T^B, \\ &= T \end{aligned} \quad (1.118)$$

$$\begin{aligned}
P^r &= P^L, \\
&= P^V, \\
&= P
\end{aligned} \tag{1.119}$$

Thus, the reservoir imposes its temperature and pressure on the system, and the temperature is uniform in the system.

The condition on the chemical potential may be written

$$\mu_2^A(T, P) = \mu_2^B(T, P) \tag{1.120}$$

Since system B consist of only the solute, the mole fraction of component 2 in system A would be the solubility of the solute in the solvent,  $x_s(T, P)$ .

$$\begin{aligned}
\mu_2^A(T, P, x_s) &= \mu_2^B \\
&= \mu_2^0(T, P)
\end{aligned} \tag{1.121}$$

From Eqs. (1.121) and (1.114)

$$\begin{aligned}
k_b T [1 + \ln f(T, P)] + k_b T \ln \frac{x_s}{x_1} &= \mu_2^0(T, P) \\
1 + \ln f(T, P) &= \frac{\mu_2^0(T, P)}{k_b T} - \ln \frac{x_s}{x_1} \\
\mu_2(T, P, x_2, x_1) &= \mu_2^0(T, P) + k_b T \ln \left[ \frac{x_2}{x_s(T, P)} \right]
\end{aligned} \tag{1.122}$$

Thus, provided the value of  $x_s$  can be measured, the expression for the chemical potential of a solute in a weak solution can be determined in terms of  $\mu_2^0(T, P)$ .

For certain weak solutions, the temperature and pressure dependence of the solubility can be separated, and the solubility written in terms of an empirical parameter, the Henry constant,  $K_h(T)$ :

$$x_s = \frac{x_1 P}{K_h(T)} \quad (1.123)$$

Thus, the solubility is determined by measuring  $K_h(T)$ .

### 1.6.5 Example C1.7-1

Suppose two components are added to a solvent to form a weak liquid solution. Give the expression for the chemical potential of the solvent and the solutes.

#### Solution

If the three components form a weak solution, there can be no interaction between the solutes. Thus, we may follow the procedure outline above to formulate the expression for the chemical potentials.

The function,  $\alpha(T, P, N_1)$ , was the amount by which the Gibbs function of the solvent was changed by adding one molecule of the first solute. Let  $\beta(T, P, N_1)$  be the amount by which the Gibbs function of the pure solvent is changed by the addition of a molecule of the second solute. Then if  $N_2$  molecules of the first solute and  $N_3$  molecules of the second solute are added to the pure solvent, the Gibbs function would be

$$G(T, P, N_1, N_2) = N_1\mu_1^0(T, P) + N_2\alpha(T, P, N_1) + k_b T(N_2 \ln N_2 - N_2) + N_3\beta(T, P, N_1) + k_b T(N_3 \ln N_3 - N_3), \quad (1.124)$$

where we have accounted for the fact that molecules in a fluid cannot be identified and after requiring the Gibbs function to be a first-order homogeneous function:

$$G(T, P, N_1, N_2) = N_1\mu_1^0(T, P) + N_2k_b T \ln \left( \frac{N_2 f_2(T, P)}{N_1} \right) + \quad (1.125)$$

$$N_3k_b T \ln \left( \frac{N_3 f_3(T, P)}{N_1} \right) \quad (1.126)$$

After taking the partial differential of  $G(T, P, N_1, N_2, N_3)$  with respect  $N_1$  and introducing the mole fractions, , the chemical potential of the solvent may be written

$$\mu_1(T, P, x_1, x_2, x_3) = \mu_1^0(T, P) - k_b T \left( \frac{x_2 + x_3}{x_1} \right) \quad (1.127)$$

and after taking the partial differential of  $G(T, P, N_1, N_2, N_3)$  with respect  $N_2$  and then with respect to  $N_3$  and introducing the solubility one finds

$$\mu_2(T, P, x_1, x_2) = \mu_2^0(T, P) + k_b T \ln \left( \frac{x_2}{x_{s2}(x_1, T, P)} \right) \quad (1.128)$$

$$\mu_3(T, P, x_1, x_3) = \mu_3^0(T, P) + k_b T \ln \left( \frac{x_3}{x_{s3}(x_1, T, P)} \right) \quad (1.129)$$

### Example C1-4

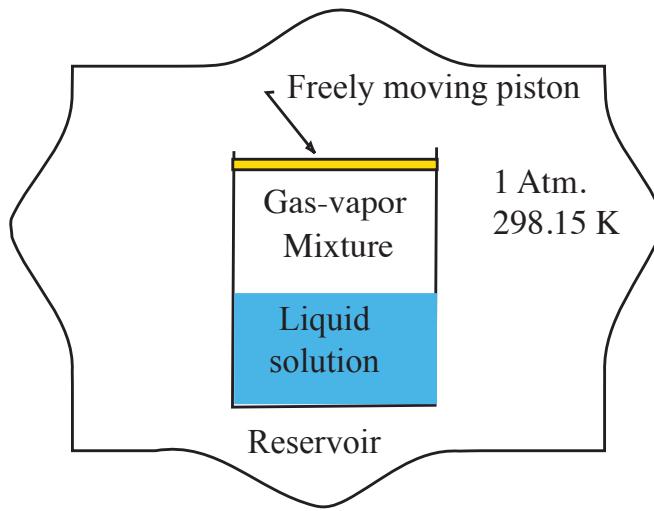
Consider the system shown in Fig. 1.4 in which moist air (an ideal gas-vapor mixture of O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O vapor) is in contact with water. Under equilibrium conditions, the water phase is a weak solution. The pure solvent may be approximated as incompressible. The walls of the piston-cylinder arrangement are impermeable, but heat conducting. The pressure and temperature of the reservoir are 101.325 kPa and 298.15 K. The Henry constant for O<sub>2</sub> is  $4.259 \times 10^4$  Atm and for N<sub>2</sub> is  $9.077 \times 10^4$  Atm.

1. What conditions must the intensive properties satisfy in order for the system to be in equilibrium?
2. For the weak solution, if

$$\exp \left[ \left( \frac{v_f}{v_g} \right) \left( \frac{P}{P_s} - 1 \right) - \left( \frac{x_2^L + x_3^L}{x_1^L} \right) \right] \rightarrow 1,$$

give the expression for the mole fraction of H<sub>2</sub>O in the moist air.

3. If the mole fraction of N<sub>2</sub> in the moist air is 2.5 times that of O<sub>2</sub>, give the values of the mole fractions of the gases in the solution when the system is in equilibrium.



**Figure 1.4:** An ideal mixture that consists of  $H_2O$  vapor and  $N_2$  is in contact weak  $H_2O$  at 25 °C and 101.325 kPa

### Solution

1. The conditions for equilibrium may be determined by considering the isolated composite system formed by the gas-vapor mixture, the weak solution, and the reservoir and applying the entropy postulate. As seen above, the reservoir imposes its temperature and pressure on the phases inside the piston-cylinder arrangement

$$P^G = P^L$$

$$= P.$$

$$T^G = T^L$$

$$= T.$$

and the chemical potentials must satisfy

$$\begin{aligned}\mu_1^L &= \mu_1^G. \\ \mu_2^L &= \mu_2^G. \\ \mu_3^L &= \mu_3^G.\end{aligned}\tag{1.130}$$

2. The chemical potential of the solvent in a weak solution is

$$\mu_1^L(T, P, x_1^L, x_2^L, x_3^L) = \mu_1^0(T, P) - \bar{R}T \left( \frac{x_2^L + x_3^L}{x_1^L} \right).$$

and since the pure solvent may be approximated as incompressible, we may introduce a reference pressure,  $P_r$ , and write

$$\mu_1^L(T, P, x_1^L, x_2^L, x_3^L) = \mu_1^0(T, P_r) + v_f(P - P_r) - \bar{R}T \left( \frac{x_2^L + x_3^L}{x_1^L} \right).$$

If the reference pressure is chosen to be the saturation-vapor pressure, then

$$\mu_1^L(T, P, x_1^L, x_2^L, x_3^L) = \mu_1^0[T, P_s(T)] + v_f(P - P_s) - \bar{R}T \left( \frac{x_2^L + x_3^L}{x_1^L} \right).\tag{1.131}$$

The chemical potential of the solvent in the gas mixture may be expressed

(1.132)

$$\mu_1(T, P, x_1^G) = \mu_1^{0V}(T, P) + \bar{R}T \ln(x_1^G)$$

but since  $\mu_1^{0V}(T, P)$  is the chemical potential of the pure vapor, approximated as an ideal gas, we may write it in terms of a reference pressure,  $P_r$ ,

$$\mu_1^G(T, P, x_1^G) = \mu_1^{0V}(T, P_r) + \bar{R}T \ln \left( \frac{P x_1^G}{P_r} \right)\tag{1.133}$$

3. One of the conditions for equilibrium requires

$$\mu_1^L = \mu_1^G$$

or

$$\mu_1^{0L}[T, P_s(T)] + v_f(P - P_s) - \bar{R}T \left( \frac{x_2^L + x_3^L}{x_1^L} \right) = \mu_1^{0V}(T, P_r) + \bar{R}T \ln \left( \frac{Px_1^G}{P_r} \right) \quad (1.134)$$

Since the reference pressure may be chosen arbitrarily, and since a chemical potential cannot be measured directly, we choose  $P_r$  so the chemical-potential terms cancel out.

We can do this because (Eq. (??))

$$\mu_1^{0L}[T, P_s(T)] = \mu_1^{0V}[T, P_s(T)] \quad (1.135)$$

then

$$v_f(P - P_s) - \bar{R}T \left( \frac{x_2^L + x_3^L}{x_1^L} \right) = \bar{R}T \ln \left( \frac{Px_1^G}{P_s} \right)$$

or

$$P_s \exp \left[ \left( \frac{v_f P_s}{\bar{R}T} \right) \left( \frac{P}{P_s} - 1 \right) - \left( \frac{x_2^L + x_3^L}{x_1^L} \right) \right] = x_1^G P$$

Since the vapor is being approximated as an ideal gas, the specific volume of the vapor at saturation may be expressed

$$\begin{aligned} \frac{\bar{R}T}{P} &= v_g \\ P_s \exp \left[ \left( \frac{v_f}{v_g} \right) \left( \frac{P}{P_s} - 1 \right) - \left( \frac{x_2^L + x_3^L}{x_1^L} \right) \right] &= x_1^G P \end{aligned}$$

For water at 25 °C  $v_f/v_g$  is  $\sim 10^{-3}$  and a weak solution  $x_2^L + x_3^L/x_1^L \ll 1$ , one finds

$$P_s = x_1^G P \quad (1.136)$$

4. The condition for equilibrium that the gas components must satisfy is (Eq. (1.129))

$$\mu_i^L = \mu_i^G$$

$$\mu_i^{0G}(T, P) + k_b T \ln \left( \frac{x_i^L K_{hi}}{x_1^L P} \right) = \mu_i^{0G}(T, P) + k_b T \ln x_i^G,$$

where we have expressed the solubility in terms of the Henry relation. Then

$$\left( \frac{x_i^L K_{hi}}{x_1^L P} \right) = x_i^G$$

For each component then

$$\left( \frac{x_2^L K_{h2}}{x_1^L} \right) = x_2^G P \quad (1.137)$$

$$\left( \frac{x_3^L K_{h3}}{x_1^L} \right) = x_3^G P \quad (1.138)$$

5. By adding Eqs. (1.136) - (1.138), one finds

$$P_s + \left( \frac{x_2^L K_{h2}}{x_1^L} \right) + \left( \frac{x_3^L K_{h3}}{x_1^L} \right) = P \quad (1.139)$$

Since

$$x_2^L = 2.5 x_3^L \quad (1.140)$$

this equation can be solved. From the given conditions one finds

$$x_2^L = 1.23 \times 10^{-5} \quad (1.141)$$

$$x_3^L = 4.91 \times 10^{-6} \quad (1.142)$$

6. Based on your results, calculate the value of

$$\exp \left[ \left( \frac{v_f}{v_g} \right) \left( \frac{P}{P_s} - 1 \right) - \left( \frac{x_2^L + x_3^L}{x_1^L} \right) \right]$$

## 1.7 Phases of a single component system

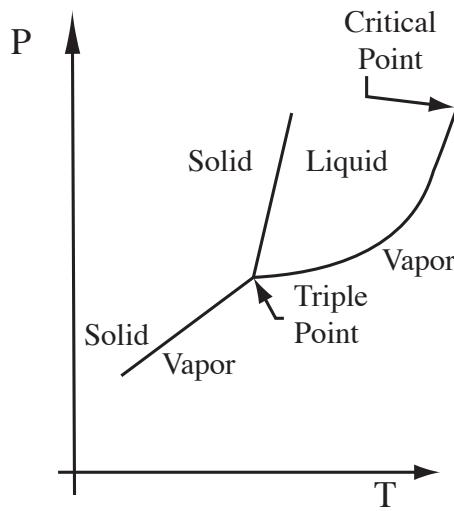
When more than one phase of a substance is present in a system, the system cannot be treated as a simple material system. The phases are distinguished by their specific volumes and entropies. Thus, the system is by definition heterogeneous, and must be treated as a composite system. We first consider single component systems in more than one phase.

A schematic of the phase diagram of a single component substance is shown in Fig. 1.5. Such a diagram is viewed as a summary of the observations in many experiments. The solid lines in this figure indicate the conditions where two phases of the substance (e.g., solid-liquid or liquid-vapor or solid-vapor) are in equilibrium. Note that for a given temperature, the diagram indicates there is **only one** pressure at which equilibrium exists when two phases are present. The inverse is also true: for a given temperature, there is only one pressure at which an equilibrium state exists between two phases of the substance. Thus, empirically it is found that there is a **unique relation** between the temperature and pressure at which equilibrium can exist between two phases of a substance. However, the phase diagram also indicates that if all three phases (solid, liquid and vapor) are in equilibrium, there is a **unique value** of the temperature and pressure. We now want to determine if the postulates can be used to understand the reason this behavior.

## 1.8 Equilibrium between a liquid and its vapor

For temperatures between the triple point and the critical point, the vapor phase is defined as the phase with the larger specific volume and the phase with the larger specific entropy. Thus by definition

$$\begin{aligned} 0 &< v^L < v^V; \\ s^L &< s^V. \end{aligned} \tag{1.143}$$



**Figure 1.5:** A phase diagram is shown for a substance that contracts on freezing.

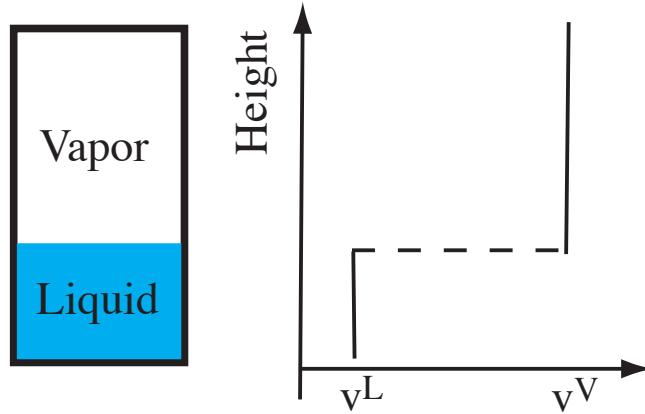
If equilibrium exists between a liquid and its vapor, the specific volume of the vapor is denoted  $v_g$  and that of the liquid as  $v_f$ .

Since we are neglecting surface effects, we take the boundary between the liquid and vapor phases to be sharp, as opposed to a gradual change that will be considered when surface effects are included. A schematic is shown in Fig. 1.6 of a composite system formed by enclosing the liquid and vapor phases of a substance in a constant volume, impermeable, adiabatic container that isolates the phases from their surroundings. The boundary between two phases is completely open: thermal energy and molecules are freely transported between the phases and the boundary can move.

The constraints required to isolate the system are:

1. The volume of the composite system,  $V_c$  is constant:

$$V_c = V^V + V^L; \quad (1.144)$$



**Figure 1.6:** Fluid phases of a component enclosed in a constant volume system.

2. the number of moles of the fluid that are in the composite system,  $N_c$ , is constant:

$$N_c = N^V + N^L; \quad (1.145)$$

3. and the total energy of the composite system,  $U_c$ , is constant:

$$U_c = U^L + U^V. \quad (1.146)$$

When the composite system has reached equilibrium, independently of the **nature of the equilibrium state, stable, metastable, or unstable** according to our postulates, the entropy of the composite system is an extremum:

$$dS_c = dS^L + dS^V. \quad (1.147)$$

If the equilibrium values of the temperature, pressure and chemical potentials in phase  $\alpha$  are denoted  $T^\alpha$ ,  $P^\alpha$ ,  $\mu^\alpha$ , Eq. (1.8) gives for each of the simple material systems that constitute the composite system

$$dS^\alpha = \left(\frac{1}{T}\right)^\alpha dU^\alpha + \left(\frac{P}{T}\right)^\alpha dV^\alpha - \left(\frac{\mu}{T}\right)^\alpha dN^\alpha \quad (1.148)$$

where  $\alpha$  is  $L$  or  $V$ . After differentiating the constraints, one finds for a virtual displacement about the equilibrium state

$$dS_c = \left(\frac{1}{T^L} - \frac{1}{T^V}\right) dU^L + \left(\frac{P^L}{T^L} - \frac{P^V}{T^V}\right) dV^L - \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V}\right) dN^L. \quad (1.149)$$

The constraints indicate that  $U^L, V^L, N^L$  may be treated as independent variables. Thus, in order for  $dS_c$  to vanish for each virtual displacement about the entropy-extremum state or the equilibrium state that has temperatures  $T^L, T^V$ , pressure  $P^L, P^V$  and chemical potentials  $\mu^L, \mu^V$  the necessary conditions for equilibrium are

$$\begin{aligned} \left( \frac{1}{T^L} - \frac{1}{T^V} \right) &= 0; \\ \left( \frac{P^L}{T^L} - \frac{P^V}{T^V} \right) &= 0; \\ \left( \frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) &= 0. \end{aligned} \quad (1.150)$$

Hence, the temperature and pressure are uniform throughout the system, but so is the chemical potential, and the chemical potential of each phase has as its independent variables  $T$  and  $P$  of that phase; thus in this case

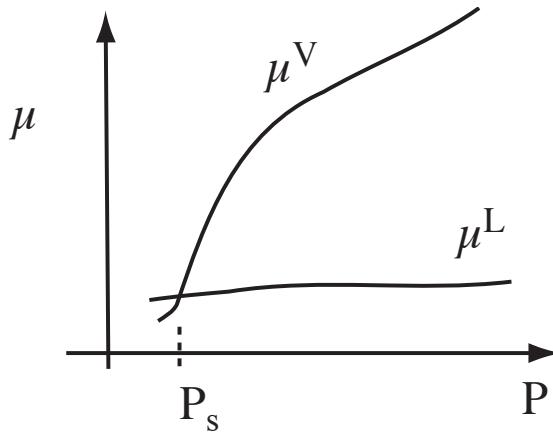
$$\mu^L(T, P) = \mu^V(T, P). \quad (1.151)$$

Two possibilities now arise: either the chemical potential “function” for the liquid phase has the same functional dependences on  $T$  and  $P$  as does the chemical potential function of the vapor phase, or these two chemical-potential functions have different functional dependences on their independent variables. If the former is true, then Eq. (1.151) is an identity and no relation between  $T$  and  $P$  is implied, but if the latter is true, it suggests that when equilibrium exists between the two phases, there is a relation between the system temperature and the system pressure.

### 1.8.1 The saturation-vapor pressure

From the Gibbs-Duhem equation for a single component system, Eq. (1.27):

$$d\mu^L = -s^L dT + v^L dP, \quad (1.152)$$



**Figure 1.7:** In an isothermal two phase system, the chemical potentials of the liquid and vapor phases can be equal at only one pressure.

and for the vapor

$$d\mu^V = -s^V dT + v^V dP. \quad (1.153)$$

Then

$$\left(\frac{\partial\mu^L}{\partial P}\right)_T = v^L, \quad (1.154)$$

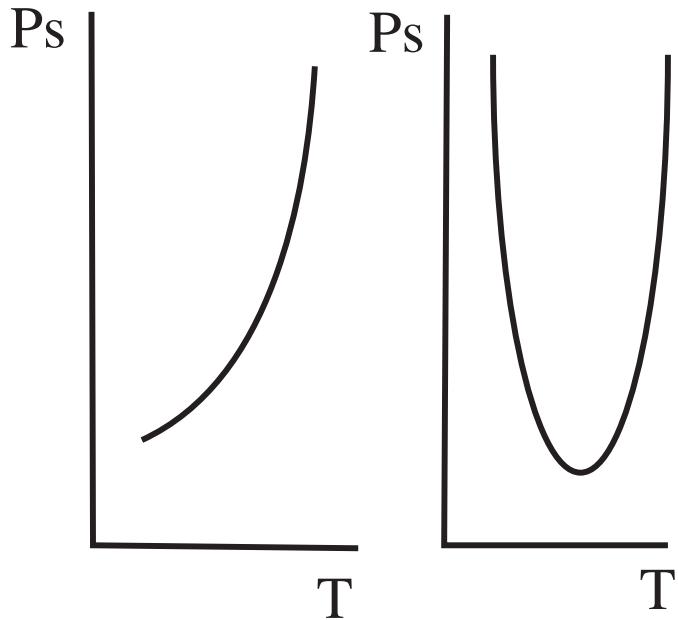
and

$$\left(\frac{\partial\mu^V}{\partial P}\right)_T = v^V, \quad (1.155)$$

but by definition of the liquid and vapor phases  $0 < v^L < v^V$ ; thus,

$$0 < \left(\frac{\partial\mu^L}{\partial P}\right)_T < \left(\frac{\partial\mu^V}{\partial P}\right)_T, \quad (1.156)$$

and Eq. (1.151) indicates that for a given  $T$ , the chemical potential functions of the liquid and vapor phases are different. But Eq. (1.151) indicates there is at least one pressure where the chemical potentials have the same value. Since the specific volumes are positive  $0 < v^L < v^V$ , the partial differentials of the chemical potentials with respect to pressure cannot vanish, and there can be only one pressure at which the chemical potentials are equal. The situation is depicted in Fig. 1.7 where the pressure  $P_s(T)$  is defined as the **saturation-vapor pressure**



**Figure 1.8:** Possible relations between  $P_s(T)$  and  $T$ .

The relation  $P_s(T)$  would exist only under conditions where both the liquid and vapor phases can exist in equilibrium. However, as indicated in Fig. 1.5, at temperatures above the critical temperature,  $T_{cr}$ , or above the critical pressure,  $P_{cr}$ , there is only one fluid phase and the substance has  $T$  and  $P$  as its independent variables.

### 1.8.2 Saturation-vapor temperature

The condition that the saturation-vapor pressure is a unique function of  $T$  can be satisfied by many different types of functions. Two of them are depicted in Fig. 1.8. Each of these functions satisfies the condition that for a given  $T$  there is only one value of  $P_s$ . However, the curve on the left indicates that if  $P_s(T)$  were inverted to write the **saturation-vapor temperature**,  $T_s(P)$ , in terms of the pressure, there **would** be a unique value of  $T_s$ . Whereas, the curve on the right in Fig. 1.8 indicates that for a given value of  $P$ , there are multiple values of  $T$  that could exist in the system.

We know that when equilibrium exists in a two phase system such as that shown in Fig. 1.6, the chemical potentials of the molecules in each phase must be equal, Eq. (1.151). We suppose that this equation may be solved for  $T_s(P)$ . For a given value of the pressure, we now want to determine how many values of  $T_s(P)$  can satisfy the conditions for equilibrium.

From the Gibbs-Duhem relation, Eq. (1.27), one finds

$$\left( \frac{\partial \mu^j}{\partial T} \right) = -s^j \quad j = L, V, \quad (1.157)$$

and from the Euler relation, Eq. (1.29),

$$u^j - Ts^j + Pv^j = \mu^j. \quad (1.158)$$

Since

$$\mu^L = \mu^V,$$

it follows

$$T(s^V - s^L) = (u^V - u^L) + P(v^V - v^L). \quad (1.159)$$

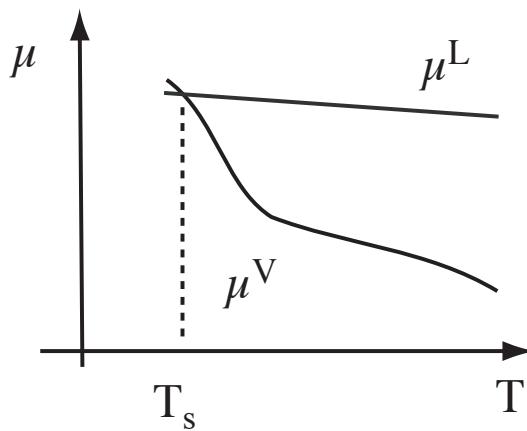
By definition of the vapor and liquid phases of a fluid, Eq. (1.143):

$$s^V > s^L > 0. \quad (1.160)$$

Thus

$$\left( \frac{\partial \mu^V}{\partial T} \right) < \left( \frac{\partial \mu^L}{\partial T} \right), \quad (1.161)$$

and the relation between the chemical potentials is as indicated in Fig. 1.9. Thus, for a given pressure in the two phase system considered, there is only one temperature at which the system would be in equilibrium. The  $P_s(T)$  relation is as indicated on the left in Fig. 1.8.



**Figure 1.9:** For a given pressure, the relation between the chemical potential functions of a liquid and its vapor is shown.

### 1.8.3 Equilibrium between a liquid and its vapor when $T$ and $v$ are the independent variables

When the two fluid phases of a single component substance, Fig. 1.6, are present in a composite system, and the phases are free to exchange energy, molecules and to expand, we have seen that  $T$  and  $P$  in the system are uniform, and if either the temperature or the pressure is specified, the other property is then fixed, e.g.,  $P_s = P_s(T)$  or  $T_s = T_s(P)$ . As indicated in Fig. 1.5, either of these relations defines the phase boundary in the phase diagram for the substance. But there is a variable not being considered when pressure is being expressed as a function of temperature, and that is the specific volume,  $v$ . In order to examine it, we consider changing the independent, intensive variables of a simple material system to  $T$  and  $v$ .

For such a system, the Helmholtz function must be a first order homogeneous function:

$$\lambda F(T, V, N) = F(T, \lambda V, \lambda N).$$

If  $\lambda$  is chosen to be  $1/N$ , then the intensive Helmholtz function,  $f$ , has  $T$  and  $v$  as its independent variables.

$$f = f(T, v) \quad (1.162)$$

One find the total differential of  $f$  may be expressed

$$df = -sdT - Pdv \quad (1.163)$$

Thus

$$P = P(T, v) \quad (1.164)$$

In Fig. 1.10, we show schematic plots of  $P$  for given  $T$  under two circumstances. In one  $T$  is greater than the critical temperature,  $T_{cr}$ , and on this curve  $P$  is a smooth function of  $T$  and  $v$ , but by contrast for a given  $T$  in the range

$$T_{tp} < T < T_{cr}$$

there is a discontinuity in  $v$  when the pressure is  $P_s(T)$ . <sup>1</sup> Below we consider the reason for the first order phase transition indicated in Fig. 1.10.

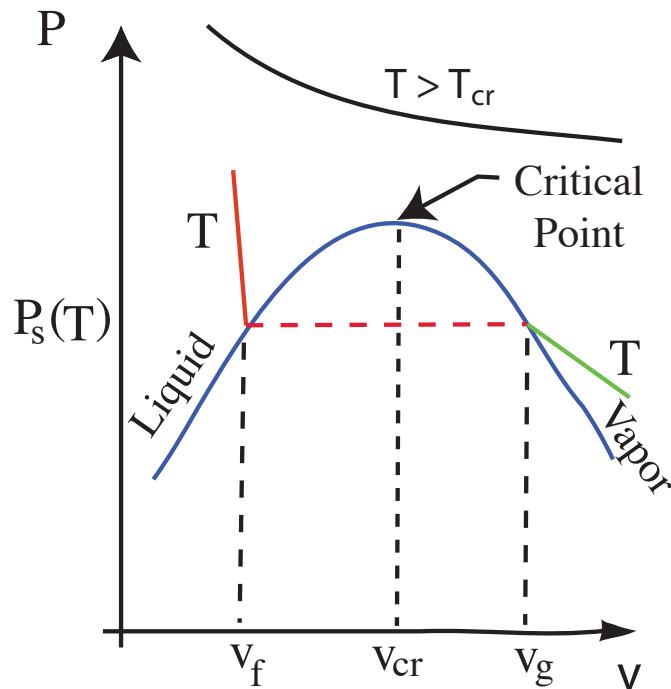
#### 1.8.4 Slope of the phase boundary between the liquid and its vapor: the Clausius-Clapeyron equation

When the two fluid phases of a single component substance are in equilibrium, we have seen that the pressure and temperature are uniform and that (1.151). If we take the temperature to be given, then this equations may be written

$$\mu^L(T, P_s) = \mu^V(T, P_s), \quad (1.165)$$

---

<sup>1</sup>Such a discontinuity is called a first order phase transition because there is discontinuity in a thermodynamic variable as opposed to discontinuity in a differential.



**Figure 1.10:** The fluid phases the system shown Fig. ?? could adopt are shown schematically.

After taking the total differential and applying the Gibbs-Duhem equation, one finds

$$-s^L dT + v^L dP_s = -s^V dT + v^V dP_s$$

or

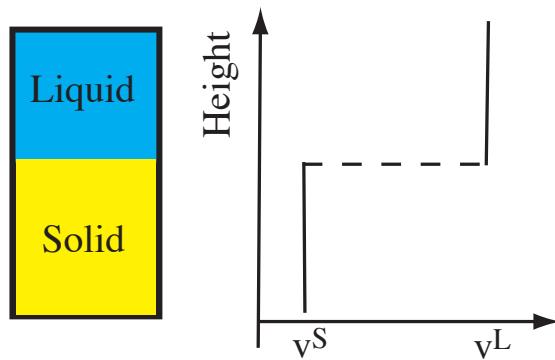
$$\frac{dP_s}{dT} = \frac{s^V - s^L}{v^V - v^L} \quad (1.166)$$

Equation ?? is the Clausis-Clayperon equation. It give the expression for the slope of the liquid-vapor phase boundary curve.

Since by definition of the fluid phases of a substance

$$s^V - s^L > 0,$$

$$v^V - v^L > 0$$



**Figure 1.11:** A liquid phase in equilibrium with a solid phase in the absence of surface effects and gravity

it follows that

$$\frac{dP_s}{dT} > 0 \quad (1.167)$$

Thus the phase boundary between the liquid and vapor phase that is shown in Fig. 1.5 is consistent with the thermodynamic postulates.

## 1.9 Equilibrium between the solid and liquid phases of a single component substance

In general, one can only say that the specific volume of a solid phase,  $v^S$ , is different than that of the liquid phase: some substances expand, notably water, on solidifying but others contract. However,  $v^S$ , like  $v^V$  and  $v^L$ , is positive and cannot vanish. Also, in general, we may say that the solid phase must be heated in order to form the liquid phase :

$$s^S < s^L$$

If the substance contracts on solidifying, then

$$v^V > v^L > v^S > 0$$

but if the substance expands

$$v^V > v^S > v^L > 0 \quad (1.168)$$

We shall neglect the off-diagonal terms in the stress tensor of the solid phase,  $\sigma_{ij}$

$$P = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}).$$

This allows the solid phase to be approximated as a simple material system.

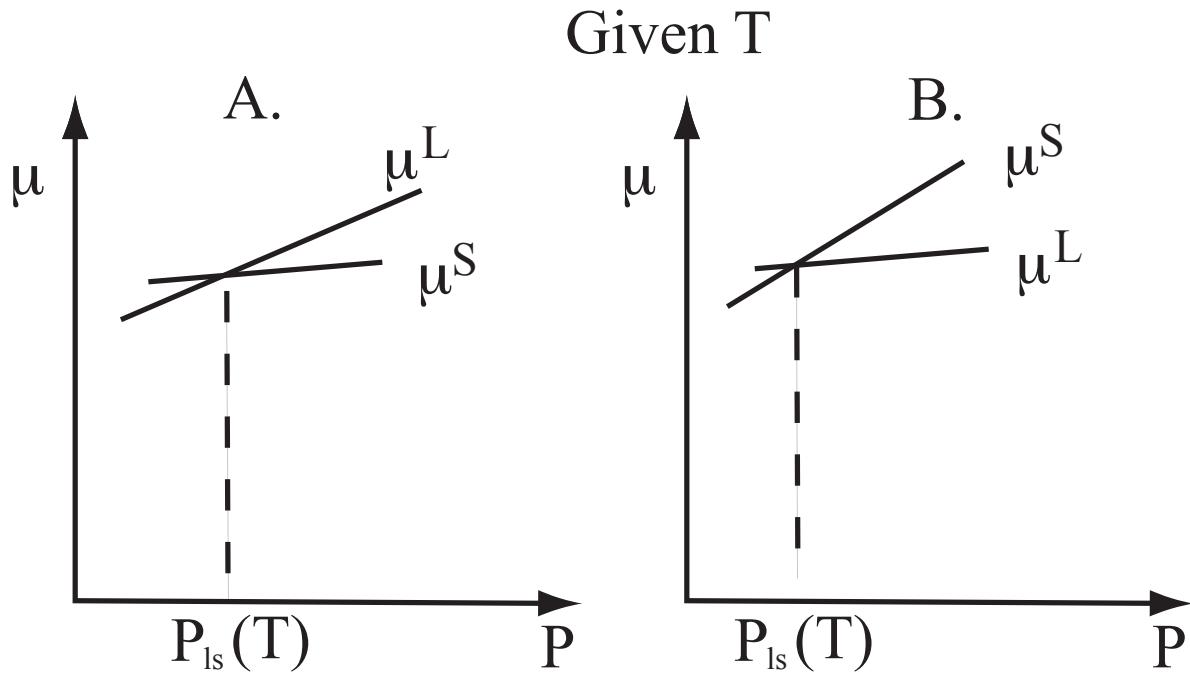
The necessary conditions for equilibrium of an isolated composite system, such as that shown in Fig. 1.11, are similar to the necessary conditions found for a liquid and vapor phases. Namely, the temperature and pressure must be uniform in the system and the chemical potentials of the molecules in each phase must have the same value.

Since the specific volume of the liquid phase is different than that of the solid phase, the chemical potential of the molecules in the liquid and those in the solid phase are different functions. This indicates there is a relation between  $T$  and  $P$ , and since the chemical potentials cannot be equal at any other values of  $T$  and  $P$ , the condition for equilibrium between the solid and liquid of a given substance at a temperature  $T$ , denoted  $P_{ls}(T)$ , is a unique function of temperature independently of whether on solidifying the material either **contracts**, Fig. 1.12A, or **expands** Fig. 1.12B.

We can determine the slope of the solid-liquid phase boundary by applying the Clausius-Clapeyron equation, (1.166). If we take the temperature as given, then

$$\frac{dP_s}{dT} = \frac{s^L - s^V}{v^L - v^S} \quad (1.169)$$

For a substance that contracts on solidifying, the slope is positive, and the phase diagram is as indicated in Fig. 1.10, but if the substance that expands on solidifying the slope is negative and the phase diagram is as indicated in Fig. 1.13.



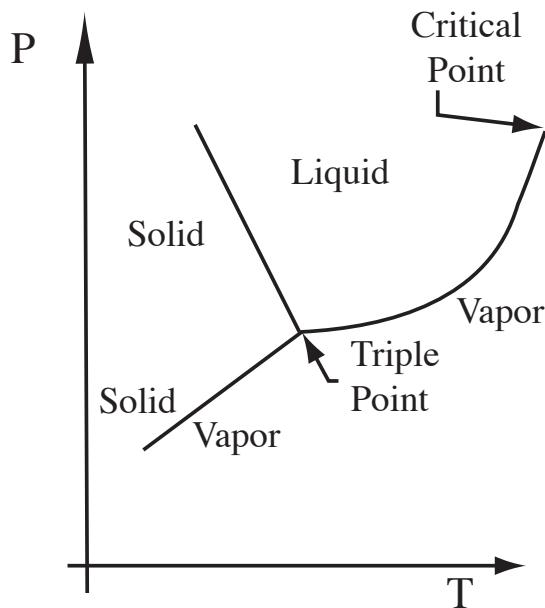
**Figure 1.12:** In A. the chemical potential of a solid which contract on solidifying is plotted, and on the right the chemical potential of a solid that expands on solidifying is shown.

### 1.9.1 Energy required to change the phase of a substance

Suppose the liquid and solid phases of a substance are present in a piston cylinder arrangement as indicated in Fig. 1.14. Initially the system is in equilibrium and there are  $N^S(i)$  moles of solid and  $N^L(i)$  of liquid present. The system is heated quasi-statically to change the number of moles of liquid. If the process is quasi-stastic, the system goes through a sequence of equilibrium states. In each of these states the chemical potential of the liquid and vapor phase would be equal so the pressure would saturation pressure,  $P_{sl}(T)$ .

The change in volume of the liquid phase

$$\begin{aligned}\Delta V^L &= v^L[N^L(f) - N^L(i)] \\ \Delta V^L &= v^L N_{sl}\end{aligned}\tag{1.170}$$



**Figure 1.13:** When the solid phase has a larger specific volume than the liquid phase, the slope of  $P_{ls}(T)$  is negative, but if the specific volume of the solid is smaller than that of the liquid, the slope is positive as seen Fig 1.5

and since there is no change in the number of moles of the system,

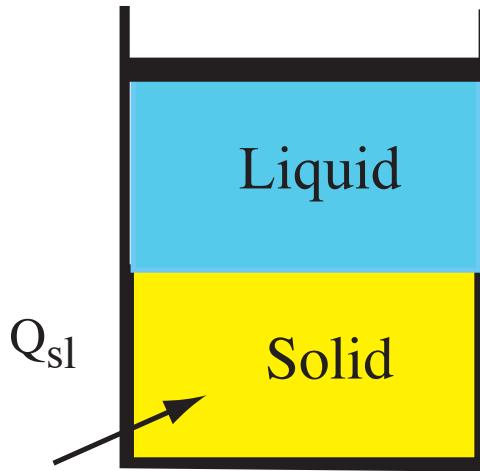
$$N_{sl} = -(N^S(f) - N^S(i))$$

For the solid phase

$$\Delta V^S = -v^S N_{sl}$$

and the total change in the system volume would be

$$\begin{aligned} \Delta V &= \Delta V^L + \Delta V^S \\ &= N_{sl}(v^L - v^S) \end{aligned} \tag{1.171}$$



**Figure 1.14:** The solid and liquid phases of a single component system are initially in equilibrium are then heated to produce more liquid.

The work,  $W_{if}$ , done during the constant pressure heating process would be

$$\begin{aligned} W_{if} &= -P_{ls}\Delta V \\ &= -P_{ls}N_{sl}(v^L - v^S) \end{aligned} \quad (1.172)$$

and the change in the internal energy of the composite system

$$\begin{aligned} \Delta U_c &= U^L(f) + U^S(f) - (U^L(i) + U^S(i)) \\ &= (N^L(f) - N^L(i))u^L + (N^S(f) - N^S(i))u^S \\ &= N_{sl}(u^L - u^S) \end{aligned} \quad (1.173)$$

and applying the conservation of thermodynamic energy

$$\begin{aligned} Q_{sl} + W_{if} &= N_{sl}(u^L - u^S) \\ Q_{sl} &= N_{sl}[(u^L - u^S) + P_{sl}((v^L - v^S))] \end{aligned} \quad (1.174)$$

$$Q_{sl} = N_{sl}[h^L - h^S] \quad (1.175)$$

The intensive Euler equation, Eq. (1.29), may be written

$$u + Pv = Ts + \mu \quad (1.176)$$

$$h = Ts + \mu \quad (1.177)$$

and  $\mu$  is constant during the quasi-static process:

$$Q_{sl} = N_{sl}(h^L - h^S) \quad (1.178)$$

$$N_{sl}T(s^L - s^S) \quad (1.179)$$

The energy per mole required to change the phase from solid to liquid,  $q_{sl}$  is the latent heat,  $\lambda_{sl}$  and it may be written

$$q_{sl} = T(s^L - s^S)$$

or

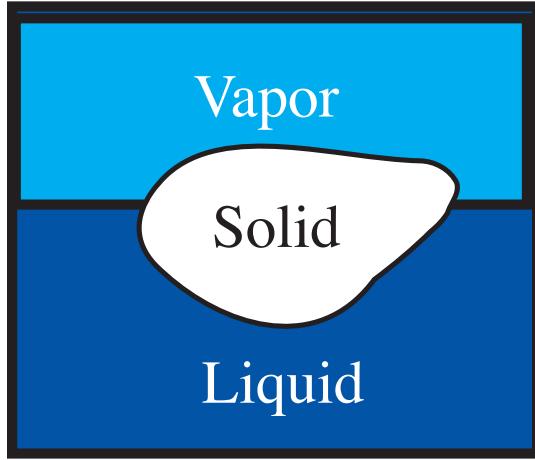
$$q_{sl} \equiv h_{sl} \quad (1.180)$$

## 1.10 Triple point of a substance

The conditions under which the three phases of a pure substance are in equilibrium is a special state in thermodynamics. If the pure substance is H<sub>2</sub>O, then the temperature in this state is used to define the temperature scale. Thus, the conditions under which three phases can be in equilibrium is of particular importance.

We consider the system shown schematically in Fig. 1.15 where the three phases of a substance are shown in an isolated composite system. The values of  $N_c$ ,  $V_c$  and  $U_c$  for the composite system are constant, and the constraints may be written:

$$N_c = N^L + N^V + N^S,$$



**Figure 1.15:** An isolated system containing three phases of a pure substance.

$$V_c = V^L + V^V + V^S.$$

$$U_c = U^L + U^V + U^S.$$

The total differential of the entropy of a simple material system is given in Eq. (1.181) and for a simple material system:

$$dS^\alpha = \left(\frac{1}{T}\right)^\alpha dU^\alpha + \left(\frac{P}{T}\right)^\alpha dV^\alpha - \left(\frac{\mu}{T}\right)^\alpha dN^\alpha, \quad (1.181)$$

where  $\alpha$  is  $L$ ,  $V$  or  $S$ . In this case, the composite system consists of three simple material systems, and the total entropy is given by

$$S_c = S^L + S^V + S^S. \quad (1.182)$$

After taking the total differential of  $S_c$ , and of the constraints, one finds after combining the results

$$\begin{aligned} dS_c = & \left(\frac{1}{T^L} - \frac{1}{T^S}\right)dU^L + \left(\frac{1}{T^V} - \frac{1}{T^S}\right)dU^V + \left(\frac{P^L}{T^L} - \frac{P^S}{T^S}\right)dV^L \\ & + \left(\frac{P^V}{T^V} - \frac{P^S}{T^S}\right)dV^V - \left(\frac{\mu^L}{T^L} - \frac{\mu^S}{T^S}\right)dN^L - \left(\frac{\mu^V}{T^V} - \frac{\mu^S}{T^S}\right)dN^L. \end{aligned} \quad (1.183)$$

For this three-phase system, there are six independent extensive variables. If we assume the system has arrived in the equilibrium state, and consider virtual displacements about the equilibrium state, then in each of these displacements, the total differential of  $dS_c$  must vanish independently of the stability of the equilibrium state. Thus, the necessary conditions for equilibrium are that the temperature is uniform in the system:

$$T^L = T^V = T^S = T,$$

the pressure is uniform in the system,

$$P^L = P^V = P^S = P,$$

and the chemical potential has the same value in each phase:

$$\mu^L(T, P) = \mu^V(T, P), \quad (1.184)$$

$$\mu^V(T, P) = \mu^S(T, P). \quad (1.185)$$

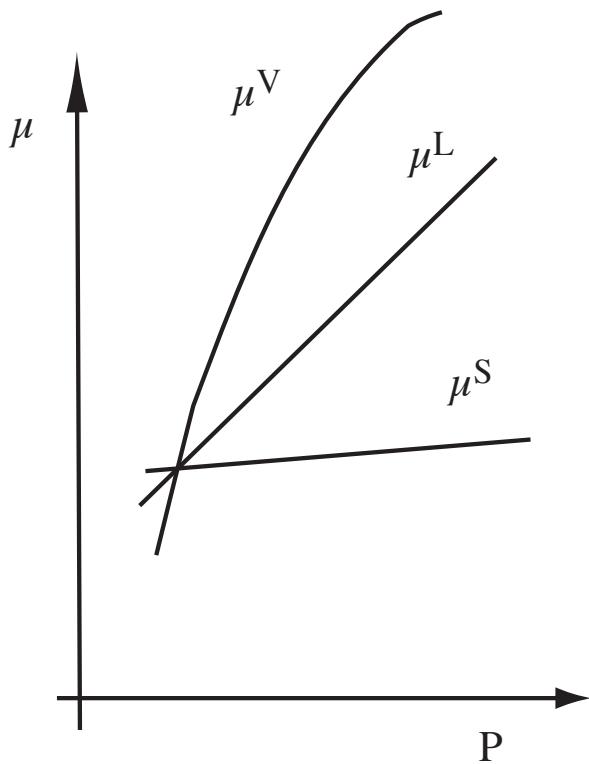
We know  $\mu^L(T, P)$ ,  $\mu^V(T, P)$  and  $\mu^S(T, P)$  are three different functions and that these chemical potentials cannot be equal in more than one state (see Fig. 1.16); thus, Eqs. 1.184 and 1.185 are viewed as two simultaneous equations in two unknowns. The temperature obtained by solving these equations simultaneously is assigned a value of 273.16 K and the pressure is measured to be 610 Pa. The temperature in degrees-celsius,  $T(^{\circ}\text{C})$ , is obtained from:

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15.$$

Thus, the temperature at the triple point of water is 0.01 °C.

## 1.11 Thermodynamic potentials and phase stability

A composite system that interacts with a reservoir may be considered an isolated composite system. The second postulate claims that when they reach an equilibrium state, their total



**Figure 1.16:** For a given temperature, since the solid, liquid and vapor phases have different values of their specific volumes, the chemical potentials cannot be equal in more than one thermodynamic state.

entropy must be an extremum. The nature of the equilibrium state (stable, metastable, unstable) depends on the nature of the extremum (absolute maximum, local maximum or a minimum). The condition for equilibrium can be translated to a condition on **a thermodynamic potential of the system alone**. The thermodynamic function that acts as the thermodynamic potential is determined by the interaction of the composite system with the reservoir. We have defined a **reservoir** as a system that is sufficiently large so that none of its intensive properties are changed even though its extensive properties are changed.

Since  $F$  and  $G$  were obtained from the Legendre transforms of  $U$  both are first-order homo-

geneous functions. Also, both are extensive functions. Below we show that each has other important properties. In particular, under different constraints, each provides a criterion for equilibrium for a composite system that interacts with a reservoir .

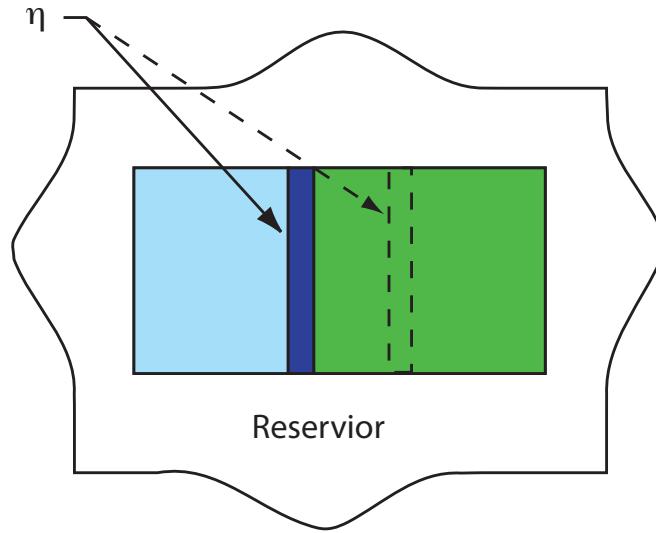
### 1.11.1 Interaction between a composite system with a reservoir

Consider the system shown in Fig. 1.17: a composite system is surrounded by a reservoir with which it can interact. For the moment, the nature of the interaction between the **composite system and the reservoir is not specified**; nor are the constraints acting within the composite system. **Initially, the composite system is supposed initially in equilibrium with a reservoir.** Then work is done on the composite system by some external agency. The work done is assumed to be done by a pure work source that does not change the entropy of anything outside the reservoir. The only change in the entropy is that of the composite system and the reservoir. An example of a pure-work source is a weight being lowered in a gravitational field by an ideal pulley system.

The work process is not necessarily quasi-static. It can be strongly non equilibrium. The composite system and the reservoir can be displaced from equilibrium as the composite system and the reservoir go from one equilibrium configuration to another. After the work process is completed, the composite system and reservoir are allowed to return to equilibrium, but in a new configuration.

Between the two equilibrium states, the thermodynamic states of the systems are not defined, but, for example, the change in the extensive properties between the initial and final state are well defined. Thus, for example, the change in the internal energy of the composite system,  $\Delta U_c \equiv U_c(f) - U_c(i)$  is well defined. The work done on the composite system, according to the energy conservation principle, changes the energy of the system and the reservoir:

$$\eta = \Delta U_c + \Delta U^R. \quad (1.186)$$



**Figure 1.17:** Non-quasistatic work is done on a composite system. The system is initially in equilibrium and finally returns to equilibrium with the reservoir, but between the two equilibrium configurations, disequilibrium can exist.

where the operator  $\Delta$  acting on a function subtracts the value of the function in the initial equilibrium state from the value of the function in the final equilibrium state.

Since the intensive properties of the reservoir are unchanged between the two equilibrium states, one finds from the Euler relation, Eq. 1.24:

$$\Delta U^R = T^R \Delta S^R - P^R \Delta V^R + \sum_{i=1}^r \mu_i^R \Delta N_i^R. \quad (1.187)$$

Since only pure work is crossing the outer boundary of the reservoir, independently of how the system interacts with the reservoir, the constraints at the **outer** boundary of the reservoir give

$$N_{ic} + N_i^R = N_{it}, \quad (1.188)$$

$$V_c + V^R = V_t. \quad (1.189)$$

where  $N_{it}$  and  $V_t$  are the total number of moles in the composite system, and their total volume, respectively. There are no changes in these quantities. The work done on the system

and the reservoir is given by

$$\eta = \Delta U_c + T^R \Delta S^R + P^R \Delta V_c - \sum_{i=1}^r \mu_i^R \Delta N_{ic}. \quad (1.190)$$

Note that the intensive properties in this expression are those of the reservoir and the extensive properties are those of the composite system. Thus, the intensive properties in this expression are unchanged between the initial and final state, but the extensive properties can change.

We now apply the second postulate. Since there is no change in entropy outside the reservoir, for any spontaneous processes induced by the work process

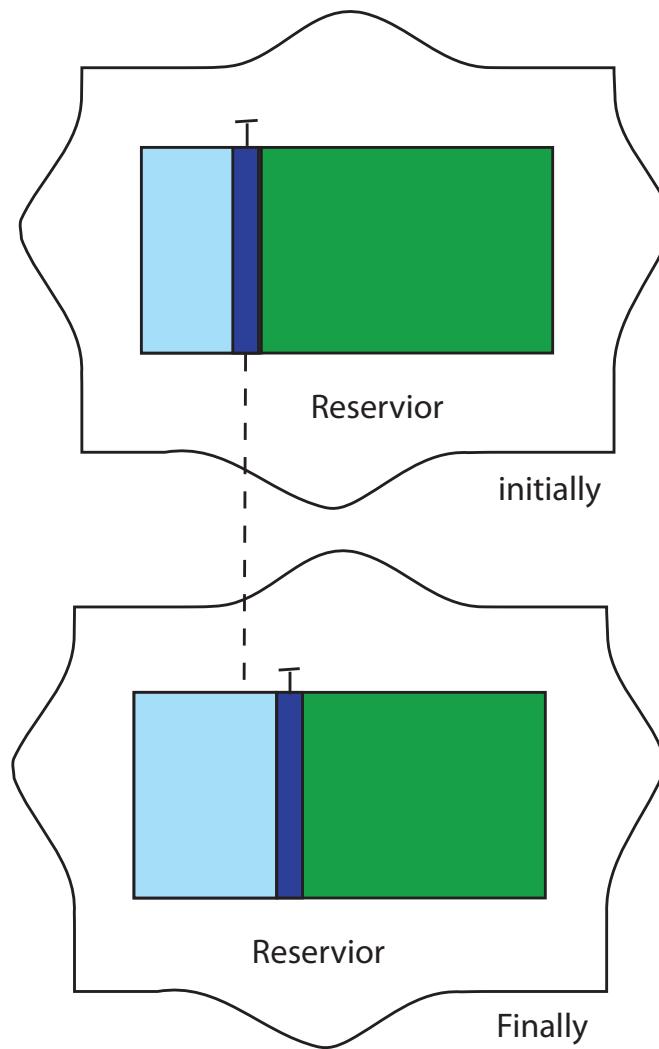
$$\Delta S_c + \Delta S^R \geq 0, \quad (1.191)$$

and Eq. (1.190) gives:

$$\eta \geq \Delta U_c - T^R \Delta S_c + P^R \Delta V_c - \sum_{i=1}^r \mu_i^R \Delta N_{ic}. \quad (1.192)$$

We emphasize that the inequality in Eq. (1.192) results from the entropy postulate. Thus, any spontaneous change that indicated the inequality is violated would indicate the entropy postulate was violated, but recall also that the entropy postulate only applies to macroscopic changes in a system. Molecular or microscopic changes are outside its range of validity. This will be discussed further when the spontaneous formation of a new phase is discussed.

For a thermodynamic function to act as a thermodynamic potential under a defined set of constraints, it must 1) provide a criterion for determining when the system is in equilibrium, and 2) if work is done by the system as the system undergoes a change in equilibrium states, the change in the thermodynamic potential must define the maximum amount of work that could be performed by the system.



**Figure 1.18:** A composite system is indicated that is in equilibrium with a surrounding reservoir when a constraint is in place. The constraint is then removed and the system is allowed to evolve for a short period of time. The constraint is replaced, and the system allowed to come to a new equilibrium state.

### 1.11.2 The Helmholtz function as the criterion for equilibrium

We first consider the composite system shown in Fig. 1.18, and suppose the system and reservoir form an isolated system. We suppose the composite system has constant volume, and number of moles but exchanges thermal energy with the reservoir.

Initially, when a constraint is in place, the system and reservoir are in a constrained equilibrium state, but then the constraint is removed and the system allowed to evolve for a short period of time, but there is no work done during the process. The constraint is then replaced and the system and reservoir allowed to come to equilibrium again. During the process then

$$\Delta V_c = 0, \quad (1.193)$$

$$\Delta N_{ic} = 0, \quad (1.194)$$

then if no work is done, Eq. (1.192) gives:

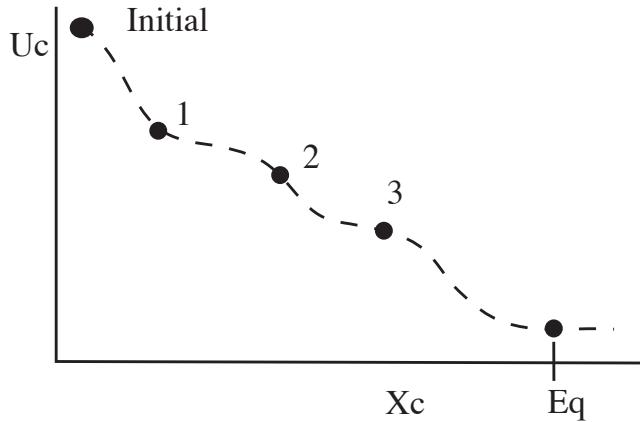
$$\begin{aligned} 0 &\geq \Delta U_c - T^R \Delta S_c \\ &= \Delta(F_c) \end{aligned}$$

thus for each process

$$F_i \geq F_f \quad (1.195)$$

In each spontaneous process that occurs when the constraint is released, the Helmholtz is decreased. If the Helmholtz function had reached its minimum value, there could be no further decrease, and we interpret that to mean the system would have reached an equilibrium state. If we wait for an arbitrarily long period of time and there is still no spontaneous change, we may conclude the system is in a stable equilibrium state.

If the constraint were removed and the system were allowed to evolve for an arbitrarily long period of time, reaching the final equilibrium state, we know that the total entropy would



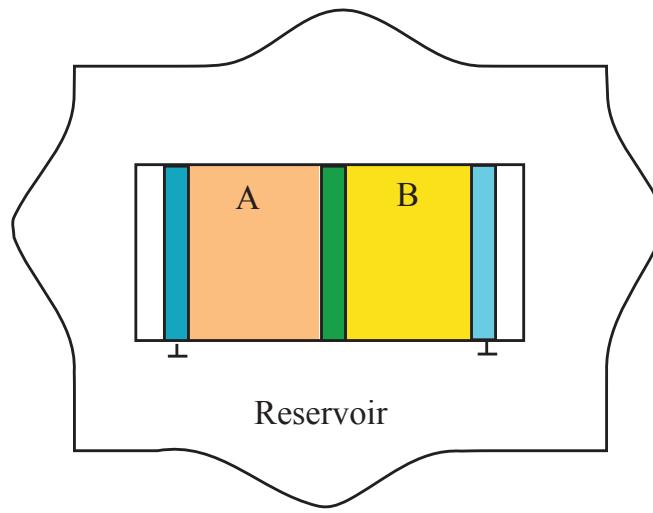
**Figure 1.19:** Each time the constraint is released on the system shown in Fig. 1.18, the function that acts as the thermodynamic potential spontaneously decreases. Then when the constraint is replaced the system comes to equilibrium again. The solid dots indicate these states. The function that acts as a thermodynamic potential depends on the constraints.

be a maximum. We wish to investigate the change in  $U_c$  as the system evolves through a sequence of constrained equilibrium states in which **the entropy is at its equilibrium value**,  $\Delta S_c = 0$ , and investigate how the internal energy changes as the system comes to equilibrium.

$$0 \geq \Delta U_c, \quad (1.196)$$

$$U_c(i) \geq U_c(f). \quad (1.197)$$

As indicated in Fig. 1.19, each time the constraint is removed,  $U_c$  decreases. This process can continue until  $U_c$  reaches its minimum value. When  $U_c$  is at its minimum value, there will be no spontaneous macroscopic changes when the constraint is released. Thus, if the entropy has its maximum value, equilibrium is reached when the energy,  $U_c$ , is a minimum.



**Figure 1.20:** Schematic of a system interacting with a surrounding reservoir. The interactions allow the reservoir to impose its temperature and pressure on the system, but no molecular exchange between the system and the reservoir are allowed.

### 1.11.3 The Gibbs interaction between a composite system and reservoir

Consider the system shown in Fig. 1.20. When the constraints are released, we suppose the constraints are such that the reservoir can impose its pressure and temperature on each of the subsystems in the composite system, but there is no molecular exchange between the composite system and the reservoir.

$$\begin{aligned}\Delta(V_c + V^R) &= 0, \\ \Delta N_{ic} &= 0, \\ \Delta(U_c + U^R) &= 0\end{aligned}\tag{1.198}$$

Then, since no work is being done on the system by an external agency, when the constraint

are released, spontaneous changes takes place, and Eq. (1.190) gives

$$G_c(1) \geq G_c(2) \quad (1.199)$$

and we conclude that equilibrium between the system and reservoir is reached only when the Gibbs function of the composite system has reached a minimum.

## 1.12 Phase transitions and phase stability

Consider a single component fluid in a piston-cylinder arrangement, and suppose it is surrounded by a temperature and pressure reservoir. We know the reservoir imposes its temperature and pressure on the fluid. Suppose the fluid is described by the van der Waals equation of state:

$$P = \frac{\bar{R}T}{v - b} - \frac{a}{v^2}. \quad (1.200)$$

The values of the constants appearing in this equation may be determined from the measured values of the fluid properties at the critical point. At this condition

$$\begin{aligned} \left( \frac{\partial P}{\partial v} \right)_{T=T_{cr}, P=P_{cr}} &= 0, \\ \left( \frac{\partial^2 P}{\partial v^2} \right)_{T=T_{cr}, P=P_{cr}} &= 0. \end{aligned} \quad (1.201)$$

When these equations are solved simultaneously, one finds expressions for  $a$  and  $b$  in terms of  $T_{cr}$  and  $v_{cr}$

$$\begin{aligned} a &= \frac{9\bar{R}T_{cr}v_{cr}}{8}, \\ b &= \frac{v_{cr}}{8}. \end{aligned} \quad (1.202)$$

$$(1.203)$$

**Table 1.1:** Properties at the critical point [1].

Fluid	$T_{cr}/\text{K}$	$P_{cr}/\text{Pa}$	$v_{cr}/(\text{m}^3/\text{mol})$
Carbon dioxide	304.1	$7.38 \times 10^6$	$9.39 \times 10^{-5}$
Hydrogen	33.2	$1.3 \times 10^6$	$6.51 \times 10^{-5}$
Water	647.3	$22.12 \times 10^6$	$5.71 \times 10^{-5}$

If these expressions for  $a$  and  $b$  are inserted into Eq. (1.200) and the result solved for the specific volume in the critical state,  $v_{cr}$ , one finds

$$v_{cr} = \frac{3\bar{R}T_{cr}}{8v_{cr}} \quad (1.204)$$

Then  $a$  and  $b$  may be expressed in terms of  $a$  and  $b$

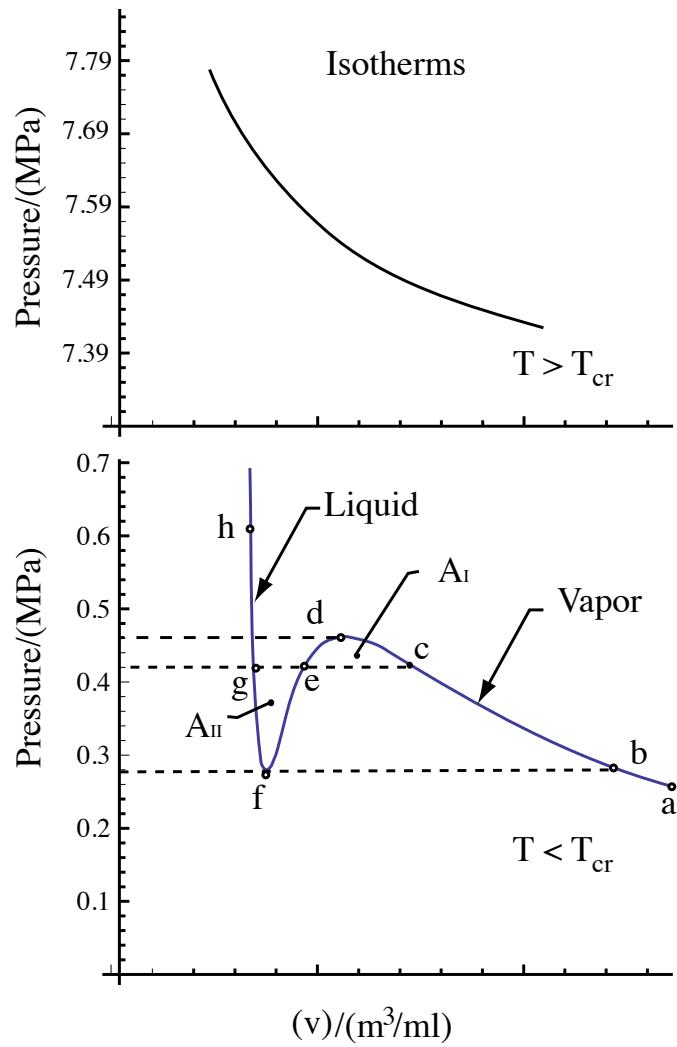
$$a = \frac{27(\bar{R}T_{cr})^2}{64P_{cr}} \quad (1.205)$$

$$b = \frac{\bar{R}T_{cr}}{8P_{cr}} \quad (1.206)$$

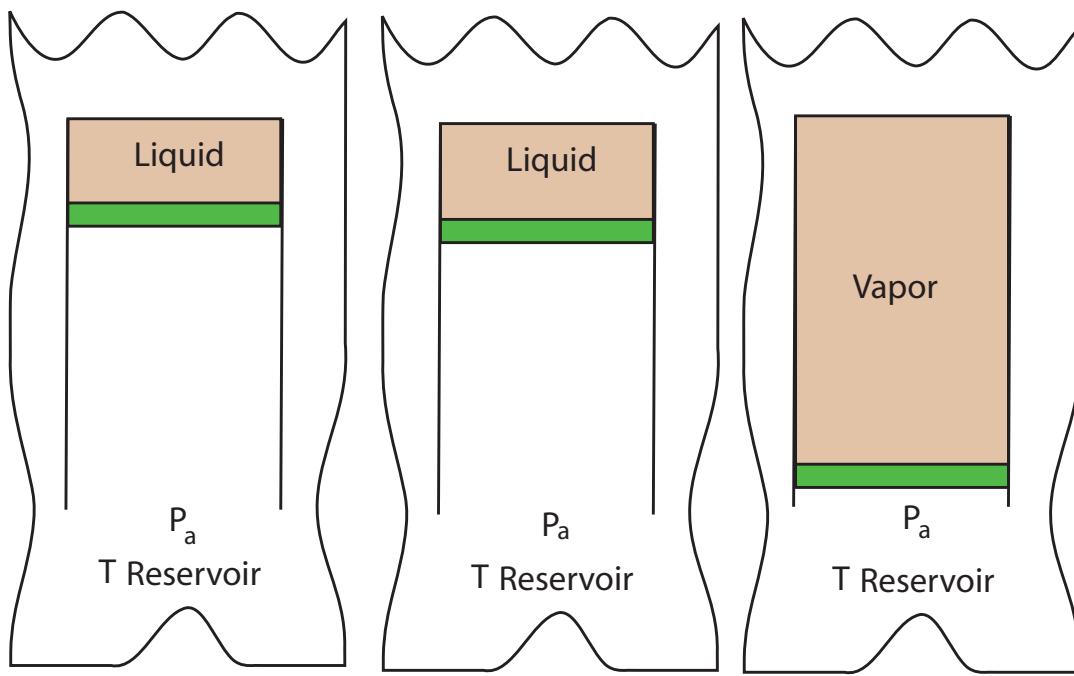
From Eq. (1.200), an isotherm may calculated using the expressions for  $a$  and  $b$  and the measured values  $T_{cr}$  and  $P_{cr}$ . In Fig. 1.21, two isotherms are shown, one for temperature above the critical point and the other below.

The critical values of the temperature and pressure for selected substances are given in Table 1.1 Note then that at pressures between 0.28 and 0.46 MPa, there are predicted to be three different configurations the system could occupy (see Fig. 1.22). An immediate question is: which configuration does the system occupy? We want to show that if the equation of state is known, then the stable, metastable and the unstable configurations of the system can be identified, and the saturation-vapor pressure can be predicted.

The isotherm below the critical point was calculated from the van der Waals equation of state:



**Figure 1.21:** Calculated van der Waals isotherm for  $CO_2$ . The upper one is for a temperature and a pressure above the critical values ( $304.2\text{ K}$  and  $7.39\text{ MPa}$ ), and the lower one is  $275.16\text{ K}$ .



**Figure 1.22:** A fluid in a piston-cylinder arrangement that is maintained isothermal and at constant pressure is predicted to have three possible configurations.

The empirical, critical point properties for three substances are listed in Table 1.1. When these empirical properties are used in Eq. (1.204) to calculate the value  $v_{cr}$ , one finds a value of  $9.1 \times 10^{-5}$ . Whereas, the measured value is  $5.71 \times 10^{-5}$ .

At present much more sophisticated equations of state are being developed, but we may use the van der Waals equation of state to illustrate how knowledge of a  $P = P(T, v)$  relation may be used to determine the stability of a phase and the saturation-vapor pressure of the liquid and vapor phases of the substance.

**Table 1.2:** Calculated values of van der Waals constants

Fluid	a/(Pa m <sup>6</sup> /mol <sup>2</sup> )	b/(m <sup>3</sup> /mol)
Carbon dioxide	4.3	$5.03 \times 10^{-4}$
Hydrogen	0.324	$3.47 \times 10^{-4}$
Water	5.45	$3 \times 10^{-4}$

## 1.13 Phase stability predicted from an equation of state

When a system is at a temperature and pressure below the critical point, the isotherm (Fig. ?? may be viewed as consisting of three physical branches. We consider the stability of each branch. Those states on the isotherm from  $a$  to  $d$  are referred to as states on branch I, those from  $d$  to  $f$  as branch II states, and those states from  $f$  to  $g$  as branch III states. The states on branch I of the substance are compressible, but on branch III of the substance, the states are almost incompressible. Thus, these branches may be labelled vapor and liquid respectively. The states on branch II cannot be labelled, at present, but the stability of the states on each branch may be determined from the thermodynamic potential which for system considered (Fig. 1.22) is the Gibbs function. Since

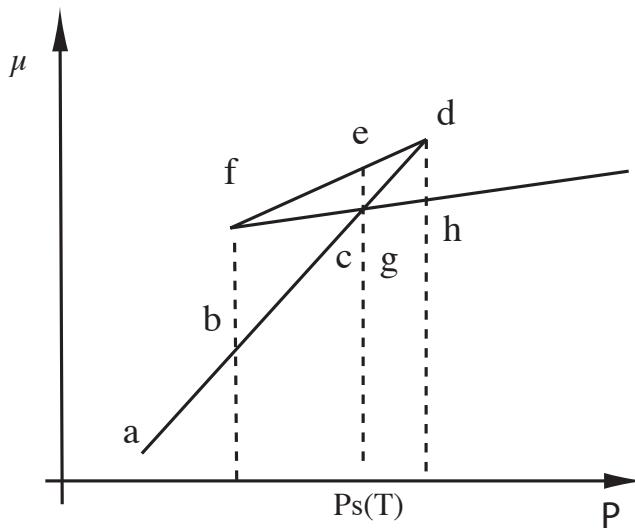
$$G = N\mu(T, P),$$

and  $N$  is constant, we need to determine the value of the chemical potential on each branch to determine the stability of the states on that branch. From the Gibbs-Duhem equation, Eq. (1.48),

$$d\mu = -sdT + vdP$$

Thus

$$\begin{aligned} \left(\frac{\partial \mu}{\partial P}\right)_T &= v. \\ \left(\frac{\partial \mu}{\partial P}\right)_T &> 0 \end{aligned} \tag{1.207}$$



**Figure 1.23:** Calculated isotherm for  $\text{CO}_2$  at  $2\text{ }^\circ\text{C}$ .

and from a calculated isotherm such as that shown in Fig. ??, one may sketch a curve showing  $\mu(T, P)$  versus  $P$ , as indicated in Fig. 1.23. Note that the chemical potential on branch I at  $P_g$  is equal the chemical potential on branch III at  $P_c$ . The chemical potentials on branch I and on branch III are different functions, and the fact that they are equal at one pressure

$$\mu^{III}(T, P_g) = \mu^I(T, P_c). \quad (1.208)$$

indicates that this pressure is the saturation-vapor pressure (See Section 2.2):

$$P_g = P_c = P_s(T)$$

Now the thermodynamic stability of the different branches can be stated. The descriptions is given in Table 1.3 Thus, once the saturation-vapor pressure is known, the stability of a phase is determined by the pressure relative to the saturation-vapor pressure.

Now we want to show the value of the saturation-vapor pressure, corresponding to a particular temperature, can be determined from the expression for the isotherm.

**Table 1.3:** Thermodynamic stability of the different branches of a van der Waals isotherm.

Branch	Pressure Range	stability
I	$P_b \leq P \leq P_s(T)$	stable
I	$P_s(T) \leq P \leq P_d$	metastable
II	$P_f \leq P \leq P_d$	unstable
III	$P_f \leq P \leq P_s(T)$	metastable
III	$P_s(T) \leq P \leq P_d$	stable

From the Gibbs-Duhem equation, Eq. (1.48), and Fig. 1.23

$$\mu(T, P_s) = \mu(T, P_a) + \int_{P_a}^{P_c} v^I dP, \quad (1.209)$$

$$\mu(T, P_s) = \mu(T, P_a) + \int_{P_a}^{P_c} v^I dP + \int_{P_c}^{P_d} v^I dP - \int_{P_f}^{P_d} v^{II} dP + \int_{P_f}^{P_g} v^{III} dP, \quad (1.210)$$

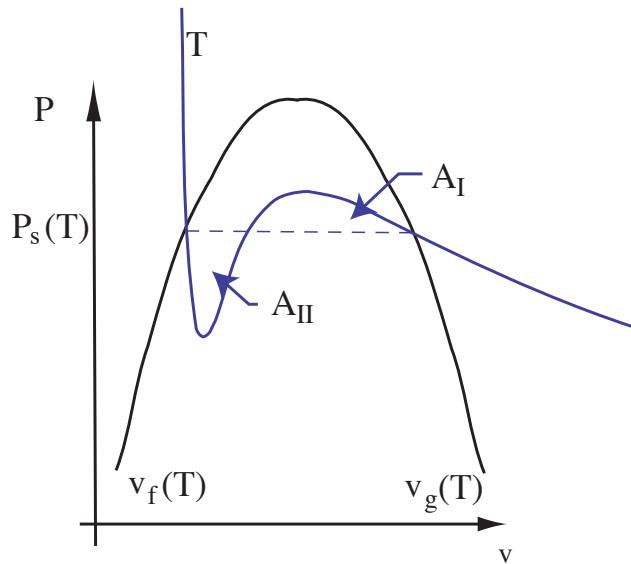
and after subtracting the first of these equations from the second

$$\int_{P_c}^{P_d} v^I dP - \int_{P_e}^{P_d} v^{II} dP = \int_{P_f}^{P_g} v^{III} dP. \quad (1.211)$$

If these integrals are interpreted as areas, then they indicate areas  $A_I$  and  $A_{II}$  defined in Fig. ?? must be equal:

$$A_I = A_{II}. \quad (1.212)$$

Thus, one plots  $P$  versus the specific volume using the isotherm relation, and obtains a curve such as that shown in Fig. ???. One then chooses the saturation-vapor pressure to be such that the areas,  $A_I$  and  $A_{II}$ , defined in Fig. 1.24, are equal. Once the value of  $P_s$  is known, one can apply the results in Table 1.3 to determine the stability of each portion of the isotherm.



**Figure 1.24:** Calculated isotherm for  $\text{CO}_2$  at  $2\text{ }^{\circ}\text{C}$ .

### 1.13.1 The absent mechanism for a liquid-vapor phase transition

We can now state the conditions necessary for a liquid-to-vapor phase transition to occur. If the pressure  $P_a$  in Fig. 1.22 is a pressure greater than  $P_s(T)$ , then as indicated in Table 1.3, the liquid phase, branch III, is stable. When the pressure on the liquid phase is reduced so  $P_a < P_s(T)$ , the liquid phase is metastable, but what event must occur in order to take the liquid out of the metastable state we cannot say at present. We can only say that the liquid phase is no longer stable. This indicates the fluid will not remain indefinitely as a liquid. When the system arrives in a stable equilibrium state again, the fluid is a vapor, but mechanism by which the transition takes place has not been established.

A similar description may be given for the transition from a vapor to a liquid.

## 1.14 Chapter 1 Problems

1. The following two functions are purported to be fundamental relations.

- a.  $S = C(NU/V)^{2/3}$ .

- b.  $S = CV^3/NU$ .

If  $C$  is a constant, can either of them be a fundamental relation?

2. Use the entropy formulation to show the ratio  $P/T$  is an intensive property of a simple-material system.
3. If the fundamental relation for a two-component simple system in the entropy formulation satisfies the following relation

$$\begin{aligned} S &= NC + NR \ln \left( U^{3/2}V/N^{5/2} \right) - N_1 R \ln \left( N_1/N \right) - N_2 R \ln \left( N_2/N \right), \\ N &= N_1 + N_2, \end{aligned} \tag{1.213}$$

where  $R = 8.314 \text{ J/mol-K}$  and  $C$  is an unspecified constant, give the expression for each of the following in terms of the indicated independent variables:

- a.  $U = U(T, V, N_1, N_2)$ ,
  - b.  $P = P(T, V, N_1, N_2)$ ,
  - c.  $\mu_1 = \mu(T, P, N_1, N_2)$ .
4. If  $s$  and  $v$  are to be chosen as the independent intensive variables for a single component simple-material:
    - a. show that  $\mu$  may be expressed in terms of these variables.

- b. If the enthalpy is defined as  $h = u + Pv$ , show that  $c_p$  may be expressed

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p .$$

5. The fundamental relation for electromagnetic radiation is

$$S = \frac{4}{3}b^{1/4}U^{3/4}V^{1/4},$$

where  $b$  is a constant. The number of particles,  $N$ , does not appear in the relation because there are no conserved particles. Suppose the universe to be an expanding electromagnetic cavity containing radiation that now has a temperature of 2.7 K, and the expansion is isentropic (constant entropy).

- a. What will be the temperature of the radiation when the volume of the universe is twice its present value?
- b. If the energy is presently  $U_I$ , give the expression for the change in energy that results of the expansion.
- c. Give the expression for the energy in terms of the volume and entropy.
- d. Since there is nothing beyond the boundary of the universe, what is the work required to expand the universe from  $V_I$  to  $2V_I$ ?
- e. Why is the energy of the universe not constant as universe expands? Show quantitatively the reason for your answer.

6. The fundamental relation for system A is

$$S^A = C(U^2VN)^{1/4}$$

and that of system B is

$$S^B = C(U^2VN)^{1/4}.$$

- What is the fundamental relation of a system formed by enclosing system A and system B in a constant volume isolated container with no restrictions on the interactions between the systems?
7. A portion of a substance,  $S = C(U^2VN)^{1/4}$  where  $C$  is a constant, is placed on either side of an impermeable, adiabatic piston that is pinned in position, and separates the volume into two portions. The portion of the substance on either side of the piston forms a simple-material system. The volume on one side of the piston is  $2 \text{ cm}^3$ , has 4 moles of the substance and is denoted side A. On the other side of the piston, there is a volume of  $3 \text{ cm}^3$  and 9 moles.
- A. Since the piston is adiabatic, there can be no exchange of energy between systems A and B. The system cannot come to thermal equilibrium, but the total entropy of the composite system,  $S_c$  can be determined. The value of  $S_c$  depends on how the energy is partitioned between the two systems, and the partitioning cannot be determined from the information given. Show a plot of

$$S_c/CU_c^{1/2}$$

as a function of  $U^A/U_c$ , and give the value of  $U^A/U_c$  at which the maximum occurs, denote it as  $U_m^A/U_c$

- B. Now suppose the piston is diathermal, determine the value of  $U^A/U_c$  at equilibrium, denote it as  $U_e^A/U_c$ .
- C. Compare on the two values  $U^A/U_c$ , and comment on the role of entropy in determining the equilibrium state.

8. The fundamental relation for a substance is

$$S = C(N_1 + N_2) + (N_1 + N_2)R \ln \left( \frac{U^{3/2}V}{(N_1 + N_2)^{5/2}} \right) - N_1 R \ln \left( \frac{N_1}{N_1 + N_2} \right) - N_2 R \ln \left( \frac{N_2}{N_1 + N_2} \right) \quad (1.214)$$

where  $R=8.314 \text{ J/(mole K)}$  and  $C$  is a constant. The substance is in a container that is divided into two portions by a rigid, diathermal piston that is fixed in position and permeable to component 1, but impermeable to component 2. Initially, on side A of the piston:

$$N_1^A = 0.75 \text{ mole}, N_2^A = 1 \text{ mole}, V^A = 5 \text{ L}, T^A = 320 \text{ K},$$

and initially on side B

$$N_1^B = 1.0 \text{ mole}, N_2^B = 0.75 \text{ mole}, V^B = 5 \text{ L}, T^B = 250 \text{ K}.$$

- After equilibrium is established, what are the values of  $N_1^A, T^A, P^A, P^B$ ?

9. A single component, ideal gas is defined as a substance that satisfies

$$\mu(T, P) = \mu(T, P_r) + \bar{R}T \ln \frac{P}{P_r}.$$

Show that for such substance, the enthalpy,  $h$  is only a function of temperature,  $h = h(T)$ .

10. The three phases of water are in equilibrium when maintained at 0.01 °C and 0.6113 kPa. The properties of the three phases at this condition are given in Table 1.4

A. Suppose the pressure is reduced to 0.4375 kPa and the temperature to  $-6^\circ \text{ C}$ . If the system is allowed to come to equilibrium at these conditions, what will be its phase?

B. If the temperature is maintained at  $-6^\circ \text{ C}$ , and the pressure is increased until equilibrium exists between the liquid and solid phases, estimate the increase in pressure.

C. A skater wants water to be present under a portion of the blade of his skate to reduce the friction between his skate and the ice. If a 100 kg skater wants to skate at

**Table 1.4:** Properties of water at the triple point [1].

phase	solid	liquid	vapor
entropy / (kJ/kg K)	-1.2210	0	9.1562
specific volume/(m <sup>3</sup> /kg)	0.0010908	0.001000	206.132
internal energy/(kJ/kg)	333.40	0	2375.33
enthalpy/(kJ/kg)	-333.4	0	2501.3

- 6 °C, and the portion of the blade of his skate that is in contact with the ice is 250 mm in length, what should be the cross-sectional thickness of his skate? Comment on the validity of your calculation.
11. When equilibrium exists between the liquid and vapour phases of a particular substance, the temperature-pressure relation for temperatures near the triple point is given by

$$\ln \frac{P}{P_r} = 15.16 - \frac{3063K}{T}$$

,

and for temperatures near the triple point when equilibrium exists between the solid and vapour phases of this substance

$$\ln \frac{P}{P_r} = 18.70 - \frac{3754K}{T},$$

where  $P_r = 1.01325 \times 10^5$  Pa.

- A. What are the values of the temperature and pressure at the triple point?
- B. If at the triple point, the specific volumes of this substance satisfies the conditions:

$$v_{tp}^V \gg v_{tp}^L \gg v_{tp}^S$$

and the vapour may be approximated as an ideal gas, what is the value of the latent heats of the solid-vapour and liquid-vapour phase transitions?

- C. What is the value of the latent heat of the solid-liquid phase transition at the triple point of the substance?
12. From the fundamental relation of a pure component, it is found that at a temperature  $T_0$ , the pressure as a function of specific volume is approximately given by

$$\begin{aligned} P &= P_1 + a(v_1 - v) & v < v_1 \\ P &= v \frac{(P_2 - P_1)}{v_2 - v_1} + \frac{(v_2 P_1 - v_1 P_2)}{v_2 - v_1} & v_1 < v < v_2 \\ P &= P_2 + a(v_2 - v) & v_2 < v \end{aligned} \quad (1.215)$$

where  $P_1, P_2, v_1, v_2, a$  are parameters of known values.

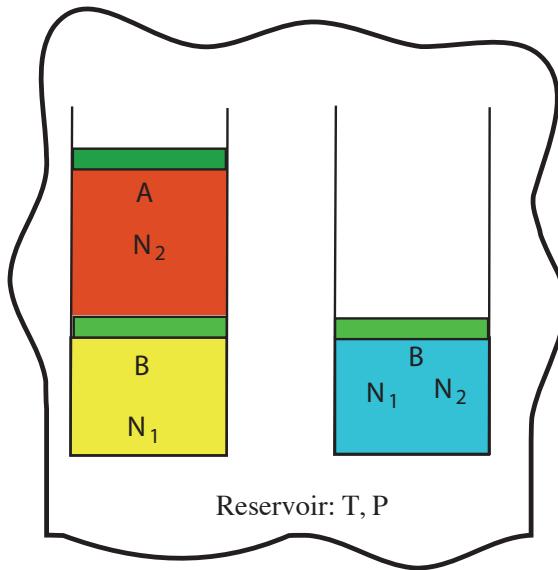
- A. Give the expression for the saturation-vapor pressure of the substance at  $T_0$  in terms of the isotherm parameters.
- B. When the substance is at temperature  $T_0$ , for what range of pressures is substance stable?
13. A cylindrical container is divided into two portions by freely-moving, rigid pistons that are diathermal and impermeable (see Fig. 1.25). Initially, in subsystem B only  $N_1$  mole of a pure liquid is present, and in subsystem A, only component 2 is present. Component 2 has as its fundamental relation

$$S = N_2 K + N_2 \bar{R} \ln \frac{U^{3/2} V}{N_2^{5/2}},$$

where  $K$  is constant. The lower piston is suddenly removed, and the system allowed to come to equilibrium. In the final state, the two components form a weak solution

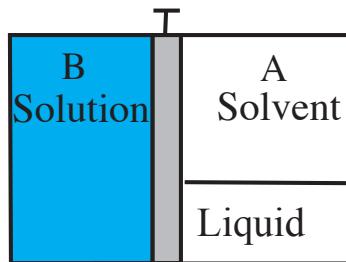
for which the saturation concentration is given by

$$x_s = \frac{x_1 P}{K_h(T)}.$$



**Figure 1.25**

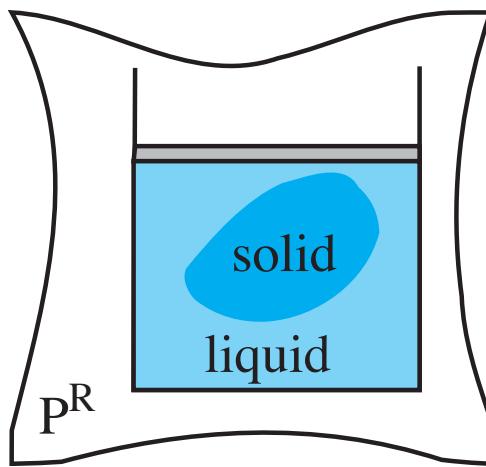
- A. What is the change in the volume of the composite system between the initial and final states?
  - B. What is the change in entropy of the composite system between the initial and final states?
14. In the system shown schematically in Fig 1.26, the solution is separated from the solvent by a membrane that is permeable only to the solvent and is diathermal. The solution contains only one solute. System B consist of the pure solvent, but in two phases. The composite system forms an isolated system.
- A. State the constraints that you use and apply the entropy postulate to determine the conditions that the intensive properties must satisfy in order for equilibrium to exist.

**Figure 1.26**

- B. When equilibrium is reached, if the solvent is water and the ratio of mole fractions is 0.1 and the temperature 100 °C, what would be the pressure in system B .
- C. If the piston unpinned and freely moving what would be the final configuration of the system? Show a sketch of the configuration you predict.
15. By definition, the freezing point of a substance is the temperature at which equilibrium exists between the solid and liquid phases when the pressure is equal to that of the surroundings. Suppose the liquid and solid phases of a pure substance are enclosed in a piston-cylinder arrangement and surrounded by a pressure reservoir, as indicated in Fig. 1.27. The piston is free to move and the cylinder walls are diathermal. The ambient pressure of the reservoir is 0.10135 MPa, and the freezing point of the pure substance in the piston-cylinder arrangement is  $T_0$ .
- A. Suppose that the liquid and solid phases are in equilibrium at  $T_0$ . Then a small amount of a new, nonvolatile substance is added to the liquid phase where the non-volatile substance immediately goes into solution, and forms a weak solution with a concentration  $x_2$ . If the latent heat for the solid-liquid phase transition,  $\lambda_{sl}$ , for the pure solvent may be expressed

$$\lambda_{sl} = T_0(s^L - s^S) \quad (1.216)$$

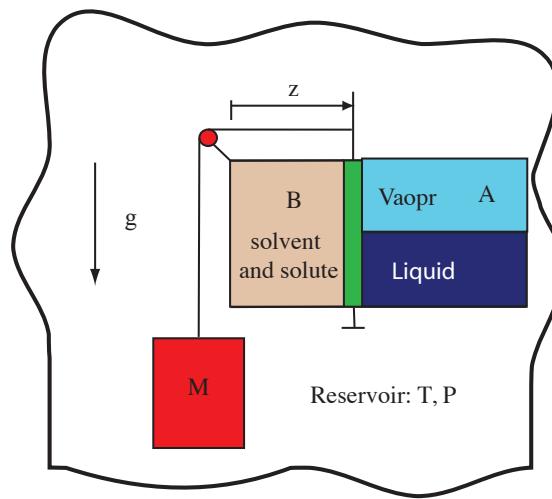
give the *approximate* expression for the freezing point of the solution.



**Figure 1.27:** Two phase system.

- B. If the solvent is water, and the freezing point of the solution is found to be  $-5\text{ }^{\circ}\text{C}$ , what is the osmotic pressure of the solution?
16. The boiling point of a liquid is defined as the temperature at which the equilibrium vapor pressure is equal to the ambient pressure. Suppose the liquid and vapour phases of a pure substance are enclosed in a piston-cylinder arrangement. The piston-cylinder system is surrounded by a reservoir. The piston is free to move and the cylinder walls are diathermal. The ambient pressure of the reservoir is  $0.10135\text{ MPa}$ , and the boiling point of the pure substance in the piston-cylinder arrangement is known to be  $T_0$ .
- A. Suppose the liquid and vapour phases are in equilibrium, that a small amount of a new, nonvolatile substance is added to the liquid phase where the nonvolatile substance immediately goes into solution and forms a weak solution. After the nonvolatile substance has gone into solution in the liquid phase, a small quantity of the solution is extracted and the osmotic pressure of the solution is measured when the solution is at  $T_0$ . It is found to be  $\Pi_0$ . If the boiling point of the solution,  $T_{BP}$ , is near that of the pure substance, give the approximate expression for the boiling point of the solution in terms of properties of the pure solvent and  $\Pi_0$ .

- B. If the solvent is water and the value of  $\Pi_0$  is 5.0 MPa, what is the boiling point of the solution?
- C. The atmospheric pressure at the top of Mount Everest is said to be 0.03652 MPa. What is the boiling point of water there? What is the boiling point of the solution in parts A and B?
17. A rigid cylinder is divided into two portions by a semi-permeable, diathermal piston of area A. On one side is a two component, weak liquid solution. On the other is the pure solvent in the two fluid phases. The piston is permeable only to the solvent. A mass M is attached to the piston by a string, as indicated in Fig. 1.28 Friction effects and any effects of gravity inside the piston-cylinder arrangement may be neglected. The total system is surrounded by a reservoir that has a temperature  $T^R$  and a pressure  $P^R$ .
- A. Initially, the piston is pinned in position. After the piston is released, it is found that when equilibrium is reached, both the liquid and vapour phases are present in system A. Use the entropy postulate to determine the necessary conditions for equilibrium.
- B. If the mass is 100 kg, the area of the piston is  $0.1 \text{ m}^2$ , the solvent is water, the temperature of the reservoir is  $25^\circ\text{C}$ , and its pressure is 2 bar, what is the concentration in the solution (moles per mole)? The molecular weight of the solute is 150.
18. Show that
- $$\left(\frac{\partial P}{\partial T}\right)_v = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_v}. \quad (1.217)$$
19. Show that
- $$Tds = c_v dT + T \frac{\alpha}{\kappa_T} dv \quad (1.218)$$
20. A liquid is enclosed in a piston-cylinder arrangement that initially has a volume of one litre and is initially at a temperature  $90^\circ\text{C}$ , and a pressure of 70.183 kPa.



**Figure 1.28:** Two phase system.

- A. If the liquid is heated to 100 °C with piston fixed rigidly in position, use a Taylor series to estimate the final pressure in the system.
- B. If the piston is free to move as the liquid is heated, estimate the final volume.

Other properties of the liquid at 90 °C are:

$$v = 0.001036 \frac{m^3}{kg}$$

$$\kappa_T = 4.63 \times 10^{-10} \frac{1}{Pa},$$

$$c_p = 4.205 \frac{kJ}{kgK},$$

$$c_v = 3.865 \frac{kJ}{kgK}$$

21. The expansivity  $\alpha \equiv \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P$  for a particular single component system is found to have

the following relation to the temperature

$$\alpha = \frac{1}{T}.$$

Show that for this substance

$$\left( \frac{\partial c_p}{\partial P} \right)_T = 0.$$

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