

Thermodynamics and Physical Kinetics

by

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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

Boulud **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 [8] 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 [9] 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, μ_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 α 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

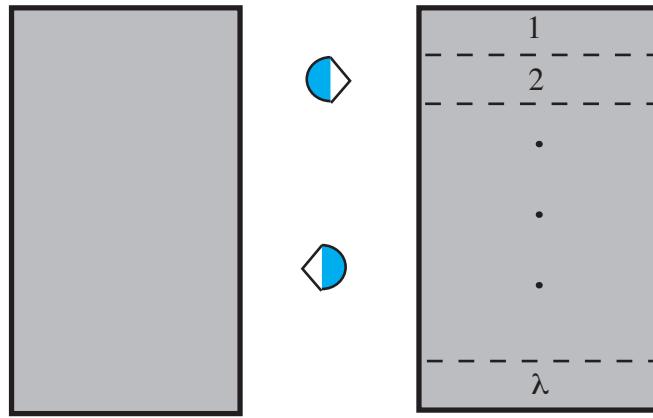


Figure 1.1: A simple-material system may be viewed as a composite system in which each subsystem consists of the same substance.

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

¹

According to the Entropy Postulate, the total internal energy of a composite system, U_c , for which each of its λ 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 λ 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:

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

¹ **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 λ 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 λ —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 λ 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 μ 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 μ 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 μ , 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 μ 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 ζ 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, κ_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, α , 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 λ 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, μ have been defined. 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, κ_T and α . 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 α

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

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

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 μ_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, κ_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, κ_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.

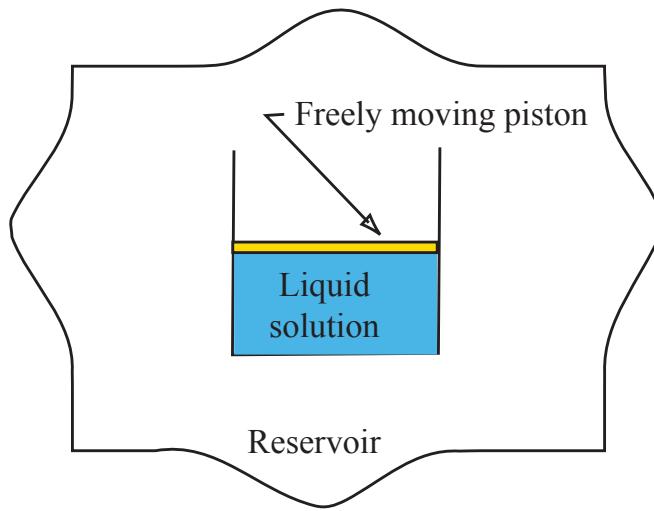


Figure 1.2: The liquid is initially pure, and the walls of the piston-cylinder relation are impermeable.

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.

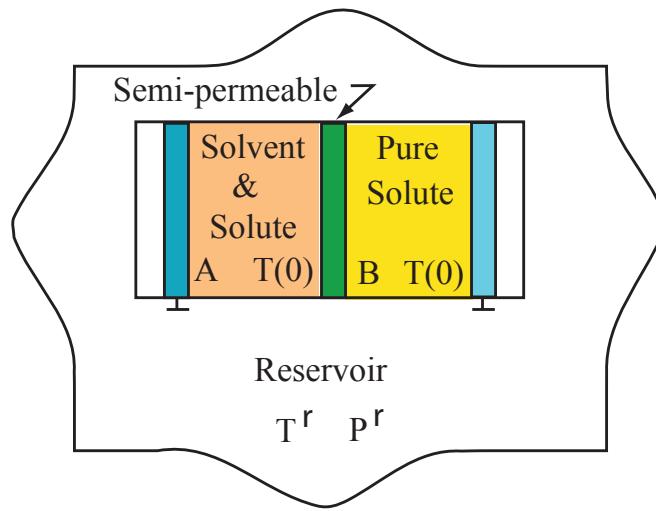


Figure 1.3: Schematic of a composite system, with subsystem A and B, that interacts with a reservoir. System A is a liquid solution and system B is pure solute. Initially the temperature of the system and the reservoir are different.

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:

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

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

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 O₂, N₂, and H₂O 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 O₂ is 4.259×10^4 Atm and for N₂ is 9.077×10^4 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 H₂O in the moist air.

3. If the mole fraction of N₂ in the moist air is 2.5 times that of O₂, give the values of the mole fractions of the gases in the solution when the system is in equilibrium.

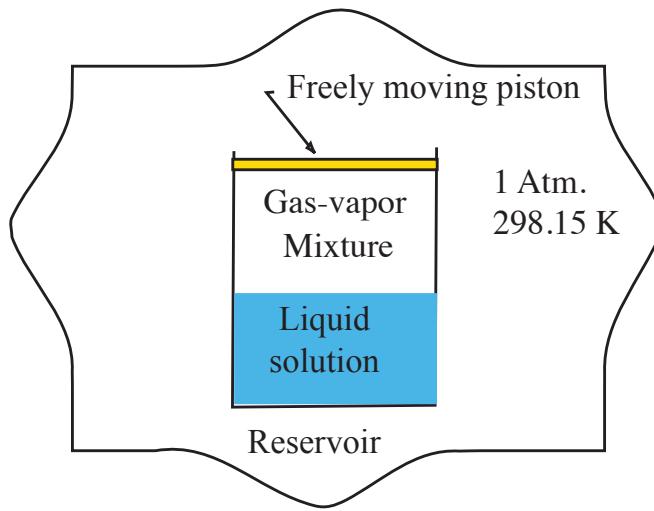


Figure 1.4: An ideal mixture that consists of H_2O vapor and N_2 is in contact weak H_2O at 25 °C and 101.325 kPa

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

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

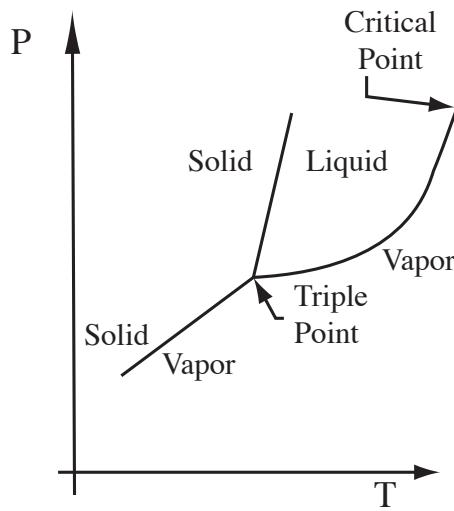


Figure 1.5: A phase diagram is shown for a substance that contracts on freezing.

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:

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

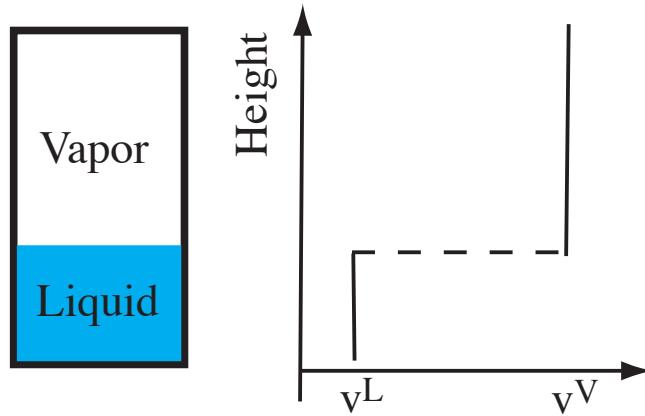


Figure 1.6: Fluid phases of a component enclosed in a constant volume system.

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 α are denoted T^α , P^α , μ^α , 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 α 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 μ^L, μ^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):

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

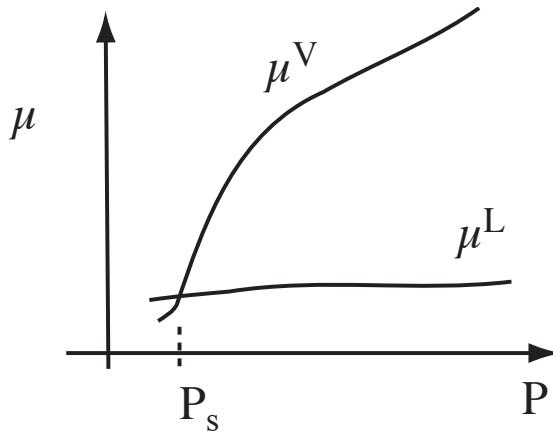


Figure 1.7: In an isothermal two phase system, the chemical potentials of the liquid and vapor phases can be equal at only one pressure.

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**

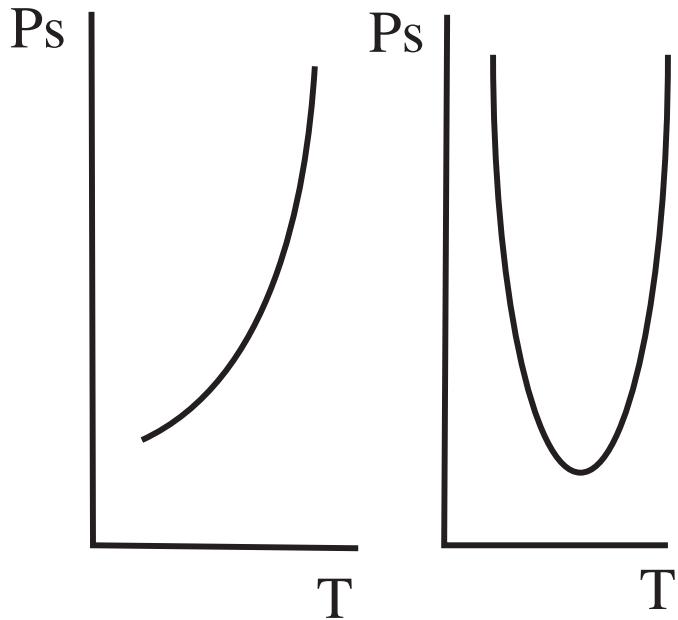


Figure 1.8: Possible relations between $P_s(T)$ and T .

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.

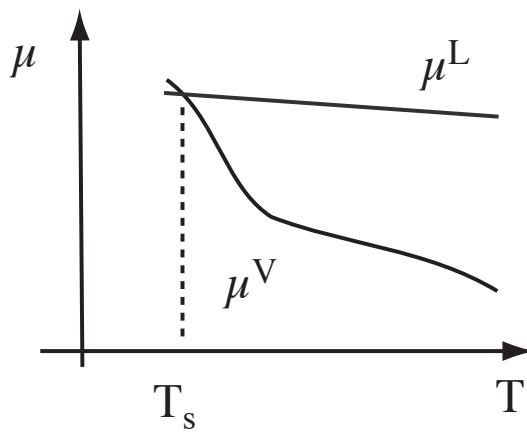


Figure 1.9: For a given pressure, the relation between the chemical potential functions of a liquid and its vapor is shown.

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 λ 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 $P_s(T)$. ¹ 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

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

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

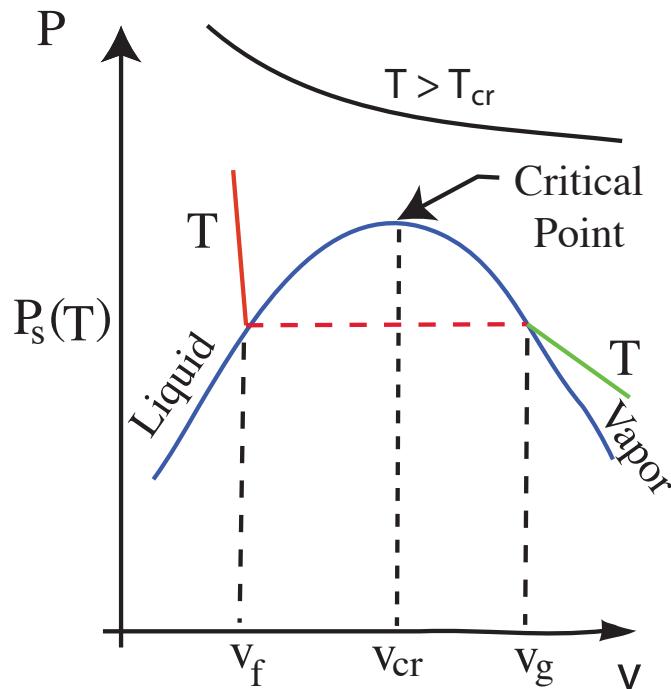


Figure 1.10: The fluid phases the system shown Fig. ?? could adopt are shown schematically.

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

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

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

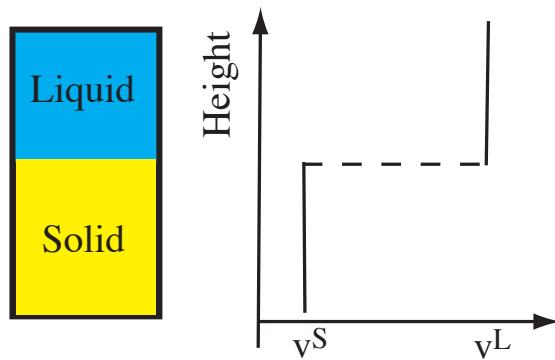


Figure 1.11: A liquid phase in equilibrium with a solid phase in the absence of surface effects and gravity

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, σ_{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.

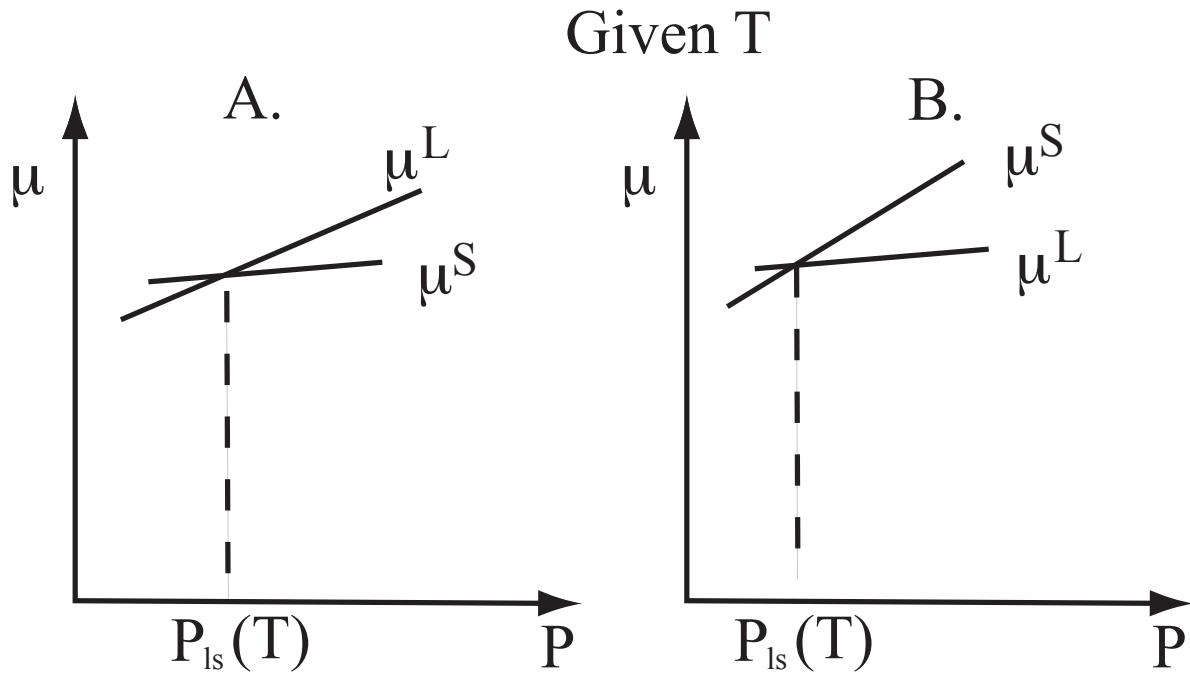


Figure 1.12: In A. the chemical potential of a solid which contract on solidifying is plotted, and on the right the chemical potential of a solid that expands on solidifying is shown.

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

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

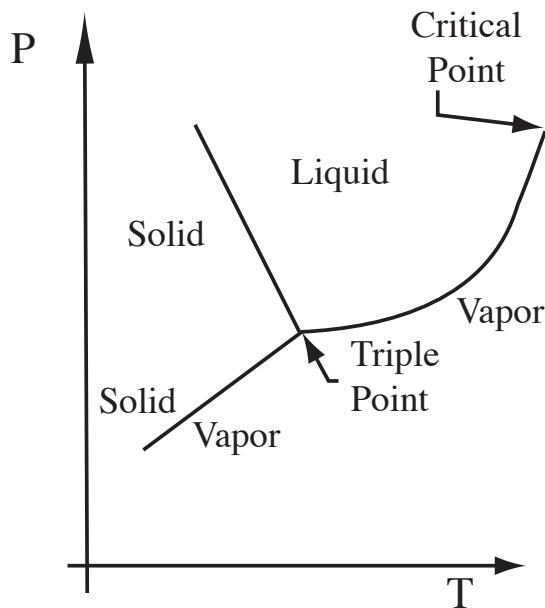


Figure 1.13: When the solid phase has a larger specific volume than the liquid phase, the slope of $P_{ls}(T)$ is negative, but if the specific volume of the solid is smaller than that of the liquid, the slope is positive as seen Fig 1.5

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

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

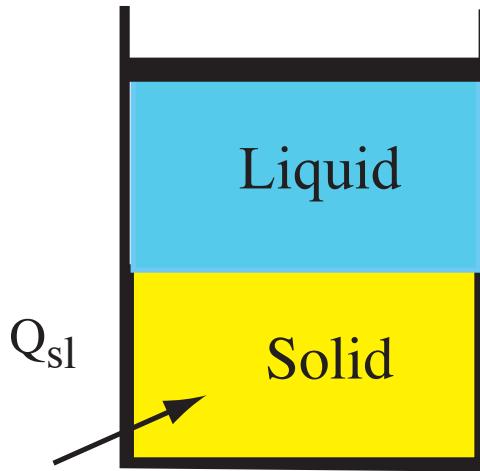


Figure 1.14: The solid and liquid phases of a single component system are initially in equilibrium are then heated to produce more liquid.

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 μ 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, λ_{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 H₂O, 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:

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

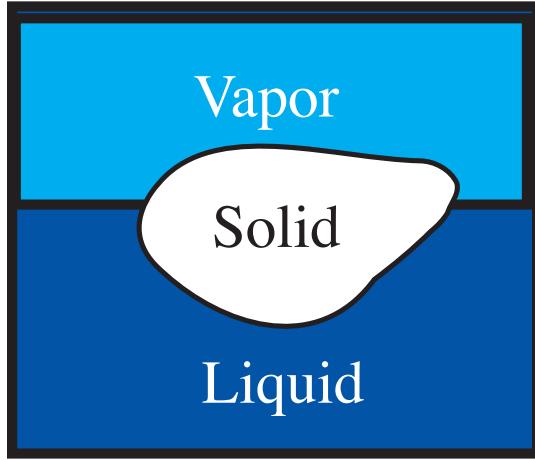


Figure 1.15: An isolated system containing three phases of a pure substance.

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

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

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 α 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 $^{\circ}\text{C}$. This definition is used to set the temperature scale for temperature measurements.

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

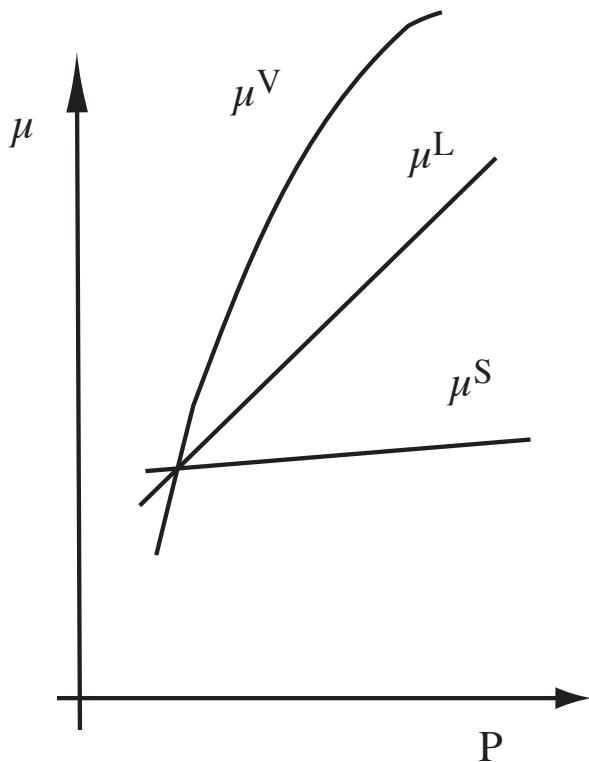


Figure 1.16: For a given temperature, since the solid, liquid and vapor phases have different values of their specific volumes, the chemical potentials cannot be equal in more than one thermodynamic state.

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:

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

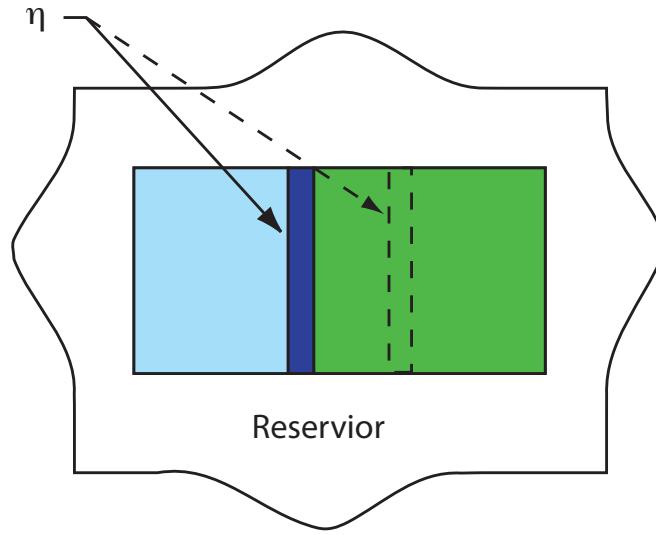


Figure 1.17: Non-quasistatic work is done on a composite system. The system is initially in equilibrium and finally returns to equilibrium with the reservoir, but between the two equilibrium configurations, disequilibrium can exist.

where the operator Δ 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.

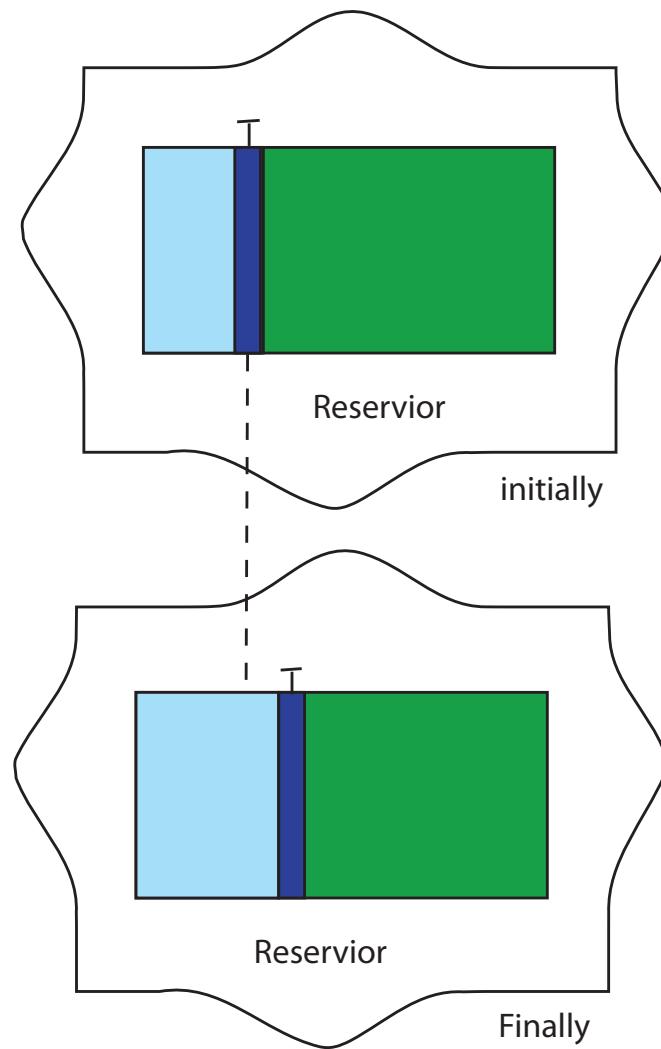


Figure 1.18: A composite system is indicated that is in equilibrium with a surrounding reservoir when a constraint is in place. The constraint is then removed and the system is allowed to evolve for a short period of time. The constraint is replaced, and the system allowed to come to a new equilibrium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

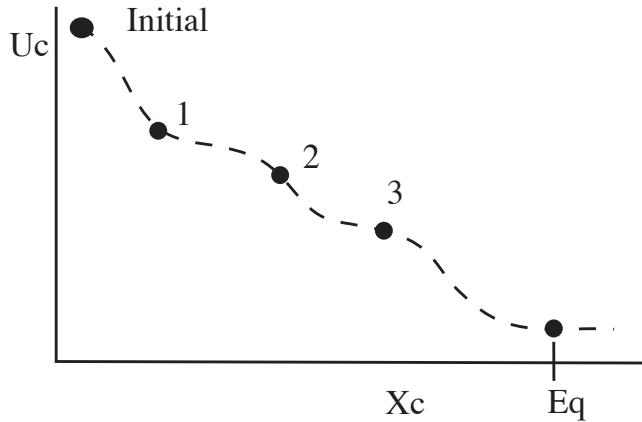


Figure 1.19: Each time the constraint is released on the system shown in Fig. 1.18, the function that acts as the thermodynamic potential spontaneously decreases. Then when the constraint is replaced the system comes to equilibrium again. The solid dots indicate these states. The function that acts as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

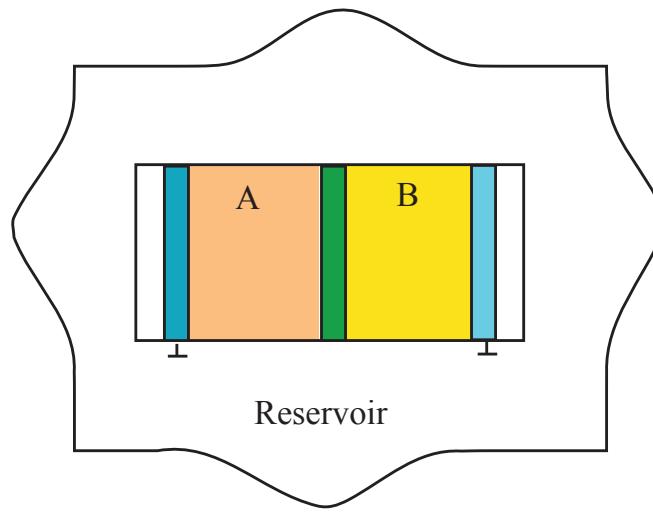


Figure 1.20: Schematic of a system interacting with a surrounding reservoir. The interactions allow the reservoir to impose its temperature and pressure on the system, but no molecular exchange between the system and the reservoir are allowed.

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 [5].

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

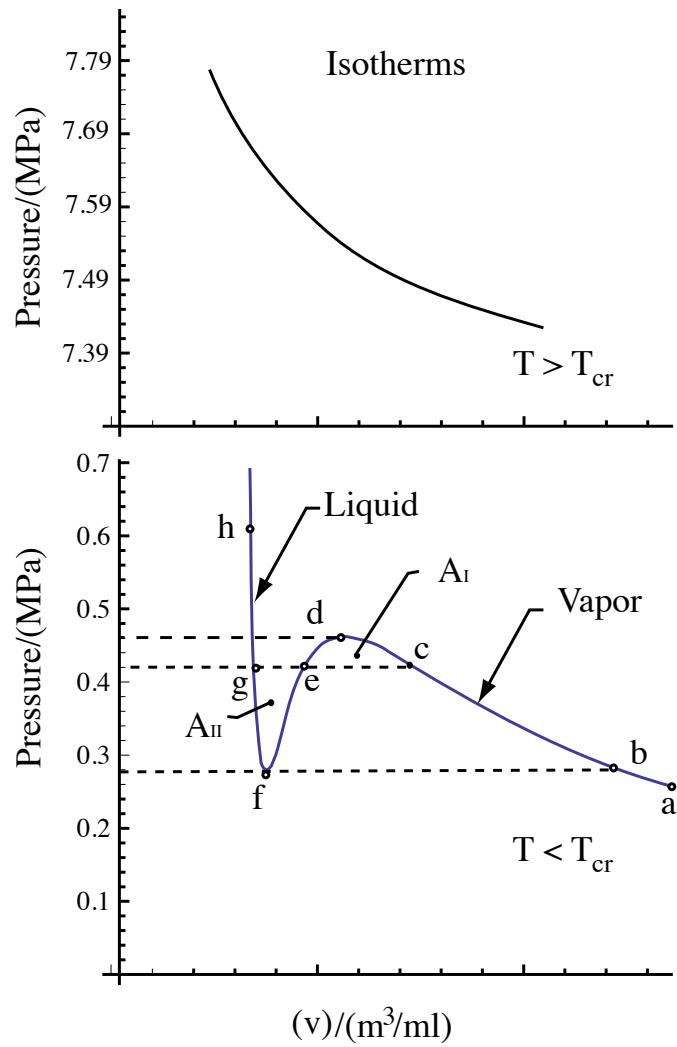


Figure 1.21: Calculated van der Waals isotherm for CO_2 . The upper one is for a temperature and a pressure above the critical values (304.2 K and 7.39 MPa), and the lower one is 275.16 K .

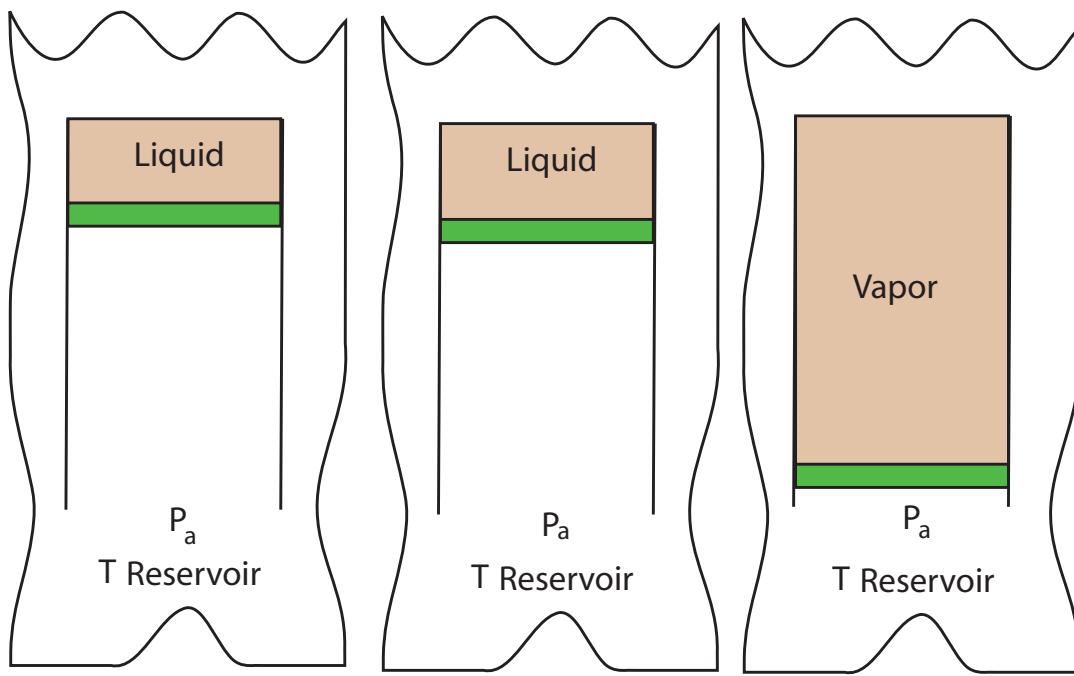


Figure 1.22: A fluid in a piston-cylinder arrangement that is maintained isothermal and at constant pressure is predicted to have three possible configurations.

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 9.1×10^{-5} . Whereas, the measured value is 5.71×10^{-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 ⁶ /mol ²)	b/(m ³ /mol)
Carbon dioxide	4.3	5.03×10^{-4}
Hydrogen	0.324	3.47×10^{-4}
Water	5.45	3×10^{-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),

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

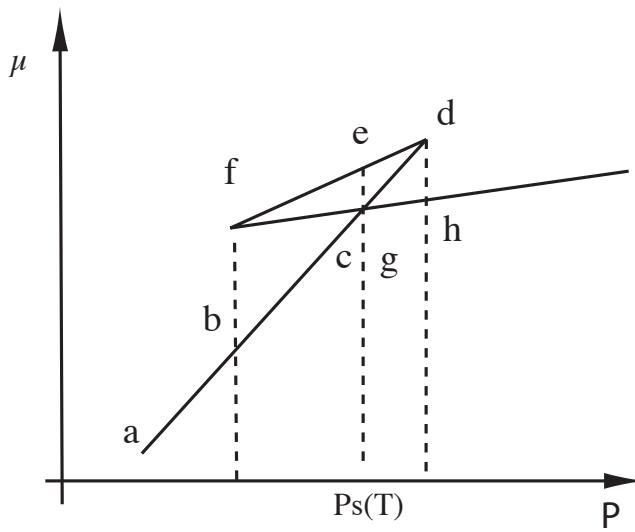


Figure 1.23: Calculated isotherm for CO_2 at $2\text{ }^\circ C$.

Thus

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

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

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

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.

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.

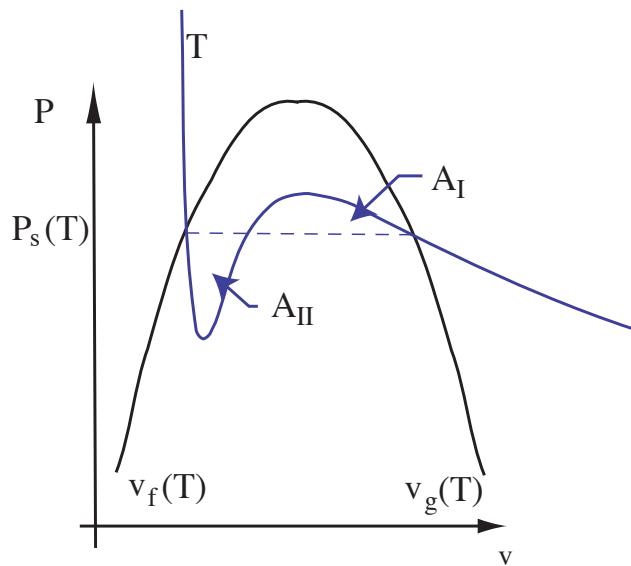


Figure 1.24: Calculated isotherm for CO_2 at $2\text{ }^{\circ}\text{C}$.

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.

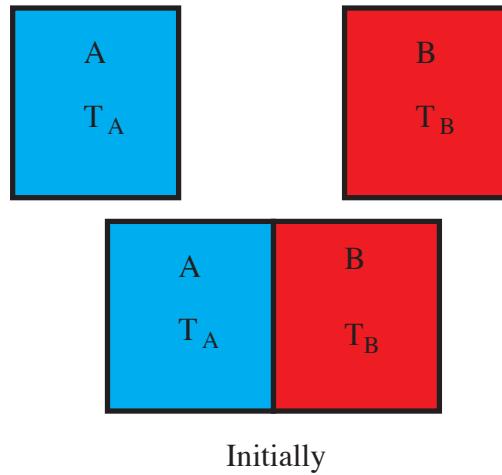


Figure 1.25: Two simple-material systems are brought together to form an isolated composite system. The substances in systems A and B are different and therefore have different fundamental relations.

1.14 The physical meaning of the thermodynamic definitions of the intensive properties

There are two concepts of the intensive properties to be considered: empirical and thermodynamic. The empirical concept is the one used when the property is to be measured, and the thermodynamic one is used when the intensive property is to be calculated or predicted. These must correspond. We show that if the postulates are valid, the thermodynamic definition of the intensive properties correspond to our physical understanding of the empirical concept.

1.14.1 Temperature of a simple-material system

The thermodynamic definition of temperature is given in Eq. (1.4). The empirical temperature has three characteristics:

1. It can be measured at a point, but we have all ready seen that the thermodynamic temperature is an intensive property; thus the thermodynamic temperature satisfies this condition.
2. **Thermal equilibrium:** Consider two simple-material systems that are brought together to form an isolated composite system (Fig. 1.25). We suppose that the systems A and B consist of different materials, and thus, have different fundamental relations: $U^A(S^A, V^A, N_1^A, \dots, N_r^A)$ and $U^B(S^B, V^B, N_1^B, \dots, N_r^B)$.

When the systems are initially brought in contact, suppose they have different temperatures, $T^A \neq T^B$, and at this time, spontaneous microscopic processes are initiated that take the system toward equilibrium. We apply the postulates to predict the conditions that the intensive properties must satisfy—individually of the molecular nature or fundamental relation of the constituent subsystems—for the composite system to be in the final, stable equilibrium state.

The empirical or experimental concept of temperature would require the two systems to have the same value of temperature once they had reached the final or stable equilibrium state, or in other words to be in thermal equilibrium. The thermodynamic definition of temperature satisfies this condition.

For the composite system to be isolated requires

$$\begin{aligned} N_{ic} &= N_i^A + N_i^B \quad 1 \leq i \leq r, \\ V_c &= V^A + V^B, \\ U_c &= U^A + U^B, \end{aligned} \tag{1.213}$$

where N_{ic} , V_c and U_c are constants. These constraints ensure the composite system is isolated, but to concentrate attention on thermal equilibrium, we add **internal constraints** and suppose the volume of the subsystems and number of moles of each

component in the subsystems are each constant:

$$\begin{aligned} V^A &= C_1, \\ V^B &= C_2, \\ N_i^A &= C_i^A, \quad \text{for } i = 1, 2 \dots r \\ N_i^B &= C_i^B \quad \text{for } i = 1, 2 \dots r \end{aligned} \tag{1.214}$$

where C_1, C_2, C_i^A, C_i^B are each constants. Note that after each these internal constraints are added, the composite system remains isolated.

The entropy postulate may be applied to determine the conditions the intensive properties must satisfy in the final equilibrium state. Thus, we suppose the composite system has arrived in the state of maximum entropy, and imagine the composite system to be subject to small, virtual displacements about this state, i.e., small displacements that are consistent with the constraints and could result from the molecular motion or microscopic processes. In these virtual displacements, each subsystem is assumed to have uniform properties, but the subsystems are not in equilibrium with each other. The constraints are satisfied, but there are no gradients in the constituent subsystems.

The entropy of the composite system S_c may be expressed

$$S_c = S^A + S^B. \tag{1.215}$$

and then

$$dS_c = dS^A + dS^B. \tag{1.216}$$

Since systems A and B are simple-material systems, we may write for each

$$dS^\alpha = \left(\frac{1}{T^\alpha}\right)dU^\alpha + \left(\frac{P^\alpha}{T^\alpha}\right)dV^\alpha - \sum_{i=1}^r \left(\frac{\mu_i^\alpha}{T^\alpha}\right)dN_i^\alpha, \tag{1.217}$$

where α is either A or B.

We may ensure the displacements are “virtual” by ensuring the constraints are satisfied. Since the volume and number of moles of each component in each subsystem is constant, one finds by differentiating the constraint conditions

$$dV^A = dV^B = 0, \quad (1.218)$$

and

$$dN_i^A = dN_i^B = 0. \quad (1.219)$$

Since the total energy is constant:

$$dU^B = -dU^A. \quad (1.220)$$

After the results obtained from differentiating the constraints are used in the expression for dS^α , the expression for dS_c may be simplified

$$dS_c = \left(\frac{1}{T^A} - \frac{1}{T^B} \right) dU^A. \quad (1.221)$$

If S_c is a maximum (or any extremum), dS_c must vanish for each virtual displacement, and since dU^A is unrestricted by the constraints—it could have any value—the only way dS_c can vanish for all values of dU^A is for the temperature of the two systems to be equal:

$$T_e^A = T_e^B. \quad (1.222)$$

Note that no consideration was made of how the system evolved to an equilibrium state. It could have evolved along the path (dashed line) in Fig. 1.1.

It was assumed that the system had arrived in a state such that S_c was an extremum. Virtual displacements about this equilibrium state were then considered. If this state were one where S_c was an absolute maximum, the state would be a stable equilibrium state. Thus, thermal equilibrium should be viewed as a **necessary condition** for equilibrium, but it alone does not **ensure** that the state is stable.

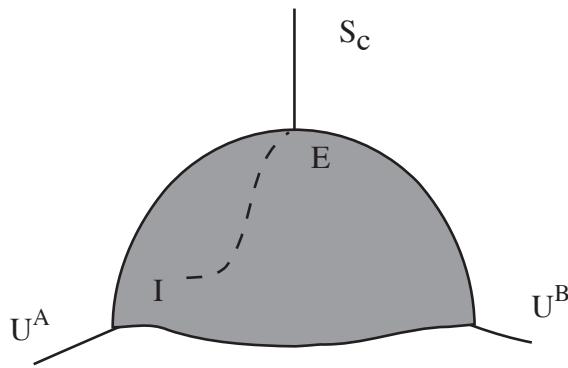


Figure 1.26: The surface shown indicates a possible relation between the entropy of a composite system and the internal energies of its subsystems.

3. Direction of thermal energy transport

Our physical idea of temperature would say that if a system of one temperature is brought in contact with another system and the second system has a different temperature than the first, the direction of the energy transport would be from the system with the higher temperature to the system with the smaller temperature. The direction of the energy transport is also necessarily independent of the molecular nature, density, pressure or phase of the substances exchanging energy.

If the composite system were in a **stable equilibrium state**, and it were subjected to a **virtual displacement** that reduced S_c so T^A to be greater than T^B . Then according to the postulate, S_c would increase to restore equilibrium

$$dS_c = \left(\frac{1}{T^A} - \frac{1}{T^B} \right) dU^A > 0. \quad (1.223)$$

Since by hypothesis $T^A > T^B$,

$$\left(\frac{1}{T^A} - \frac{1}{T^B} \right) < 0, \quad (1.224)$$

and in order for $dS_c > 0$, $dU^A < 0$.

In other words, in order for the system to return to its original state, the energy transport must be from the system with the higher temperature to the one with the lower temperature. Thus, the thermodynamics definition of temperature satisfies another the concepts of the empirical temperature.

We postpone the discussion of the metastable and unstable states until we consider surface phases in the Chapter.

1.15 Pressure of simple-material system

The concept of pressure in thermodynamics is more complex than in mechanics. The pressure in a simple-material system is related to the system boundaries, and there are three different boundary types that must be considered. If the boundary is impermeable, molecules cannot cross the boundary; a boundary in which only certain molecular species can be transported is semi-permeable; a molecularly unrestricted boundary is completely permeable or open. The boundary between a liquid and its vapor, for example, is open. We consider this boundary in the in the next Chapter when we consider the equilibrium size of a vapor bubble immersed in a liquid.

We first consider the systems shown in Fig. 1.27. The mass, M , is attached to the piston–cross-sectional area α —as indicated, by a cord of length L that does not elongate, and is thermally nonconducting. The system is in a gravitational field, but we neglect any effects of the field on the properties of systems A and B. Each is a simple-material system. System A consists of a two component fluid, N_1 and N_2 . and system B of a fluid of component N_1 .

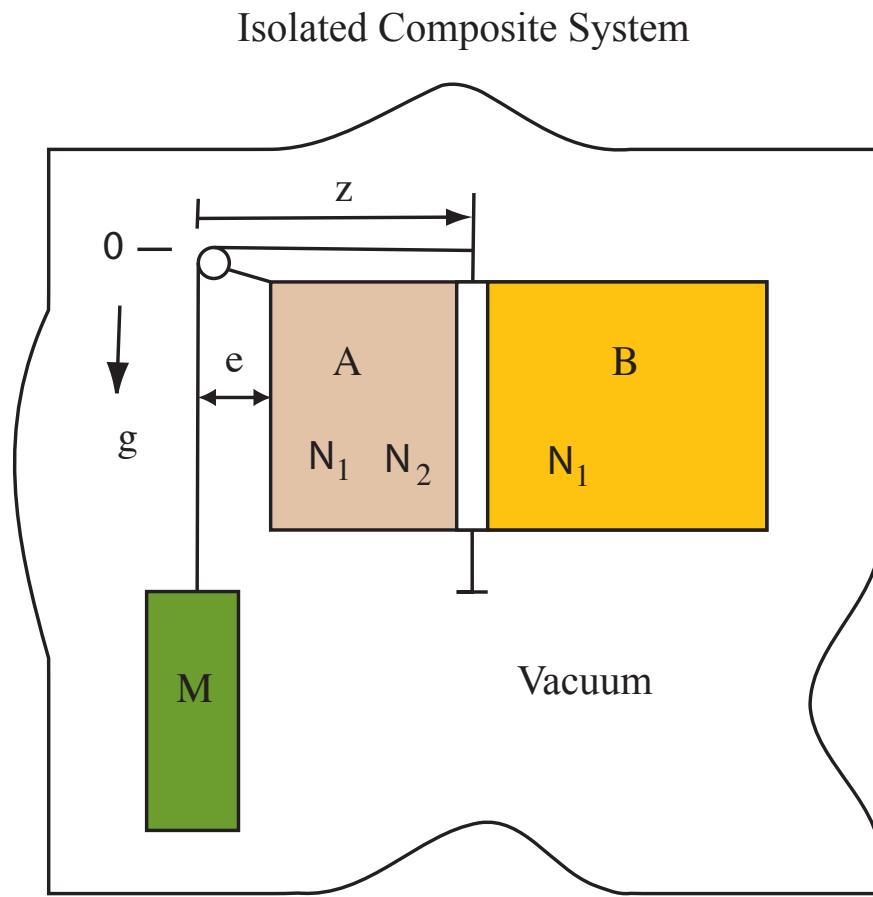


Figure 1.27: Apparatus for examining the thermodynamic definition pressure. We approximate the enclosed system is an isolated composite system.

1.15.1 Pressure as defined in mechanics

In mechanics, the pressure of a static fluid is viewed as a compressive stress—force per unit area that acts normal to a plane—and equilibrium requires only that there is a force balance, independently of whether the piston is permeable or impermeable. After the piston is unpinned and has come to equilibrium, a force balance would give (see Fig. 1.28):

$$Mg - P^A \alpha + P^B \alpha = 0. \quad (1.225)$$

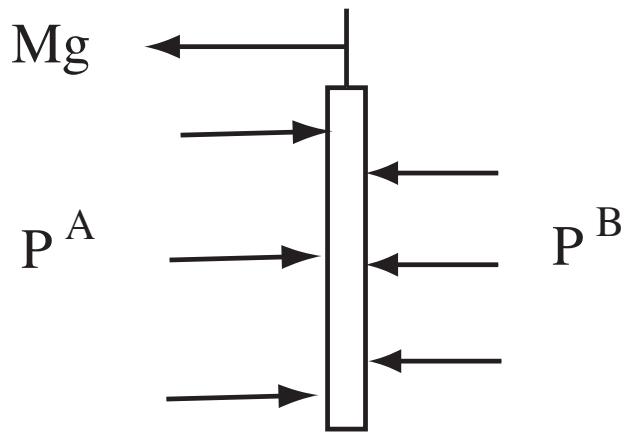


Figure 1.28: Free body diagram of the piston in the system shown in Fig. 1.27.

or

$$P^A = P^B + \frac{Mg}{\alpha}. \quad (1.226)$$

1.15.2 Pressure as defined in thermodynamics: the impermeable piston

From a thermodynamic point of view, we now want to determine the relation between the pressures in the systems A and B of the composite system shown in Fig. 1.27. We neglect any change in the thermodynamic state of the mass M , but its potential energy is not neglected. In particular, its potential energy is changed by a change of its height in the field. This height ht is given by

$$ht = z - L. \quad (1.227)$$

where h is the position of the centre-of-mass of the weight. The potential energy, PE, may be expressed

$$PE = Mg(z - L). \quad (1.228)$$

Thus, as z increases the weight is raised in the field, and the potential energy of the weight increases.

Now suppose the piston is impermeable and is unpinned. Since we are neglecting any change in the thermodynamic state of the mass M , the composite system is thermodynamically isolated, and we may apply the entropy postulate to determine the conditions for equilibrium

The constraints are: N_1^A , N_1^B , N_2^A are each constant and

$$\begin{aligned} U_c &= U^A + U^B + U^M + Mg(z - L) \\ V_c &= V^A + V^B \end{aligned} \quad (1.229)$$

where V_c and U_c are each constants. There is also a relation between z and the volume of system A:

$$V^A = (z - e)\alpha. \quad (1.230)$$

We suppose the system has evolved to the final equilibrium state and consider virtual displacements about the equilibrium state, then from the constraints

$$\begin{aligned} dU^M &= 0 \\ dU^A &= -dU^B - Mgdz \\ dV^B &= -dV^A \\ dV^A &= \alpha dz \end{aligned} \quad (1.231)$$

The entropy of the composite system, S_c , is given by

$$S_c = S^A + S^B + S^M, \quad (1.232)$$

and since we are neglecting any change in the thermodynamic state of the mass M, the total differential of the entropy

$$dS_c = dS^A + dS^B. \quad (1.233)$$

and when Eq. 1.237 is applied for each subsystem, one finds, after making use of the results obtained from the differential of the constraints that

$$dS_c = \left(\frac{1}{T^B} - \frac{1}{T^A} \right) dU^B + \left(\frac{P^A \alpha}{T^A} - \frac{P^B \alpha}{T^B} - \frac{Mg}{T^B} \right) dz. \quad (1.234)$$

and in order for dS_c to vanish in all the virtual displacements

$$\begin{aligned} T^A &= T^B \\ \frac{P^A \alpha}{T^A} &= \frac{P^B \alpha}{T^B} + \frac{Mg}{T^B} \end{aligned} \quad (1.235)$$

This result is equivalent to the result found from mechanics, So the concept of pressure in mechanics is equivalent to that in thermodynamics provided the boundary on which the pressure acts is impermeable.

1.15.3 Pressure as defined in thermodynamics: the permeable piston

Now suppose the piston separating systems A and B in Fig. 1.27 is semi-permeable . Component 1 can transfer across the piston, but component 2 cannot. Also, suppose system A consists of a weak liquid solution in which component 1 is the solvent, and it may be approximated as incompressible, and system B consist of pure component 1 also in the liquid phase.

After the constraint is released, the system evolves to an equilibrium state where the entropy is a maximum. We consider virtual displacements about this state. On differentiating these

constraints, one finds

$$\begin{aligned}
 dU^M &= 0 \\
 dU^A &= -dU^B - Mg dz \\
 dV^B &= -dV^A \\
 dN_1^A &= -dN_1^B \\
 dN_2^A &= 0
 \end{aligned} \tag{1.236}$$

Following the method outlined above, one finds

$$dS_c = \left(\frac{1}{T^B} - \frac{1}{T^A} \right) dU^B + \left(\frac{P^A \alpha}{T^A} - \frac{P^B \alpha}{T^B} - \frac{Mg}{T^B} \right) dz + \left(\frac{\mu_1^A}{T^A} - \frac{\mu_1^B}{T^B} \right) dN_1^A. \tag{1.237}$$

Note that in this case, the constraints leave three variables unrestricted, dU^A , dz and dN_1^A . Since they are independent and dS_c must vanish for all virtual displacement about a state for which the entropy is a maximum, we have three conditions for equilibrium:

$$\begin{aligned}
 T^A &= T^B, \\
 &= T. \\
 P^A &= P^B + \frac{Mg}{\alpha}. \\
 \mu_1^A &= \mu_1^B.
 \end{aligned} \tag{1.238}$$

Since system A is known to be a weak solution with an incompressible liquid solvent, the chemical potential of component 1 in system A may be written, Eq. 1.112

$$\mu_1 = \mu_1^0(T, P) - k_b T \frac{x_2}{x_1}$$

and since the liquid solvent is incompressible, we may introduce a reference pressure, P_{rA} , and write

$$\mu_1^A(T, P^A) = \mu_1^0(T, P_{rA}) + v_f(P^A - P_{rA}) - k_b T \frac{x_2}{x_1}$$

In system B, we know the liquid is incompressible

$$\mu_1^B(T, P^B) = \mu_1^0(T, P_{rB}) + v_f(P^B - P_{rB}) \quad (1.239)$$

Since the condition for equilibrium requires $\mu_1^A(T, P^A)$ and $\mu_1^B(T, P^B)$ to be equal, if we choose $P_{rA} = P_{rB}$

$$P^A = P^B + \frac{k_b T x_2}{v_f x_1} \quad (1.240)$$

Thus, the thermodynamic pressure must satisfy two conditions Eqs. 1.239 and 1.240: the pressures must be such that there is force balance and the condition that the chemical potentials of the transport component are equal. If Eqs. 1.239 and 1.240 are solved simultaneously one finds

$$\frac{x_2}{x_1} = \frac{M g v_f}{k_b T \alpha} \quad (1.241)$$

Thus, if the piston is impermeable, the thermodynamic definition of pressure corresponds with the concept of pressure as defined in mechanics. Both concepts indicate a force balance must exist under equilibrium conditions, but a force balance is not sufficient for thermodynamic equilibrium.

It should also be noted that the results given in Eqs. 1.239 were obtained totally from the entropy postulate. Thus, the entropy postulate contains the condition that the forces must be in balance in order for equilibrium to exist. In this sense, the entropy postulate contains the equilibrium postulate of continuum mechanics.

1.16 The chemical potential and its relation to molecular transport

Suppose the **isolated**, composite system shown in Fig. 1.29 is separated into two portions by a semi-permeable, rigid, diathermal membrane that is pinned in position. Component-1

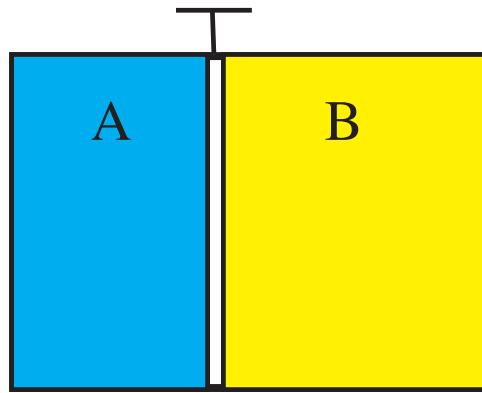


Figure 1.29: Schematic of a system consisting of r -components that is separated into two simple-material systems by a rigid membrane that is pinned in position. Only component-1 is transported across the membrane.

moves freely between the two simple-material systems, system-A and system-B, but none of the other components $i = 2, 3 \dots r$ are transported across the diathermal, semi-permeable membrane. Since the composite system is isolated, we may use us the entropy postulate to determine the conditions for equilibrium.

The internal constraints are:

- the total number of moles of component 1 in the composite system is shared between the subsystems:

$$N_{1c} = N_1^A + N_1^B. \quad (1.242)$$

where N_{1c} is a constant.

- The mole numbers of other component in systems A and B are each constant.
- The total internal energy of the composite system, U_c , is likewise constant:

$$U_c = U^A + U^B. \quad (1.243)$$

- The volume of each of the subsystems, V^A and V^B , are constant.

If the isolated composite system has evolved to an equilibrium state, the entropy of the composite system will be an extremum. Thus, we only determine the necessary conditions for the system to be in a stable equilibrium state.

Suppose the composite system is subject to small virtual displacements about the equilibrium state. Postulate 2.6 requires that in this state, the total differential of S_c vanishes, and Postulate 2.4 indicates that S_c is given by

$$S_c = S^A + S^B. \quad (1.244)$$

For $\alpha = A$ or B

$$dS^\alpha = \left(\frac{1}{T^\alpha}\right)dU^\alpha + \left(\frac{P^\alpha}{T^\alpha}\right)dV^\alpha - \sum_{i=1}^r \left(\frac{\mu_i^\alpha}{T^\alpha}\right)dN_i^\alpha. \quad (1.245)$$

After differentiating the constraint conditions and S_c and combining the results, one finds

$$dS_c = \left(\frac{1}{T^A} - \frac{1}{T^B}\right)dU^A - \left(\frac{\mu_1^A}{T^A} - \frac{\mu_1^B}{T^B}\right)dN_1^A. \quad (1.246)$$

Thus, there are two independent variables, U^A and N_1^A , and in order for dS_c to vanish for all possible values of dU^A and dN_1^A , their coefficients must vanish:

$$\frac{1}{T^A} = \frac{1}{T^B}, \quad (1.247)$$

and

$$\frac{\mu_1^A}{T^A} = \frac{\mu_1^B}{T^B}. \quad (1.248)$$

When these two relations are satisfied, thermal equilibrium must exist in the system, and the chemical potential of the component transferred across the membrane must have the same value in systems A and B, but there are no restrictions on the chemical potentials of the other components. However, it should be emphasized that the chemical potential of component 1 can depend on the number of moles of each of the other components as well as the number of moles of component 1 that are present in a simple-material system:

$$\mu_1 = \left(\frac{\partial U(S, V, N_1 \dots N_r)}{\partial N_1}\right)_{S, V, \dots N_j \dots} \quad j \neq 1, \quad (1.249)$$

or

$$\mu_1 = \mu_1(S, V, N_1 \dots N_r). \quad (1.250)$$

Thus μ_1 has as its independent variables $S, V, N_1 \dots N_r$. The concentration of one component in the system affects the chemical potential of another component.

1.16.1 Direction of molecular transport

To determine the direction of molecular transport, we suppose the system is in a stable equilibrium state, and a fluctuation occurs as a result of molecular motion that makes $\mu_1^A > \mu_1^B$, but T^A remains equal to T^B in spite of the fluctuation. This would lower the entropy from its absolute maximum value. Thus, in order for the composite system to return to its equilibrium state $dS_c > 0$. From Eq. (1.246)

$$dS_c = -\frac{1}{T}(\mu_1^A - \mu_1^B)dN_1^A > 0. \quad (1.251)$$

The factor multiplying dN_1^A is negative; thus in order to satisfy the inequality $dN_1^A < 0$. Hence, component 1 is transferred from the system with the higher chemical potential to the system with the lower chemical potential. Physically, in an isothermal system, the chemical potential acts as the potential for mass transport in much the same way as temperature acts as the potential for energy transport.

1.17 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

$$\begin{aligned} S &= NC + NR \ln \left(U^{3/2}V/N^{5/2} \right) - N_1 R \ln \left(N_1/N \right) - N_2 R \ln \left(N_2/N \right), \\ N &= N_1 + N_2, \end{aligned} \tag{1.252}$$

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 μ 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

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

and that of system B is

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

- 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 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 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

$$S = C(N_1 + N_2) + (N_1 + N_2)R \ln \left(\frac{U^{3/2}V}{(N_1 + N_2)^{5/2}} \right) - N_1 R \ln \left(\frac{N_1}{N_1 + N_2} \right) - N_2 R \ln \left(\frac{N_2}{N_1 + N_2} \right) \quad (1.253)$$

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° 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° 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 [5].

phase	solid	liquid	vapor
entropy / (kJ/kg K)	-1.2210	0	9.1562
specific volume/(m ³ /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

$$\begin{aligned} P &= P_1 + a(v_1 - v) & v < v_1 \\ P &= v \frac{(P_2 - P_1)}{v_2 - v_1} + \frac{(v_2 P_1 - v_1 P_2)}{v_2 - v_1} & v_1 < v < v_2 \\ P &= P_2 + a(v_2 - v) & v_2 < v \end{aligned} \quad (1.254)$$

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

- A. Show a sketch of the isotherm, and 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 as a single phase? Show the range on your sketch of the isotherm.
13. A cylindrical container is divided into two portions by freely-moving, rigid pistons that are diathermal and impermeable (see Fig. 1.30). 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

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

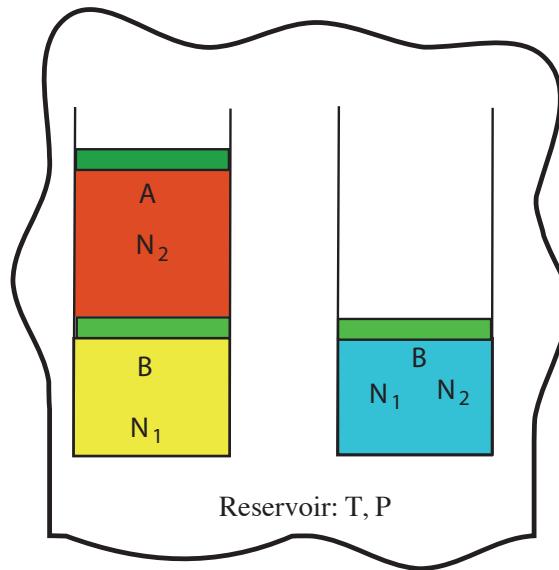
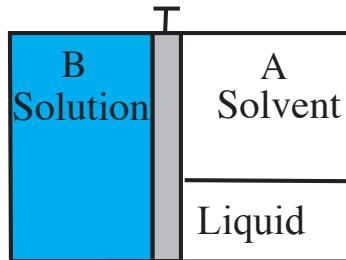


Figure 1.30

- 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 1.31, the solution is separated from the solvent by a membrane that is permeable only to the solvent and is diathermal. The weak solution in system B contains only one solute. Initially system A consists of pure liquid solvent that does not fill the volume of system A. Both systems are at the same temperature, T_I . The composite system forms an isolated system.
- A. When equilibrium is reached both fluid phases are present in 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 1.31**

- B. If the system is in equilibrium, the solvent is water, 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, and give a justification for your answer.
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. 1.32. 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 nonvolatile 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, λ_{sl} , for the pure solvent may be expressed

$$\lambda_{sl} = T_0(s^L - s^S) \quad (1.255)$$

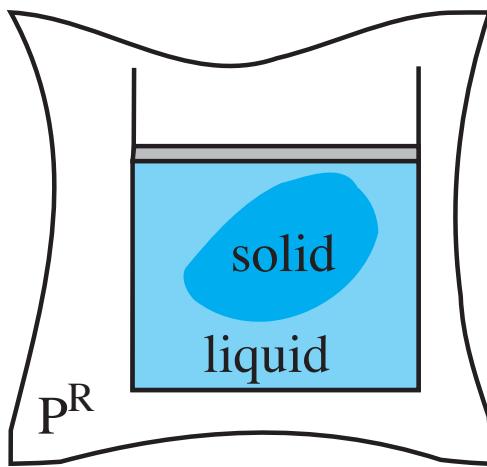


Figure 1.32: Two phase system.

- give the *approximate* expression for the freezing point of the solution.
- 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 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 Π_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 Π_0 .

B. If the solvent is water and the value of Π_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. 1.33. 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 vapor 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 m^2 , the solvent is water, the temperature of the reservoir is 25°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

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_v}. \quad (1.256)$$

19. Show that

$$Tds = c_v dT + T \frac{\alpha}{\kappa_T} dv \quad (1.257)$$

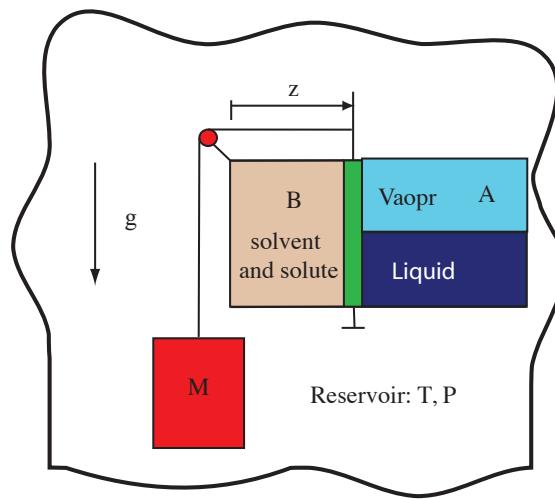


Figure 1.33: Two phase system.

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 °C, and a pressure of 70.183 kPa.

- 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

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

Chapter 2

Thermodynamics of surface phases

In the previous Chapter we dealt with simple-material systems. Now we to generalize the approach so that we may consider systems for which surface effects or important.

Consider the system shown schematically in Fig 2.1 in which the liquid-vapor phases of a multicomponent substance are enclosed in a rigid volume. For the present we will neglect gravitational effects, and suppose the vapour phase is suspended in the liquid phase. Depending on the size of the vapor phase, the energy associated with the liquid-vapor surface phase may be larger than that associated with the bulk vapor. Thus, in some circumstances, it is important to take this surface phase into account. We consider a thermodynamic model of a surface phase that is based on the approach developed by Gibbs [9]. We start by considering a liquid-vapor surface phase.

2.1 Thermodynamic description of the boundary between two fluid phases

The actual surface region where the fluid makes a transition from the liquid to the vapor is a volume, the interphase. In this region a large change in the specific volume of the fluid takes place over a very small distance. In many circumstances, the extent of the interphase is only a few molecular diameters. The extent of this volume—the interphase—is not easily defined, nor is the variation of the molar density in this region. Thus, we shall adopt an approximation, introduced by Gibbs [9], in which the interphase volume is replaced by a surface, called the dividing surface. In the Gibbs approximation, the vapor and liquid phases are treated as simple material systems, and as indicated in Fig. 2.1, the molar density of each phase is assumed uniform right up to the dividing surface. Strictly speaking there are two types of surface phases present in the system shown schematically in Fig. 2.1, a liquid-vapor and liquid-solid phase. For the purposes of this discussion, we will ignore the solid-liquid phase because it is not changed when we consider virtual displacements about the equilibrium state, but we will consider solid-liquid phases when we consider a sessile droplets.

One of the important issues raised by this approximation is where to place the two-dimensional liquid-vapor surface phase. The total number of moles of component i , in the composite system, N_{ci} , is given by

$$N_{ci} = N_i^L + N_i^V + N_i^{LV}, \quad (2.1)$$

where N_i^{LV} is the excess number of moles of component i . It is the number of moles that would have been present if both phases had been uniform right up to the dividing surface. Its value is determined by the non-uniformity of the molar densities in the interphase. Note then that N_{ci} is the physical quantity, but N_i^L , N_i^V and N_i^{LV} are quantities defined by the Gibbs model of the system. They depend on where the dividing surface is placed.

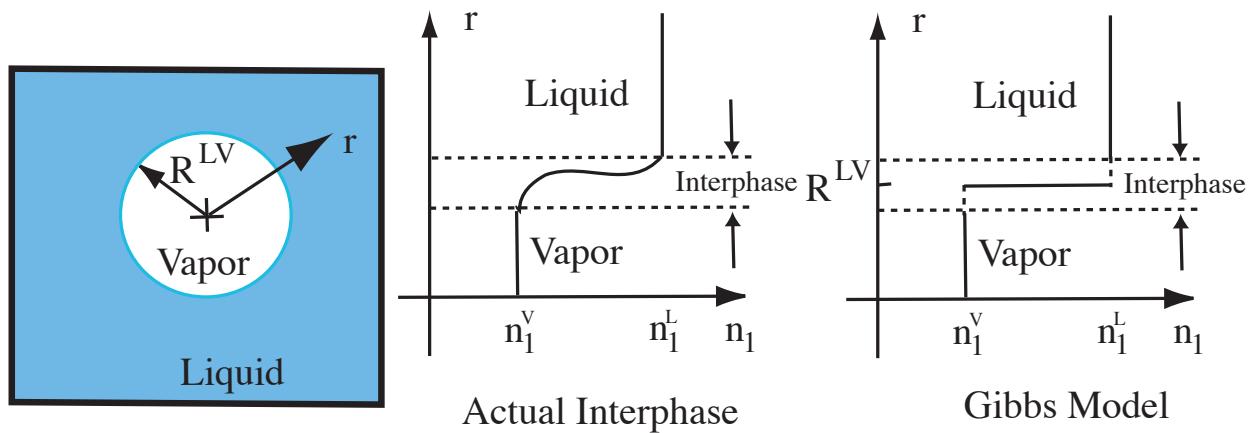


Figure 2.1: A three phase system: a liquid, a vapor and a liquid-vapor surface phase. The molar density changes sharply in the interphase that is a few molecular diameters in thickness. In the Gibbs model of the interphase, a dividing surface is placed at R^{LV} , and the molar densities are assumed to have their bulk values right up to the dividing surface.

Since the interphase volume is replaced by a surface, the system volume, V_c , a physical quantity, is expressed in terms of two model quantities: the volume of the liquid, V^L , and that of the vapor, V^V

$$V_c = V^L + V^V. \quad (2.2)$$

If we suppose the physical quantities, N_{ci} , V_c and the bulk molar densities of the liquid and vapor phases, n_i^L , n_i^V , are known, then in terms of the model quantities

$$N_{ci} = n_i^L V^L + n_i^V (V_c - V^L) + N_i^{LV}. \quad (2.3)$$

Note that we do not have enough information to solve Eq. (2.3) because it contains two unknowns: N_i^{LV} , V^L . Also note that N_i^{LV} can be positive or negative depending on the value chosen for V^L , or in other words, depending on where the dividing surface is placed. One might consider closing the system of equations, by applying conservation of energy, but that cannot close the equations since a new unknown property of the interphase is introduced each time a new conservation equation is proposed. For example, if conservation of energy is considered, the excess internal energy U^{LV} is introduced:

$$U_c = U^L + U^V + U^{LV} \quad (2.4)$$

We proceed by introducing the intensive properties of the bulk-phases on a per unit volume basis, rather than on a per mole basis. In general, the internal energy of a bulk phase is a first-order homogeneous function,

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

If λ is chosen to be $1/V$, and internal energy per unit volume is denoted ϑ , the entropy per unit volume as σ and the number of moles of each component per unit volume as n_i , then the intensive internal energy of a bulk phase may be expressed

$$\vartheta = \vartheta(\sigma, n_1, n_2, \dots, n_r). \quad (2.5)$$

Then the physical quantity, the total internal energy of composite system, U_c , may be expressed in terms of model quantities

$$U_c = V^L \vartheta^L + V^V \vartheta^V + U^{LV}. \quad (2.6)$$

where U^{LV} is the excess internal energy that results from replacing the three-dimensional interphase by a two-dimensional surface. Thus, even if the bulk-phase properties, ϑ^L , ϑ^V , n_i^L and n_i^V , are taken as known Eqs. (2.3) and (2.6) do not form a closed set because a new unknown, U^{LV} was added when the expression for the internal energy was added. A similar result is found if the physical quantity entropy is considered:

$$S_c = \sigma^L V^L + \sigma^V (V - V^L) + S^{LV}. \quad (2.7)$$

where S^{LV} is the excess entropy.

2.1.1 Extensive and intensive properties of a surface phase

In this chapter, we will consider three types of surface phases: liquid-vapor (LV), solid-vapor (SV) and solid-liquid, (SL). We now define the independent **extensive** variables of a surface phase which we denote as a Σ -phase. Thus, Σ can be LV, SV, or SL.

We use the same principle as applied for a bulk phase (see Chapter 1) to define the independent extensive variables of the internal energy of a surface phase. This requires that we identify the extensive variables that determines the internal energy of a Σ -phase.

1. We suppose the internal energy of the Σ -phase can be changed by heating. Thus, one of the independent variables is the surface entropy, S^Σ .
2. Another means of changing the internal energy of a Σ -phase is by changing its extent or its surface area, A^Σ . It is possible to imagine that the energy of a Σ -phase can be changed by changing its curvature, but we will suppose that the position of the dividing surface can be chosen so the curvature of the surface does not change its energy. Such a surface is called the “surface of tension”.
3. The number of moles of each component associated with a Σ -phase, N_i^Σ , would also be expected to influence the internal energy of a Σ -phase.

Thus, in summary the internal energy of the Σ -phase can be expressed:

$$U^\Sigma = U^\Sigma (S^\Sigma, A^\Sigma, N_1^{LV}, N_2^{LV} \dots N_r^{LV}) . \quad (2.8)$$

We define the temperature of a Σ -phase, T^Σ , and the chemical potential of each adsorbed component, μ_i^Σ in analogy with the definitions used for a bulk phase:

$$T^\Sigma = \left(\frac{\partial U^\Sigma}{\partial S^\Sigma} \right)_{A^\Sigma, N_1^\Sigma, N_2^\Sigma \dots N_r^\Sigma} . \quad (2.9)$$

$$\mu_i^\Sigma = \left(\frac{\partial U^\Sigma}{\partial N_i^\Sigma} \right)_{S^\Sigma, A^\Sigma, N_j^\Sigma, j \neq i} . \quad (2.10)$$

But we have a new independent variable, A^Σ . We use it to define the surface tension, γ^Σ :

$$\gamma^\Sigma = \left(\frac{\partial U^\Sigma}{\partial A^\Sigma} \right)_{S^\Sigma, N_1^\Sigma, N_2^\Sigma \dots N_r^\Sigma}. \quad (2.11)$$

Below we investigate the question of whether we have defined the physical surface tension that is observed in the laboratory.

2.1.2 Entropy postulate for a composite system that contains surface phases

We formalize the discussion above by stating the entropy postulate, and we state this postulate so it refers to any surface phase.

1. The internal energy of a surface phase may be expressed

$$U^\Sigma = U^\Sigma (S^\Sigma, A^\Sigma, N_1^{LV}, N_2^{LV} \dots N_r^{LV}). \quad (2.12)$$

and U^Σ is a first-order homogeneous function of its independent variables:

$$\lambda U^\Sigma = U^\Sigma (\lambda S^\Sigma, \lambda A^\Sigma, \lambda N_1^{LV}, \lambda N_2^{LV} \dots \lambda N_r^{LV}). \quad (2.13)$$

2. We may use the definitions of T^Σ , μ_i^Σ , and γ^Σ to express the total differential of U^{LV} as

$$dU^\Sigma = T^\Sigma dS^\Sigma + \gamma^\Sigma dA^\Sigma + \sum_{i=1}^r \mu_i^\Sigma dN_i^\Sigma, \quad (2.14)$$

and we assume U^Σ is well enough behaved mathematically so we may write

$$dS^\Sigma = \frac{1}{T^\Sigma} dU^\Sigma - \frac{\gamma^\Sigma}{T^\Sigma} dA^\Sigma - \sum_{i=1}^r \frac{\mu_i^\Sigma}{T^\Sigma} dN_i^\Sigma. \quad (2.15)$$

3. The entropy of a surface phase, S^Σ , cannot be negative:

$$S^\Sigma \geq 0. \quad (2.16)$$

4. If any surface phase is in a state for which

$$\left(\frac{\partial U^\Sigma}{\partial S^\Sigma} \right)_{A^\Sigma, N_1 \dots N_r} = 0, \quad (2.17)$$

then the entropy vanishes in this state.

5. 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 α bulk phases and β surface phases in a particular isolated composite system

$$S_c = \sum_{i=1}^{\alpha} S^i + \sum_{j=1}^{\beta} S^{\Sigma j}. \quad (2.18)$$

6. 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.

2.1.3 Examination of the definition of the liquid-vapor surface tension for a single component system

We now ask if the quantity we are calling surface tension of the liquid-vapor interface:

$$\gamma^{LV} = \left(\frac{\partial U^{LV}}{\partial A^{LV}} \right)_{S^{LV}, \mathbf{N}^{LV}}. \quad (2.19)$$

is the physical surface tension.

As the first step towards answering this question, we apply the entropy postulate to determine the conditions for equilibrium for the system shown in Fig. 2.1. We suppose it is a single component system and neglect any change in the solid-liquid phase. Thus, the total entropy for the system shown in Fig. 2.1 is given by

$$dS_c = dS^L + dS^V + dS^{LV}. \quad (2.20)$$

If the system is isolated, then U_c , V_c , and N_c are constants, where

$$U_c = U^L + U^V + U^{LV},$$

$$V_c = V^L + V^V, \quad (2.21)$$

$$N_c = N_i^L + N_i^V + N^{LV}. \quad (2.22)$$

The expression for the differentials of the bulk-phase entropy have been previously introduced, and from Eq. (2.14) the expression for dS^{LV} may be obtained. One then finds from Eq. (2.20)

$$\begin{aligned} dS_c = & \left(\frac{1}{T^V} - \frac{1}{T^L} \right) dU^V + \left(\frac{1}{T^{LV}} - \frac{1}{T^L} \right) dU^{LV} + \left(\frac{-P^L}{T^L} + \frac{P^V}{T^V} \right) dV^V \\ & - \frac{\gamma^{LV}}{T^{LV}} dA^{LV} - \left(\frac{\mu^{LV}}{T^{LV}} - \frac{\mu^L}{T^L} \right) dN^L - \left(\frac{-\mu_i^V}{T^V} - \frac{\mu^L}{T^L} \right) dN^L. \end{aligned} \quad (2.23)$$

Now we want to consider virtual displacements about an equilibrium state. Thus, we must establish the relation between dA^{LV} and dV^V .

A schematic of a surface element is shown in Fig. 2.2. The area of the element before the displacement is A_1

$$A_1 = (R_1 d\alpha)(R_2 d\beta). \quad (2.24)$$

Now we suppose the element undergoes an axisymmetric displacement to area A_2

$$A_2 = [(R_1 + dR_1)d\alpha][(R_2 + dR_2)d\beta], \quad (2.25)$$

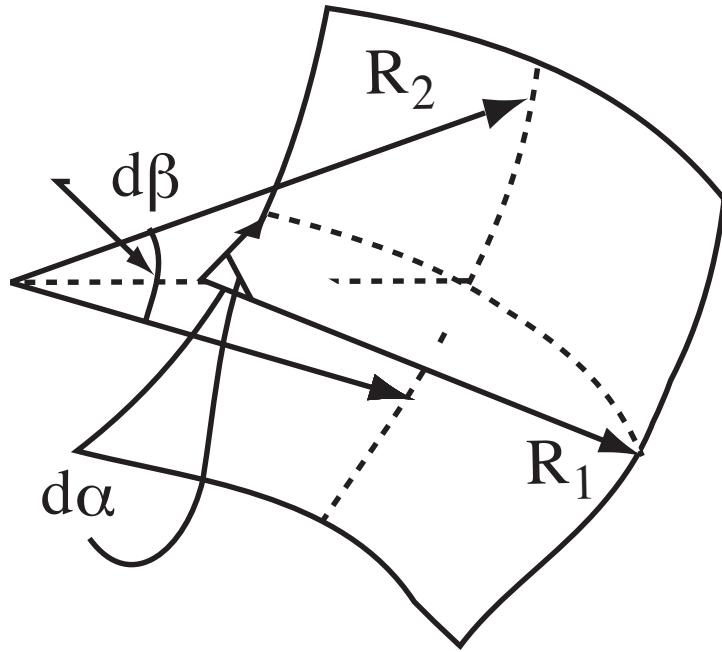


Figure 2.2: At a point on a curved surface, two radii of curvature can be defined.

and to first order in dR_1 and dR_2

$$A_2 = R_1 R_2 d\alpha d\beta + (R_2 dR_1 + R_1 dR_2) d\alpha d\beta. \quad (2.26)$$

For the axisymmetric surface displacement that we consider, each radius is assumed to be displaced by the same amount:

$$dR_1 = dR_2 \equiv dN \quad (2.27)$$

Thus

$$\begin{aligned} dA &\equiv dA_2 - dA_1, \\ dA &= (R_2 dR_1 + R_1 dR_2) d\alpha d\beta, \end{aligned} \quad (2.28)$$

$$dA = (R_2 + R_1) d\alpha d\beta dN. \quad (2.29)$$

and the change in the volume of the vapor phase may be written

$$dV = A_1 dN, \quad (2.30)$$

$$dV = (R_2 R_1) d\alpha d\beta dN. \quad (2.31)$$

After inserting Eqs. (2.29) and (2.31) into Eq. (2.23), the result may be written

$$\begin{aligned} dS_c &= \left(\frac{1}{T^V} - \frac{1}{T^L}\right)dU^V + \left(\frac{1}{T^{LV}} - \frac{1}{T^L}\right)dU^{LV} \\ &+ \left[\left(\frac{-P^L}{T^L} + \frac{P^V}{T^V}\right)(R_1 R_2) - (R_1 + R_2)\frac{\gamma^{LV}}{T^{LV}}\right]d\alpha d\beta dN \\ &- \left(\frac{\mu^{LV}}{T^{LV}} - \frac{\mu^L}{T^L}\right)dN^L - \left(\frac{\mu_i^V}{T^V} - \frac{\mu_i^L}{T^L}\right)dN_i^L. \end{aligned} \quad (2.32)$$

In an equilibrium state, dS must vanish for all virtual displacements:

$$\begin{aligned} \frac{1}{T^L} &= \frac{1}{T^V} = \frac{1}{T^{LV}}, \\ \frac{P^V}{T^V} &= \frac{P^L}{T^L} + \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\frac{\gamma^{LV}}{T^{LV}}, \\ \frac{\mu^L}{T^L} &= \frac{\mu^V}{T^V} = \frac{\mu^{LV}}{T^{LV}}. \end{aligned} \quad (2.33)$$

Thus, the thermodynamic definition of surface tension leads to the prediction that the pressure inside the surface of curvature is greater than that outside, and the assumed dependence of internal energy on the excess number of moles has led to a chemical potential for the excess moles appearing in the conditions for equilibrium.

2.1.4 Independent intensive variables of the liquid-vapor surface tension

An intensive thermodynamic property of a LV-phase is one that does not depend on the size of the phase. The entropy postulate requires that the excess internal energy be a first order homogeneous function of its independent variables:

$$\lambda U^{LV} = U^{LV} (\lambda S^{LV}, \lambda A^{LV}, \lambda N_1^{LV}, \lambda N_2^{LV} \dots \lambda N_r^{LV}). \quad (2.34)$$

After differentiating Eq. 2.34 with respect to λ and making use of the definition of the intensive properties of the LV-phase, $T^{LV}, \gamma^{LV}, \mu_i^{LV}$, one finds

$$U^{LV} = T^{LV} S^{LV} + \gamma^{LV} A^{LV} + \sum_{i=1}^r \mu_i^{LV} N_i^{LV} \quad (2.35)$$

This is the Euler equation for a LV-phase. It gives a relation between the extensive properties that depend on the size of the LV-phase and the intensive properties that are independent of the size of the phase. The extensive properties are: $U^{LV}, S^{LV}, A^{LV}, N_i^{LV}$, and the intensive properties are: $T^{LV}, \gamma^{LV}, \mu_i^{LV}$.

From the Euler equation for an LV-phase, one may obtain the expression for the total differential of U^{LV} . When this expression is set equal to the expression for the dU^{LV} given in Eq. (2.14), one finds the Gibbs-Duhem equation for the surface phase

$$\sum_{i=1}^r N_i^{LV} d\mu_i^{LV} = -S^{LV} dT^{LV} - A^{LV} d\gamma^{LV}, \quad (2.36)$$

On dividing through by A^{LV} :

$$d\gamma^{LV} = -\sigma^{LV} dT^{LV} - \sum_{i=1}^r n_i^{LV} d\mu_i^{LV}. \quad (2.37)$$

The number of moles in the surface phase, n_i^{LV} , are referred to as adsorbed. They are viewed as being bound there by molecular forces. This equation is called the Gibbs adsorption equation. It is an essential equation of understanding surface phenomena. It indicates the independent variables of the surface tension are T^{LV} and μ_i^{LV} :

$$\gamma^{LV} = \gamma^{LV}(T^{LV}, \mu_1^{LV}, \mu_2^{LV}, \dots, \mu_r^{LV}) \quad (2.38)$$

For a single component system, Eq. 2.37 reduces to

$$d\gamma^{LV} = -\sigma^{LV} dT^{LV} - n^{LV} d\mu^{LV}, \quad (2.39)$$

and since the conditions for equilibrium require

$$\begin{aligned} d\mu^{LV} &= d\mu^V \\ &= d\mu^L \end{aligned}$$

and since the Gibbs-Duhem equation gives

$$d\mu^L = -s^L dT + v_f dP^L \quad (2.40)$$

and combining the Gibbs-Duhem equation with Eq. 2.39 give

$$d\gamma^{LV} = (-\sigma^{LV} + n^{LV} s^L) dT - (n^{LV} v_f) dP^L \quad (2.41)$$

In other words, the surface tension γ^{LV} may be expressed in terms of the T^L and P^L , but it is generally found experientially that the pressure dependence of γ^{LV} is negligible, and we shall make this approximation in what follows:

$$\gamma^{LV} = \gamma^{LV}(T). \quad (2.42)$$

2.1.5 Comparison of the surface tension as defined in continuum mechanics with that defined in thermodynamics

In continuum mechanics the concept of the liquid-vapor interface is that of a membrane in a state of tension, τ . The equilibrium condition is established by requiring a force balance. The pressure in the liquid, P^L , is assumed uniform in that phase, and the pressure in the vapor phase is also assumed uniform at P^V . For simplicity, we assume the vapor phase is spherical, ($R_1 = R_2 = R$).

The conditions for equilibrium may be determined by considering a force balance on a cross section through the bubble. The forces acting on the section are indicated in Fig. 2.3. Then

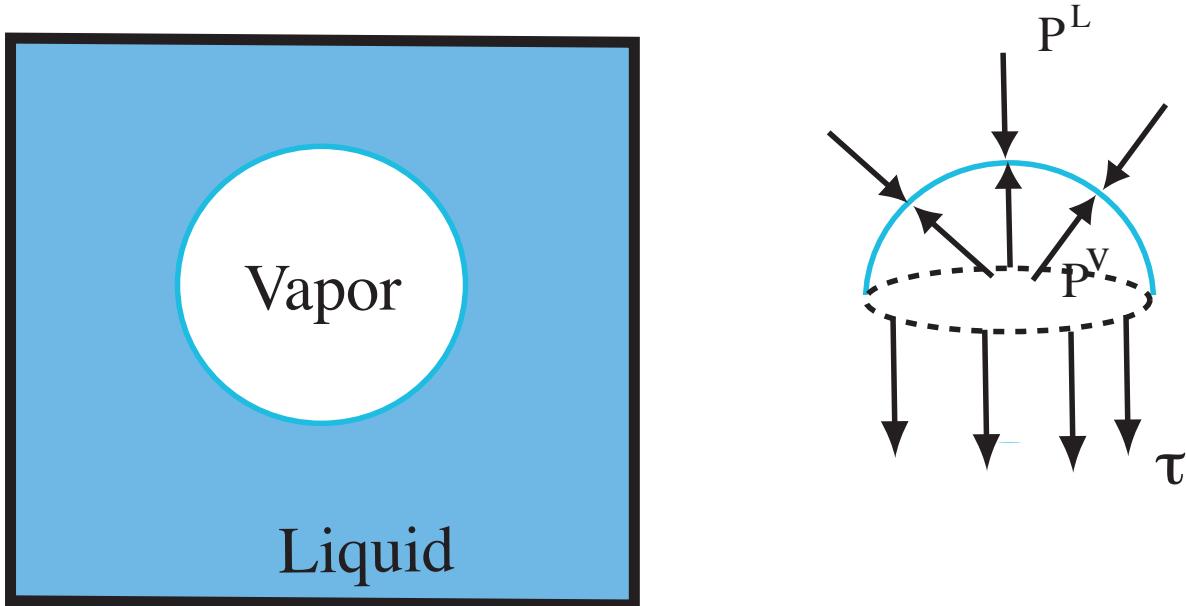


Figure 2.3: Continuum concept of forces on acting at liquid-vapor surface.

spherical coordinates may be used to calculate the net-pressure force in the z-direction that acts on an element of surface,

$$dA = R^2 \sin \theta d\theta d\phi.$$

$$0 = \int_0^{2\pi} d\phi \int_0^{\pi/2} R^2 (P^V - P^L) (\cos \theta) \sin \theta d\theta - \int_0^{2\pi} \tau R d\phi. \quad (2.43)$$

From Eq. (2.43), one finds

$$P^V - P^L = \frac{2\tau}{R}. \quad (2.44)$$

Now we consider the results obtained from thermodynamics. When Eq. (2.33) is applied to the circumstances indicated in Fig. 2.3, one finds the conditions for equilibrium are:

1. Thermal equilibrium must exist:

$$\begin{aligned} T^L &= T^V, \\ &= T^{LV}, \\ &= T. \end{aligned} \tag{2.45}$$

2. Mechanical equilibrium or a force balance:

$$P^V - P^L = \frac{2\tau}{R_\epsilon}. \tag{2.46}$$

where we have added the subscript ϵ on R to emphasize that this is the radius of the bubble that satisfies **necessary condition for equilibrium**.

3. The chemical potential in all three phases must be equal

$$\begin{aligned} \mu^L(T, P^L) &= \mu^V(T, P^V) \\ &= \mu^{LV}. \end{aligned} \tag{2.47}$$

Note that the necessary conditions for thermodynamic equilibrium includes a condition on the chemical potentials that is completely absent from the continuum mechanics approach, but this condition imposes a condition on the pressures. If the liquid phase is approximated as incompressible and the vapor phase as an ideal gas, Eq. 2.47 may be written in terms of the saturation-vapor pressure of the fluid:

$$\mu^L(T, P_s) + v_f(P^L - P_s) = \mu^V(T, P_s) + \bar{R}T \ln \frac{P^V}{P_s}$$

since $\mu^L(T, P_s)$ is equal $\mu^V(T, P_s)$, this condition simplifies to

$$P^V = P_s \exp \left[\frac{v_f}{v_g} \left(\frac{P^L}{P_s} - 1 \right) \right] \tag{2.48}$$

and when this relation is combined with Eq. 2.46, one obtains the expression for R_ϵ :

$$R_\epsilon = \frac{2\gamma^{LV}}{P_s \exp \left[\frac{v_f}{v_g} \left(\frac{P^L}{P_s} - 1 \right) \right] - P^L} \tag{2.49}$$

Thus, if the P^L and the T^L were measured, the equilibrium radius of the bubble, R_ϵ , could be predicted from the conditions for equilibrium.

By contrast, if the P^L and the T^L were measured the continuum expression for the equilibrium radius could not be used to predict the equilibrium radius because the expression for the equilibrium still contains the unknown P^V .

2.1.6 Stability of a vapor bubble in an isolated two phase, single component system

The necessary conditions for equilibrium in an isolated system that contains a vapor bubble are given in Eqs. 2.33. If the liquid phase is approximated as incompressible and the vapor phase as an ideal gas, the radius of the equilibrium sized bubble, R_ϵ may be expressed in terms of the T and P^L as indicated in Eq. 2.49. Thus, R_ϵ is a property of the liquid phase:

$$R_\epsilon = R_\epsilon(T^L, P^L) \quad (2.50)$$

Thus whether or not there is a bubble present in the liquid phase has the property R_ϵ .

However, we must separate two concepts: one is the physical size of a bubble. The physical radius of a bubble is the size of a bubble that you would see if you looked into the system (Fig. 2.4), but the physical radius is not necessarily equal to R_ϵ , the radius of an equilibrium sized bubble. For example, a physical bubble can only have a positive radius, but the value of R_ϵ can be negative or positive.

The difference in these concepts is illustrated in Fig. 2.4. For a single component system, in order for R_ϵ to be positive, the pressure in the liquid phase must be less than $P_s(T)$. As indicated in Section 1.13 a liquid phase is *not the stable phase* when the liquid-phase pressure, P^L , is less than the saturation-vapor pressure, $P_s(T)$. Now we can say that if $P^L < P_s(T)$, a physical bubble could be in equilibrium when in the liquid phase, but a question is raised:

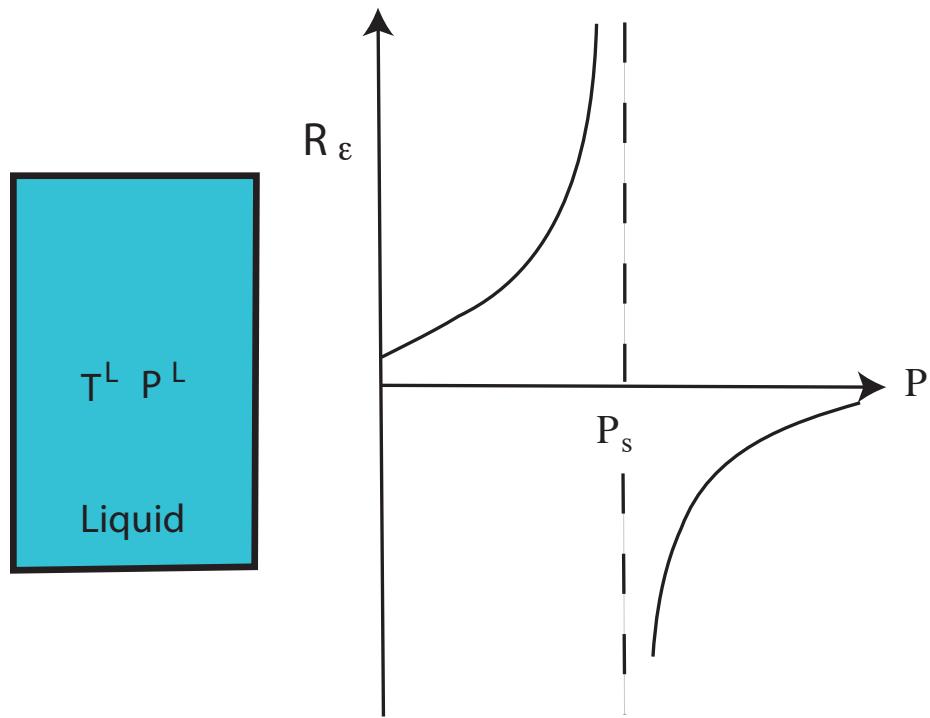


Figure 2.4: A liquid phase has a property R_ϵ whether or not a bubble is present in the system.

what kind of the equilibrium state.

2.2 Transition out of a metastable state

Now we ask what would happen if a bubble formed spontaneously in a liquid phase and the conditions in the liquid phase were such that the thermodynamic potential were an extremum. If the thermodynamic potential is denoted B , this means only that

$$dB = 0$$

for all virtual displacement about the state where the thermodynamic potential is an extremum. The potential could be an absolute maximum, a local maximum, a local minimum,

or absolute minimum, among other possibilities.

We consider two cases: one, a vapor bubble in a single component liquid, and the other, a gas-vapor mixture inside a surface of tension and immersed in a liquid-gas solution.

2.2.1 Thermodynamic potential when a surface phase separates two bulk phases.

We suppose a bulk phase, superscript L , surrounds another fluid phase, superscript G , and these two bulk phases are separated by surface phase, LG , and all three phases are enclosed in piston cylinder arrangement. The piston-cylinder arrangement is surrounded by a large volume of the same bulk phase, Fig. 2.5. Note that if the piston moves there is no change in the energy of the solid-fluid phase; thus we neglect the solid-fluid phase interface in the analysis.

We first construct the thermodynamic potential of the system in general and then apply it to the particular cases. Note that the pressure in the G -phase is different than that in the L -phase. Thus, the Gibbs function is not the thermodynamic potential for the composite system.

The energy of the composite system, U_c is given by

$$U^L + U^G + U^{LG} + U^R = U_c \quad (2.51)$$

The Euler relation may be applied for the reservoir:

$$U^R - T^R S^R + P^R V^R = \sum_{i=1}^r N_i^R \mu_i^R \quad (2.52)$$

When the piston is unpinned spontaneous processes occur to take isolated system toward equilibrium. In the these processes:

$$\Delta(U^L + U^G + U^{LG} + U^R) = 0 \quad (2.53)$$

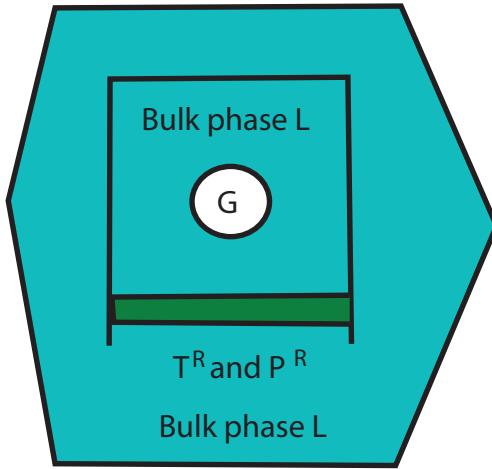


Figure 2.5: A Bulk phase surrounds another fluid phase and they are separated by a surface phase and enclosed in a piston-cylinder arrangement.

and

$$\Delta(S^L + S^G + S^{LV} + S^R) \geq 0 \quad (2.54)$$

When Eqs. (2.51) - (2.54) are combined, they give

$$0 \geq \Delta(U^L - T^R S^L + P^L V^L) + \Delta(U^G - T^R S^G) + \Delta(U^{LG} - T^R S^{LG} + P^R \Delta V^G). \quad (2.55)$$

and since $P^R = P^L$, thermodynamics potentials that have been previously defined may be introduced:

$$0 \geq \Delta(G^L + F^G + F^{LG} + P^L V^G). \quad (2.56)$$

We may now define a new function

$$B \equiv (G^L + F^G + F^{LG} + P^L V^G), \quad (2.57)$$

and as indicated by Eq. (2.56), every spontaneous change would decrease B . Thus, when a system come to the stable equilibrium state, B would be a minimum. Hence, it acts as the thermodynamic potential for a system such as that shown in Fig. 2.5.

2.2.2 Vapor bubble radius when the thermodynamic potential is an extremum

Suppose the phase labelled L in Fig. 2.5 is a single component liquid and the phase inside the surface of curvature is the vapor of that liquid. We apply the B potential to determine the bubble radius when B is an extremum. Thus, we assume that the system has come to a state where B is an extremum, that the reservoir has imposed its temperature on all phases, that it has imposed its pressure on the liquid phase, and the vapor phase is spherical. Then

$$\begin{aligned} dB &= dG^L + dF^G + dF^{LV} + P^L dV^G \\ &= (\mu^L dN^L) + (-P^V dV^V + \mu^V dN^V) + (\gamma^L V dA^{LV} + \mu^{LV} dN^{LV}) + P^L dV^V. \end{aligned} \quad (2.58)$$

The constraints require

$$dN^L = -N^V - N^{LV}.$$

$$dV^V = 4\pi R^2 dR.$$

$$dA^{LV} = 8\pi R dR.$$

and when combined with Eq. (2.58)

$$dB = (\mu^V - \mu^L) dN^G + (\mu^{LV} - \mu^L) dN^V + (-4\pi R^2 P^V + 4\pi R^2 P^L + \gamma^L V 8\pi R) dR. \quad (2.59)$$

Since B is an extremum, i.e., a local maximum, local minimum, or an absolute minimum or other extremum, dB must vanish for all virtual displacements about the extremum. Any of these states could be considered a virtual state, since each would satisfy the constraints.

The conditions for B to be an extremum are

$$\mu^L = \mu^V = \mu^{LV} \quad (2.60)$$

$$P^V = P^L + \frac{2\gamma^{LV}}{R_\epsilon} \quad (2.61)$$

where R_ϵ is radius of the vapor phase when the B-potential is a extremum. We have seen before (Section 2.1.5) that when Eqs. (2.60) and (2.61) are satisfied, the liquid is approximated as incompressible and the vapor as an ideal gas:

$$R_\epsilon = \frac{2\gamma^{LV}}{P_s \exp[\frac{v_f}{v_g}(\frac{P^L}{P_s} - 1)] - P^L} \quad (2.62)$$

Note that R_ϵ only depends on temperature and pressure; thus, as long as the constraint are satisfied R_ϵ is a constant. Also, recall that $P^L < P_s$; thus $R_\epsilon > 0$.

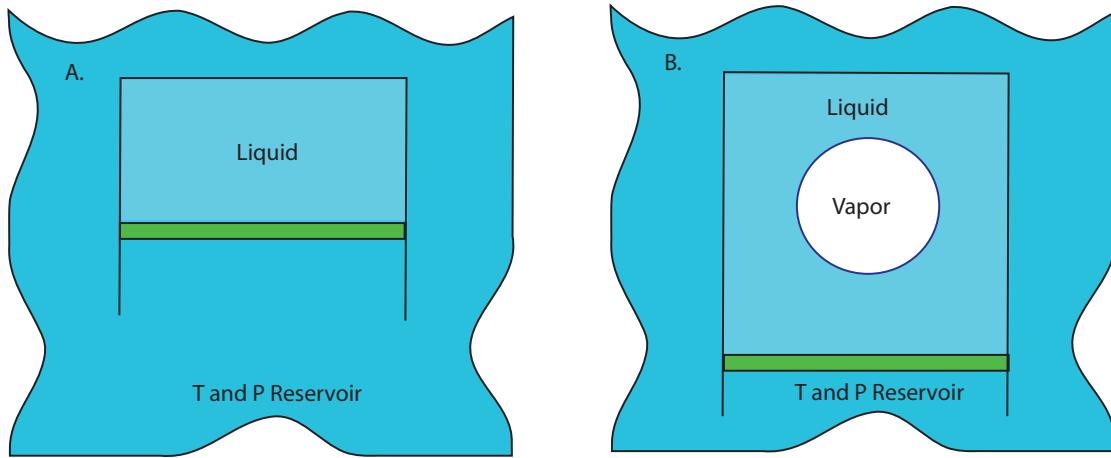


Figure 2.6: Two virtual states of the system.

2.2.3 Stability a single component liquid phase maintained at constant temperature with $P^L < P_s$

When there is no vapor bubble in the system shown in Fig. 2.6A, the B-potential, denoted B_0 , reduces to only the Gibbs function:

$$B_0 = N_c \mu^L(T, P^L).$$

If a bubble formed spontaneously—as a result of the molecular motion—in the liquid phase, Fig. 2.6B, the B-potential, Eq (2.57), would become

$$B = N^L \mu(T, P^L) + (-P^V V^V + N^V \mu^V) + (\gamma^{LV} A^{LV} + N^{LV} \mu^{LV}) + P^L V^V.$$

N_c is not changed by the formation of the vapor phase; thus

$$B_0 = (N^L + N^V + N^{LV})\mu(T, P^L).$$

and $B - B_0$ may be written

$$B - B_0 = (-P^V + P^L)V^V + N^V(\mu^V - \mu^L) + N^{LV}(\mu^{LV} - \mu^L) + \gamma^{LV}A^{LV}. \quad (2.63)$$

Now assume that the system is in one of extremum states of B-potential and consider virtual displacements about this state. In order for the system to be in an extremum state Eqs. (2.60)-(2.62) must be satisfied. These are conditions on the intensive properties, and when these conditions are imposed

$$B - B_0 = \left(-\frac{2\gamma^{LV}}{R_\epsilon}\right)\left(\frac{4\pi R^3}{3}\right) + \gamma^{LV}(4\pi R^2)$$

gathering terms

$$B - B_0 = 4\pi\gamma^{LV}\left(R^2 - \frac{2R^3}{3R_\epsilon}\right) \quad (2.64)$$

A plot of $B - B_0$ is shown in Fig. 2.7 in two circumstances. The plot in Fig. 2.7A is for $P^L > P_s(T)$ or $R_\epsilon < 0$. In the case the homogeneous liquid phase is stable: no matter how large the perturbation—the spontaneous formation of a spherical vapor bubble—the system returns to the homogeneous liquid phase.

The plot in Fig. 2.7B is for $P^L < P_s(T)$ or $R_\epsilon > 0$. In this case R_ϵ defines the perturbation required to take the liquid out of homogeneous metastable state, and to initiate the formation of the homogeneous vapor.

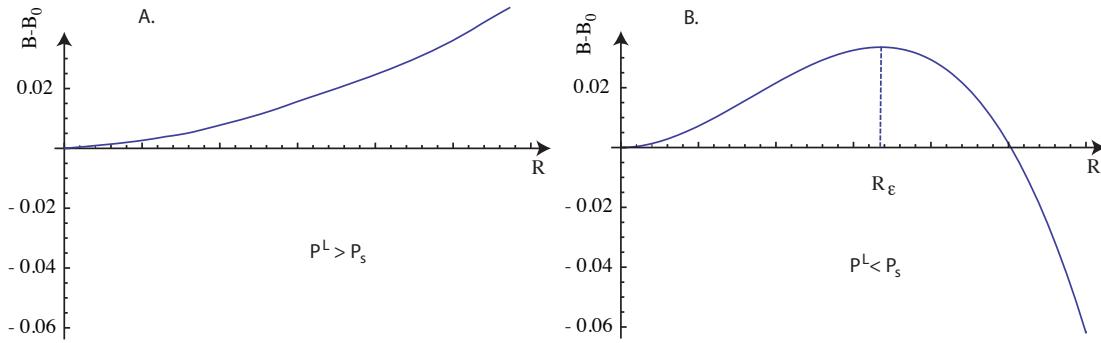


Figure 2.7: The stability of the system shown in Fig. 2.6 depends on the pressure in the liquid phase: if $P^L > P_s(T)$ the system is stable. No matter what size bubble forms spontaneously in the system, the system returns to the homogeneous liquid phase, as indicated in Fig. A. By contrast, as indicated in Fig. B, if $P^L < P_s(T)$, R_ϵ is positive and defines the perturbation required to take the liquid out of its homogeneous metastable state and to initiate the formation of the vapor phase.

2.2.4 Metastable Liquid-Gas Solution

Consider the system shown in Fig. 2.8. The thermodynamic potential is the B function, and it may be written as indicated in Eq. (2.57). We now want to use B to determine the states for which it is an extremum for the system under consideration. In these states the temperature is uniform and equal to that of the reservoir; the liquid-phase pressure is equal to that of the reservoir, and the number of moles of each component in the system is a constant.

If the gas-vapor bubble is present, we shall assume it to be spherical;

$$\begin{aligned} N_i &= N_i^L + N_i^G + N_i^{LG}, \quad i = 1, 2; \\ A^{LV} &= 4\pi R^2, \\ V^G &= \frac{4\pi R^3}{3}. \end{aligned} \tag{2.65}$$

The states for which B is an extremum may be determined by requiring $dB = 0$ for all

virtual displacements about the extremum state.

$$dB = \left(\sum_i^2 \mu_i^L dN_i^L \right) + (-P^G dV^G \sum_i^2 \mu_i^G dN_i^G) + (\gamma^{LV} dA^{LV} + \sum_i^2 \mu_i^{LG} dN_i^{LV}) + P^L dV^G \quad (2.66)$$

After differentiating the constraints, and combining the result with Eq. (2.66)

$$dB = \left(\sum_i^2 (\mu_i^G - \mu_i^L) dN_i^G \right) + \sum_i^2 (\mu_i^{LV} - \mu_i^L) dN_i^{LV} + (-4\pi R^2 P^G + 4\pi R^2 P^L + 8\pi \gamma^{LV} R) dR \quad (2.67)$$

Since dB must vanish for all values of dN_i^G , dN_i^{LV} and dR , the necessary conditions for equilibrium are

$$\begin{aligned} \mu_i^L &= \mu_i^G \\ &= \mu_i^{LG} \\ P^G &= P^L + \frac{2\gamma^{LV}}{R_\epsilon} \end{aligned} \quad (2.68)$$

We now want to determine the expression for the radius of curvature of the surface phase for the system shown in Fig. 2.8. For simplicity, we suppose the solubility of the gas is defined as indicated in Eq. (1.123). Also, we suppose the phase inside the surface of curvature is an ideal gas mixture.

The chemical potentials of the components in the solution have been previously obtained (see Section 1.6.4):

$$\mu_1^L(T, P^L, x_1, x_2) = \mu_1^0(T, P^L) - \bar{R}T \left(\frac{x_2}{x_1} \right). \quad (2.69)$$

This chemical potential of the solvent may be expressed in terms of $P_s(T)$ provided the liquid phase satisfies the condition that

$$\begin{aligned} |\kappa_T(P^L - P_s)| &\ll 1 : \\ \mu_1^L(T, P^L, x_1, x_2) &= \mu_1^0(T, P_s) + v_f(P^L - P_s) - \bar{R}T \left(\frac{x_2^L}{x_1^L} \right). \end{aligned} \quad (2.70)$$

For the solute in the liquid solution

$$\mu_2^L(T, P^L, x_2, x_s) = \mu_2^0(T, P^L) + \bar{R}T \ln \left(\frac{x_2^L}{x_s} \right). \quad (2.71)$$

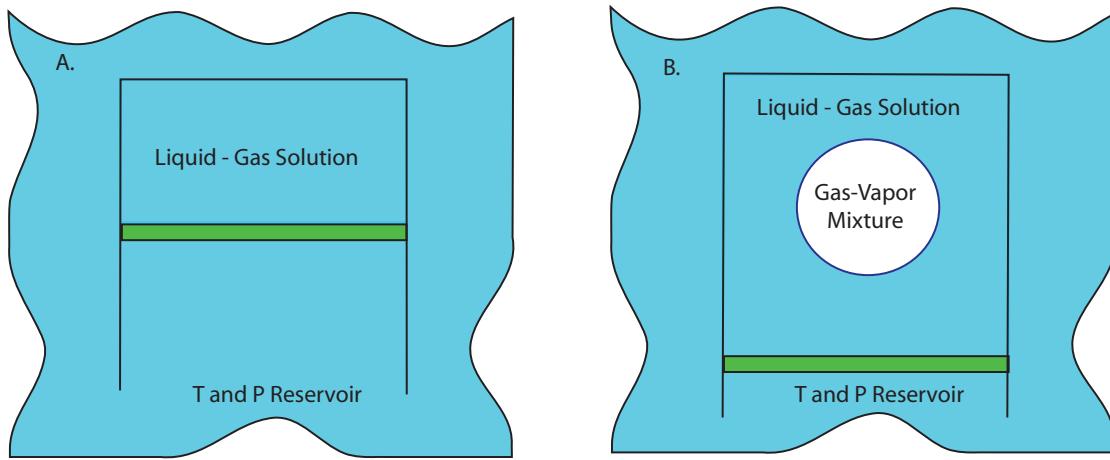


Figure 2.8: A system is depicted in two virtual states. The stability of these states is determined by the B function.

For the ideal gas mixture inside the surface of curvature, the chemical potential of either component may be expressed

$$\mu_i^G(T, P^G, x_i^G) = \mu_i^0(T, P^G) + \bar{R}T \ln x_i^G. \quad (2.72)$$

and from the definition of the chemical potential for an ideal gas

$$\mu^0(T, P) = \mu(T, P_r) + \bar{R}T \ln\left(\frac{P}{P_r}\right). \quad (2.73)$$

When Eq. (2.73) is applied in Eq. (2.72), the reference pressure may be chosen to be $P_s(T)$:

$$\mu_1^G(T, P^G, x_1^G) = \mu_1^0(T, P_s) + \bar{R}T \ln \frac{x_1^G P^G}{P_s}. \quad (2.74)$$

According to the conditions for an extremum of B , Eq. (2.33),

$$\mu_1^G(T, P^G, x_1^G) = \mu_1^L(T, P^L, x_1^L),$$

and from these conditions

$$x_1^G P^G = P_s \exp\left[\frac{v_f}{\bar{R}T}(P^L - P_s) - \frac{x_2^L}{x_1^L}\right]. \quad (2.75)$$

Since component 2 is an ideal gas, the temperature T must be above its critical temperature. Thus, a saturation-vapor pressure for this substance at this temperature would not exist. Hence, we proceed slightly differently for this component. When Eq. (2.73) is applied in Eq. (2.72) and P_r chosen to be P^L one finds

$$\mu_2(T, P^G, x_2^G) = \mu_2^0(T, P^L) + \bar{R}T \ln \frac{P^G x_2^G}{P^L}. \quad (2.76)$$

When Eqs. (2.76) and (2.71) are used in the conditions for equilibrium, one finds

$$x_2^G P^G = \frac{x_2^L P^L}{x_s}, \quad (2.77)$$

and by adding Eqs. (2.77) and (2.75), one finds

$$P^G = P_s \exp\left[\frac{\bar{R}T}{v_f}(P^L - P_s) - \frac{x_2^L}{x_1^L}\right] + \frac{x_2^L P^L}{x_s}. \quad (2.78)$$

Then the expression for the radius of curvature of the surface phase when equilibrium exists in the system may be obtained from the general conditions for equilibrium given in Eq. (2.33). If the surface phase radius, under equilibrium conditions, is denoted as R_ϵ , then

$$R_\epsilon = \frac{2\gamma^{LV}}{P_s \exp\left[\frac{v_f}{RT}(P^L - P_s) - \frac{x_2^L}{x_1^L}\right] + \frac{x_2^L P^L}{x_s} - P^L}. \quad (2.79)$$

We emphasize that R_ϵ is the radius of the gas-vapor mixture when the thermodynamics potential is an extremum. It is expressed in terms of the properties of liquid phase; thus a property of the liquid-gas solution.

We note for future reference that in order for R_ϵ to be positive P^L must satisfy

$$P^L < P_s \exp\left[\frac{v_f}{RT}(P^L - P_s) - \frac{x_2^L}{x_1^L}\right] + \frac{x_2^L P^L}{x_s} \quad (2.80)$$

2.2.5 Virtual states of a liquid-gas solution

In system shown in Fig. 2.8, the pressure in the liquid phase and temperature of the system are controlled by a surrounding reservoir. The total number of moles of each component, N_1, N_2 is constant.

We want to determine the size of the gas-vapor phase in the virtual states from the values of the controlled properties. We neglect the adsorption in the surface phase and approximate γ^{LG} as being a function only of T alone.

It is easier to apply the conservation conditions if R_ϵ is written in terms of the total number of moles in each phase, $N_1^L, N_2^L, N_1^G, N_2^G$. From the expression for the solubility, Eq. (1.123):

$$N_s = \frac{N_1^L P^L}{K_h}, \quad (2.81)$$

and then Eq. (2.79) becomes

$$R_\epsilon = \frac{2\gamma^{LV}}{P_s \exp[\frac{v_f}{RT}(P^L - P_s) - \frac{N_2^L}{N_1^L}] + \frac{N_2^L K_h}{N_1^L} - P^L}. \quad (2.82)$$

We now want to determine the expression for R_ϵ as a function of the total number of moles, N_1, N_2 and the gas-vapor phase volume, V^G . If we neglect the number of moles adsorbed

$$N_2 = N_2^L + N_2^G. \quad (2.83)$$

The partial pressure of the gas component in V^G is given in Eq.(2.77) after making use of the Henry expression for the solubility:

$$P_2^G = \frac{N_2^L K_h}{N_1^L}. \quad (2.84)$$

The number of moles of component 2 in the gas-vapor mixture is given by

$$N_2^G = \frac{N_2^L K_h V^G}{N_1^L \bar{R} T}. \quad (2.85)$$

When Eq. (2.85) is substituted into Eq. (2.83), the result may be written

$$\frac{N_2^L}{N_1^L} = \frac{N_2 \bar{R} T}{N_1^L \bar{R} T + K_h V^G}. \quad (2.86)$$

The partial pressure of the vapor in the gas-vapor phase is given by Eq. (2.75) and may now be written

$$P_1^G = \eta P_s, \quad (2.87)$$

where

$$\eta = \exp\left[\frac{v_f}{\bar{R}T}(P^L - P_s) - \frac{N_2 \bar{R}T}{N_1^L \bar{R}T + K_h V^G}\right]. \quad (2.88)$$

Since

$$N_1 = N_1^L + N_1^G,$$

one finds from Eq. (2.87) and the ideal-gas relation

$$N_1^L = N_1 - \frac{\eta P_s V^G}{\bar{R}T}. \quad (2.89)$$

After substituting Eqs. (2.86) and (2.89) into Eq. (2.82), one finds as the expression for R_ϵ

$$R_\epsilon = \frac{2\gamma^{LV}}{\eta P_s + \frac{K_h N_2 \bar{R}T}{N_1 \bar{R}T - \eta P_s V^G + V^G K_h} - P^L} \quad (2.90)$$

Since the gas-vapor phase is being approximated as spherical

$$V^G = \frac{4\pi R^3}{3}. \quad (2.91)$$

Equations (2.90), (2.91), and (2.88) constitute a closed system of equations for the thermodynamic property R_ϵ as a function of the physical radius, R of the gas-vapor phase. Note the value of η must be determined from an iteration procedure. Under normal conditions, it is very near unity.

In Fig. 2.9, a plot of R_ϵ as function of the physical radius, R , for a particular case is shown. When R_ϵ is equal R , the system is in a state where the thermodynamic potential is an extremum, i.e., virtual state. The stability of the state is determined by the nature of the extremum.

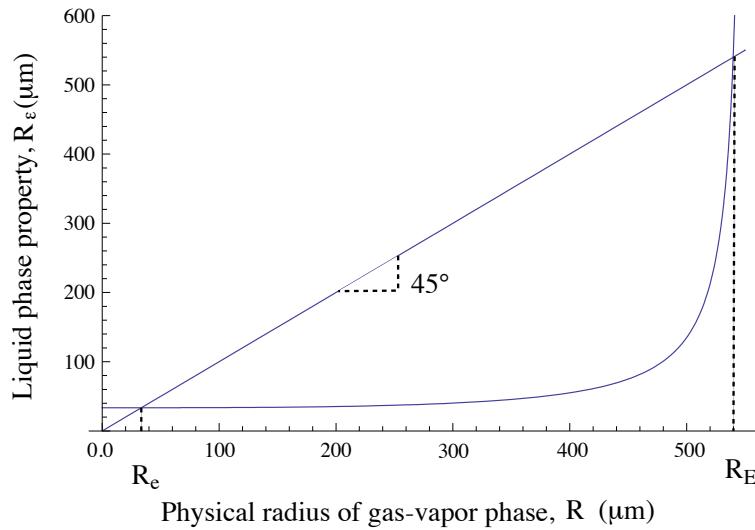


Figure 2.9: For the system shown in Fig. 2.8, the reservoir pressure was taken to be 1.01325×10^5 Pa and the temperature to be 30 °C. The solvent was water, and there were 0.0553 mol present. The solute was nitrogen and there were 0.6476 μmol present. Note the two possible equilibrium radii of the gas-vapor phase are predicted.

2.2.6 Stability of the virtual states

For the conditions considered in Fig. 2.8, the analysis indicates there are two radii of the gas-vapor mixture, R_e, R_E for which the B potential is an extremum, Fig. 2.9. We examine the B potential in these states.

If there is no gas-vapopr phase present

$$\begin{aligned}
 B &= B_0 \\
 &= G^L \\
 B_0 &= N_1\mu_1(T, P^L, N_1, N_2) + N_2\mu_2(T, P^L, N_1, N_2)
 \end{aligned} \tag{2.92}$$

The chemical potentials in the state are constants. We denote them as μ_{10} and μ_{20}

$$\mu_{10} = \mu_1^0(T, P) - \bar{R}T \frac{N_2}{N_1} \quad (2.93)$$

$$\mu_{20} = \mu_2^0(T, P) + \bar{R}T \ln \frac{N_2 K_h}{N_1 P} \quad (2.94)$$

Now we want to form the expression for the B function when $R = R_\epsilon$. In a virtual state, when a bubble of radius R_ϵ is present

$$\mu_i^L(R, R_\epsilon) = \mu_i^G(R, R_\epsilon) = \mu_i^{LV}(R, R_\epsilon) = i = 1, 2. \quad (2.95)$$

$$P^V - P^L = \frac{2\gamma}{R_\epsilon} \quad (2.96)$$

Combining Eqs. (2.86) and (2.89) gives

$$\frac{N_2^L}{N_1^L} = \frac{N_2 \bar{R}T}{N_1 \bar{R}T - \eta P_s V^G + K_h V^G} \quad (2.97)$$

and $\mu_1^L(R, R_\epsilon)$ may be written

$$\mu_1^L(R, R_\epsilon) = \mu_1^0(T, P) - \bar{R}T \left(\frac{N_2 \bar{R}T}{N_1 \bar{R}T - \eta P_s V^G + K_h V^G} \right). \quad (2.98)$$

The change in the chemical potential of component 1:

$$\mu_1^L(R, R_\epsilon) - \mu_{10} = \bar{R}T \frac{N_2(K_h V^G - \eta P_s V^G)}{N_1(N_1 \bar{R}T - \eta P_s V^G + K_h V^G)} \quad (2.99)$$

Following a similar procedure for component 2, one finds from Eqs. (2.71), (2.86) and (2.89)

$$\mu_2(R, R_\epsilon) = \mu_2^0(T, P) + \bar{R}T \ln \frac{K_h N_2 \bar{R}T}{P^L(\bar{T}N_1 - \eta P_s V^G + K_h V^G)} \quad (2.100)$$

and the change in the chemical potential of component 2

$$\mu_2(R, R_\epsilon) - \mu_{20} = \bar{R}T \ln \left(\frac{\bar{R}T N_1}{(N_1 \bar{R}T - \eta P_s V^G + K_h V^G)} \right) \quad (2.101)$$

The thermodynamic potential is then

$$B(R, R_\epsilon) = N_1 \mu_1(R, R_\epsilon) + N_2 \mu_2(R, R_\epsilon) - P^G V^G + \gamma^{LV} A^{LV} + P^L V^G \quad (2.102)$$

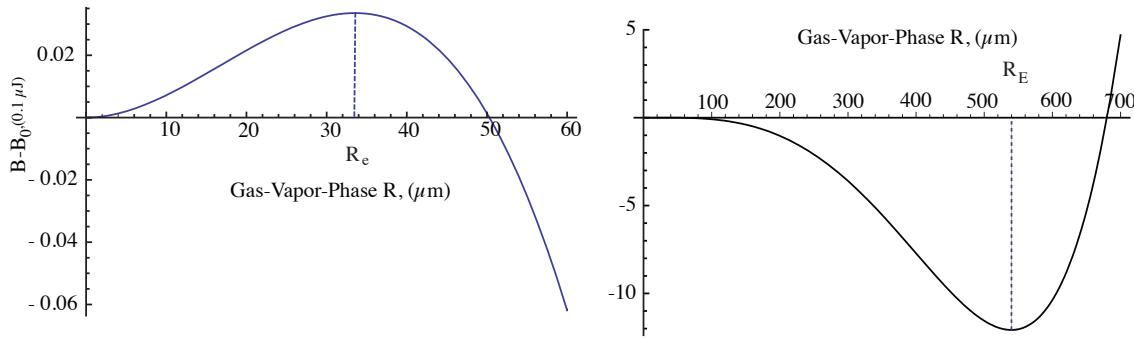


Figure 2.10: A plot of $B(R) - B_0$ for the system shown in Fig. 2.8. As shown in Fig. 2.12, there are two possible equilibrium sizes for the gas-vapor phase. One corresponding to a gas-vapor phase of radius R_e and the other corresponding to radius of R_E . As seen in this figure the one corresponding to R_e is an unstable equilibrium, but the one corresponding to R_E is a stable equilibrium radius.

After subtracting Eq. (2.92) from Eq. (2.102) and making use of the constraints Eq. (??)

$$\begin{aligned} B(R, R_\epsilon) - B_0 &= N_1(\mu_1(R, R_\epsilon) - \mu_1(T, P^L, N_1, N_2)) \\ &+ N_2(\mu_2(R, R_\epsilon) - \mu_2(T, P^L, N_1, N_2)) + (\gamma^{LV} A^{LV} + P^L V^G - P^G V^G) \end{aligned} \quad (2.103)$$

and from Eqs. (2.99) and (2.101)

$$\begin{aligned} B(R, R_\epsilon) - B_0 &= N_2 \bar{R} T \left(\frac{(K_h V^G - \eta P_s V^G)}{(N_1 \bar{R} T - \eta P_s V^G + K_h V^G)} \right) \\ &+ N_2 \bar{R} T \left(\ln \left(\frac{\bar{R} T N_1}{(N_1 \bar{R} T - \eta P_s V^G + K_h V^G)} \right) + 4\pi \gamma^{LV} (R^2 - 2R^3/3R_\epsilon) \right) \end{aligned} \quad (2.104)$$

The calculated values of

$$B(R, R_\epsilon) - B_0$$

for the system shown schematically in Fig. 2.8 may be seen in Fig. 2.10.

As seen there, the thermodynamic potential at R_e is a maximum. The usual concept of equilibrium supposes that if a system is subjected to a small displacement from the extremum state, the system would return to the equilibrium state. However, as indicated in Fig. ??, it is predicted that a *gas-vapor phase* of size R_e is unstable. In such a state, if the gas-vapor phase is displaced slightly from the R_e , the system does not return, but is predicted to continue in the direction of the displacement.

This unusual virtual state has been the subject of an experimental investigation [1], as described in the following section.

The virtual state corresponding to a gas-vapor phase having a radius R_E is an stable equilibrium state. The extremum of B is a minimum. Thus, if the gas-vapor phase is present and of size R_E , the gas-vapor phase will return to R_E when it is subjected to a small displacement from this state.

The stability of the *liquid-gas solution* must be distinguished from that of a *gas-vapor phase*. If a liquid-gas-solution is in a system such as that shown in Fig. ??, and the properties and constraints are such that $R_e > 0$, then the *liquid-gas solution* is *metastable*. The value of the property R_e defines the size of a gas-vapor phase that must be formed spontaneously, as a result of molecular motion, to take the system out of the metastable state. The value of R_e defines the threshold size of the “perturbation” required to form the new phase. Note that the system itself, as a result of the molecular motion, provides the perturbation.

If the molecular motion produces a gas-vapor phase greater than R_e , then thermodynamics predicts the gas-vapor phase will grow to size R_E . However, thermodynamics cannot predict when the molecular motion will produce a gas-vapor phase of size R_e . That is a condition addressed in physical kinetics.

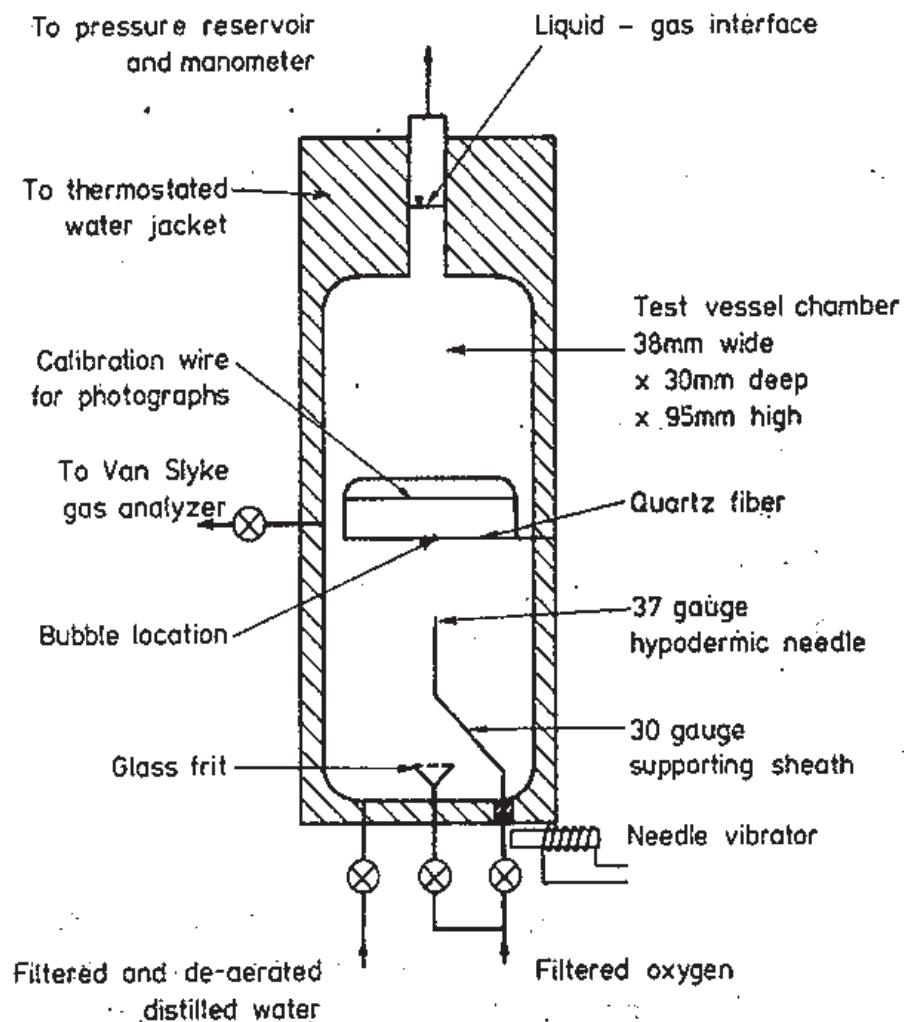


Figure 2.11: Apparatus used to examine the predicted behavior of a H_2O-O_2 phase enclosed in a liquid-vapor surface phase and immersed in a H_2O-O_2 [1].

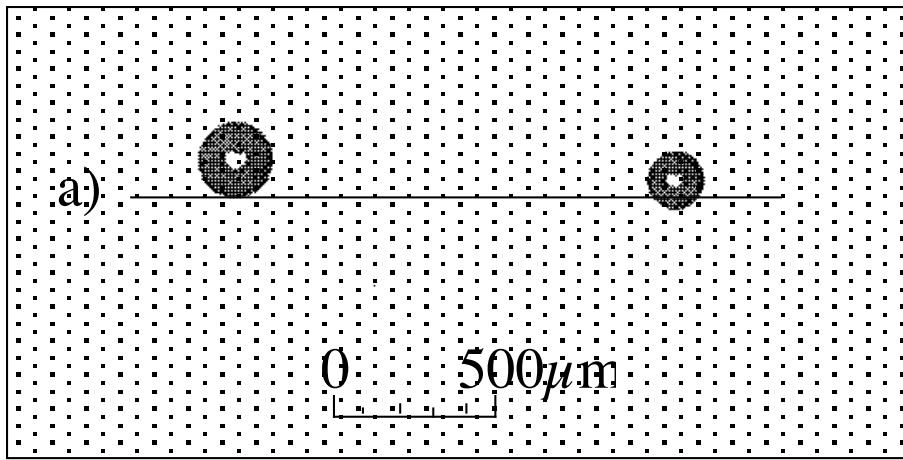


Figure 2.12: Two bubbles photographed when present in a H_2O-O_2 solution at 20 ± 0.1 $^{\circ}C$, 158 mm Hg, $n_2/n_s = 0.9585 \pm 0.0114$.

2.2.7 Experimental examination of an unstable equilibrium state

An investigation [1] has been performed of the R_e state using the apparatus shown schematically in Fig. ???. The pressure and the gas concentration were chosen so an equilibrium-sized gas-vapor phase was easily visible through a light microscope. After the liquid-gas solution was prepared and placed in the apparatus shown in fig:C3Fig38 gas-vapor bubbles were injected into the liquid with a vibrating 37 gauge needle. This produced bubbles with radii of $\sim 100\mu\text{m}$. As the bubbles rose through the liquid because buoyancy, some of them hit on the quartz fibre and stuck to it. When two bubbles were caught on the fibre, and one was greater than R_e and another was smaller, their behavior was photographed. One such photograph is shown in Fig. ??.

The bubbles are far enough apart so that they do not directly interact with one another, but each interacts with the surrounding liquid-gas solution. The thermodynamic conditions are such that the value of R_e for the solution lies between the physical radii of the bubbles. Thus, the radius of the larger bubble is greater than the value of R_e , and the radius of the

Table 2.1: Conditions at which homogeneous nucleation of a vapor occurred in ethyl ether [6, 7].

T ^L (°C)	P ^L (kPa)	P _s (kPa)	v _f (m ³ /mmol)	γ ^{LV}	R _e (nm)	mcs-L	mcs-V
153	777	1,857	0.123	0.00286	5.65	923	58
160.3	1,366	2,109	0.139	0.00224	6.55	1,278	90
170	2,089	2,491	0.170	0.00147	8.25	2,085	179

smaller bubble is less than the value of R_e . Hence the larger bubble is predicted to grow while simultaneously the smaller one is predicted to diminished in size. The photographed behavior is shown in Fig. 2.13.

The subsequent behaviour of the bubbles after the initial time is shown in Fig. 2.13. As seen there, simultaneously and in the same liquid-gas solution the smaller bubble dissolved while the larger one grew. This is certainly the behavior that would be expected since the radius of the smaller one was less the R_e , but the radius of larger one was greater than R_e .

2.2.8 A violation of the second postulate of thermodynamics?

Note that the spontaneous formation of a gas-vapor phase of size R_e in a homogeneous system such as that shown Fig. 2.8 corresponds to a spontaneous decrease in the entropy of an isolated system (the reservoir and the liquid-vapor solution). If the spontaneous change were “macroscopic” it would be a contradiction of the second postulate of thermodynamics!

Careful experiments have been conducted to determine if such event do occur and if they do, under what conditions. The spontaneous appearance of a new phase within an original phase is referred to as “homogeneous” nucleation, as opposed to “heterogeneous” nucleation that involves a solid surface.

Although we cannot yet consider the rate of homogeneous nucleation, the thermodynamic

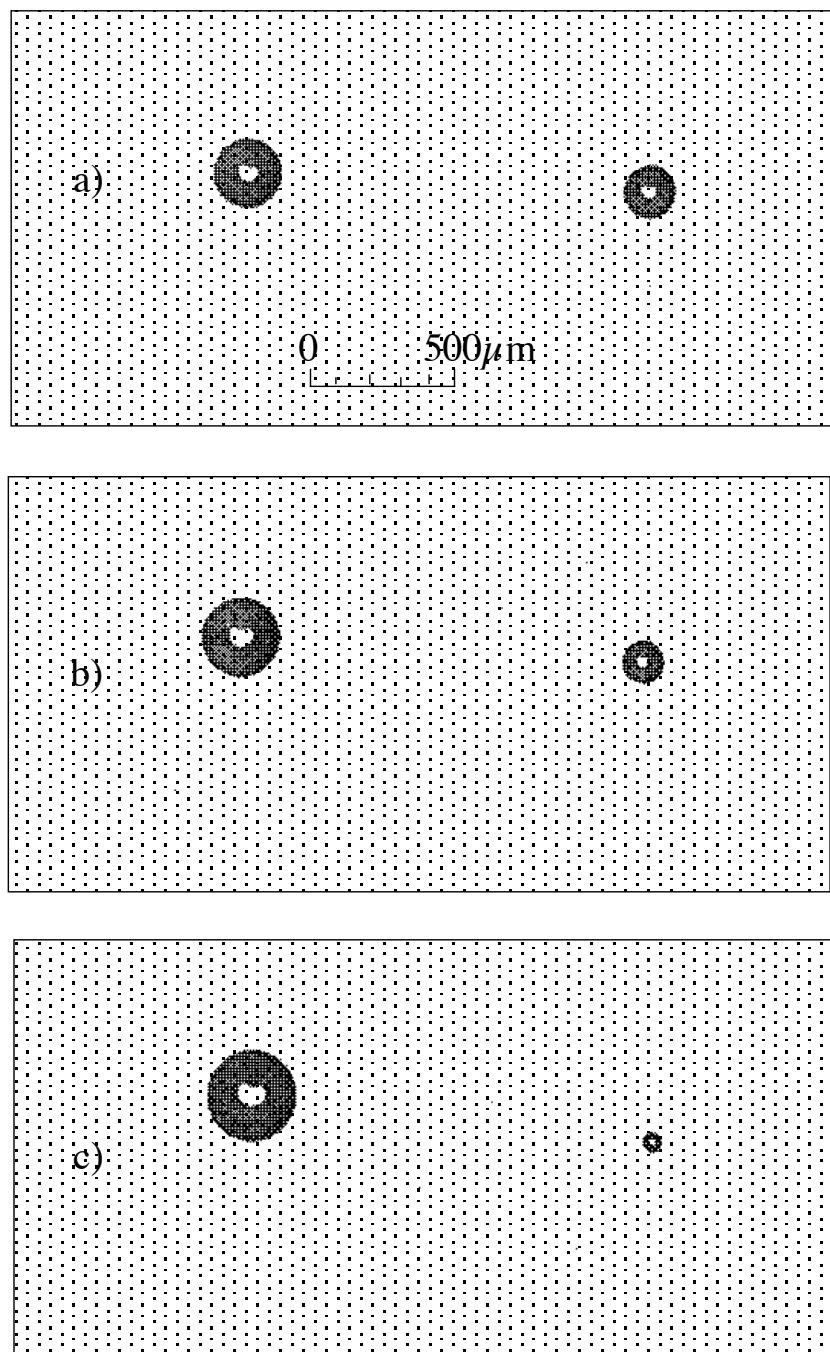


Figure 2.13: Subsequent behavior of bubbles shown initially in Fig. ?? [1].

Table 2.2: Conditions at which homogeneous nucleation of a vapor occurred in ethyl ether [6, 7].

T ^L	P ^L	P _s	v _f	γ ^{LV}	R _e	in R _e ^L	in R _e ^V
°C	kPa	kPa	m ³ /mmol	N/m	nm	mcs	mcs
153	777	1,857	0.123	0.00286	5.65	923	58
160.3	1,366	2,109	0.139	0.00224	6.55	1,278	90
170	2,089	2,491	0.170	0.00147	8.25	2,085	179

conditions under which this could occur has been addressed in Section 2.2.6. For this purpose, we consider the nucleation of a vapor phase within a liquid phase of ethyl ether (diethyl ether) [6, 7, 10, 11]. The conditions at three temperatures under which the nucleation of a vapor phase within liquid were observed are listed in Table 2.2. Note that in each case the pressure in the liquid was less than the saturation-vapor pressure. Thus, the liquid phase was metastable (see Table 1.3). This may be viewed as the necessary condition for a spontaneous phase change. The critical temperature of ethyl ether is 194.6 °C.

Mechanistically, as indicated by the last three columns: in a volume defined by R_e , the number of molecules within the liquid (mcs) is of order 10^3 , but afterwards nucleation of vapor-gas bubble, the number is reduced to roughly 10^2 . Thus, the nucleation event may be viewed as a fluctuation in density in which, molecule spontaneously leave a volume within a liquid phase. This indicates there is a limit to the validity of the thermodynamic postulates: they do not apply to changes brought about by a few 100 molecules. Also note that radius of nucleate bubble is less than 10 nm.

2.3 Surface tension of a solid

A procedure similar to that used to define the surface tension of a liquid-vapor interface may be used to define the surface tension of a solid, but we first want to understand what is meant by the surface tension of a solid. We suppose the solid is non-evaporating, and that its lattice is as depicted in Fig. 2.14A. Suppose, the lattice is cleaved to form a surface (Fig. 2.14B). As a result of the cleaving, the atoms near the surface move to new lattice positions, creating new energy. This surface energy results in what is called the surface tension of the solid. When only the atoms (or molecules) of the solid are interacting, the surface tension is a material property of the solid, denoted γ^{S0} .

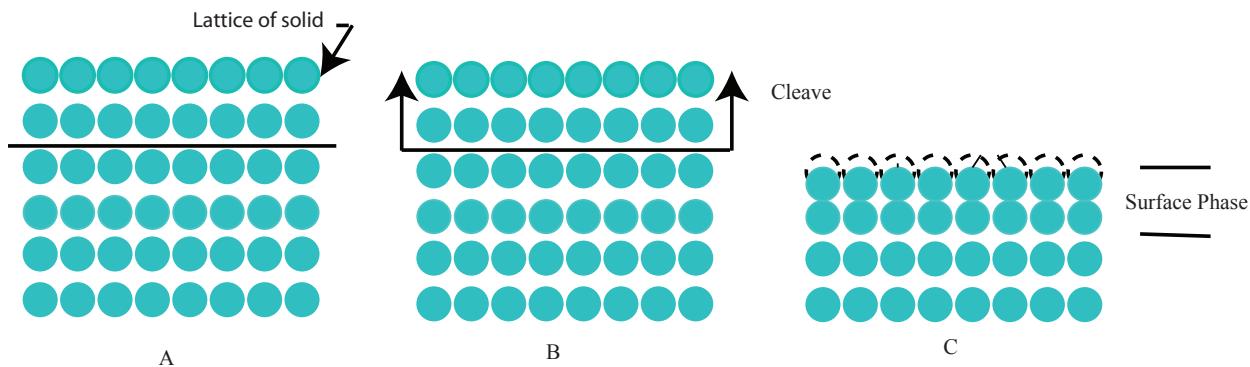


Figure 2.14: In A the lattice structure of a solid is depicted; in B a solid surface is formed by cleaving a solid. In C the movement of the surface atoms to new positions is depicted. This movement brings the surface atoms so they interact with those below create in new energy the accounted for thermodynamically by U^{SV} .

We use the Gibbs dividing surface concept to define the position of the solid surface. The position of the dividing surface is indicated by z^{S0} in Fig. 2.15. In terms of the Gibbs model, the internal energy of the surface phase when it is exposed to an absolute vacuum is denoted U^{S0} , and the thermodynamic energy of a composite system consisting of a solid phase and

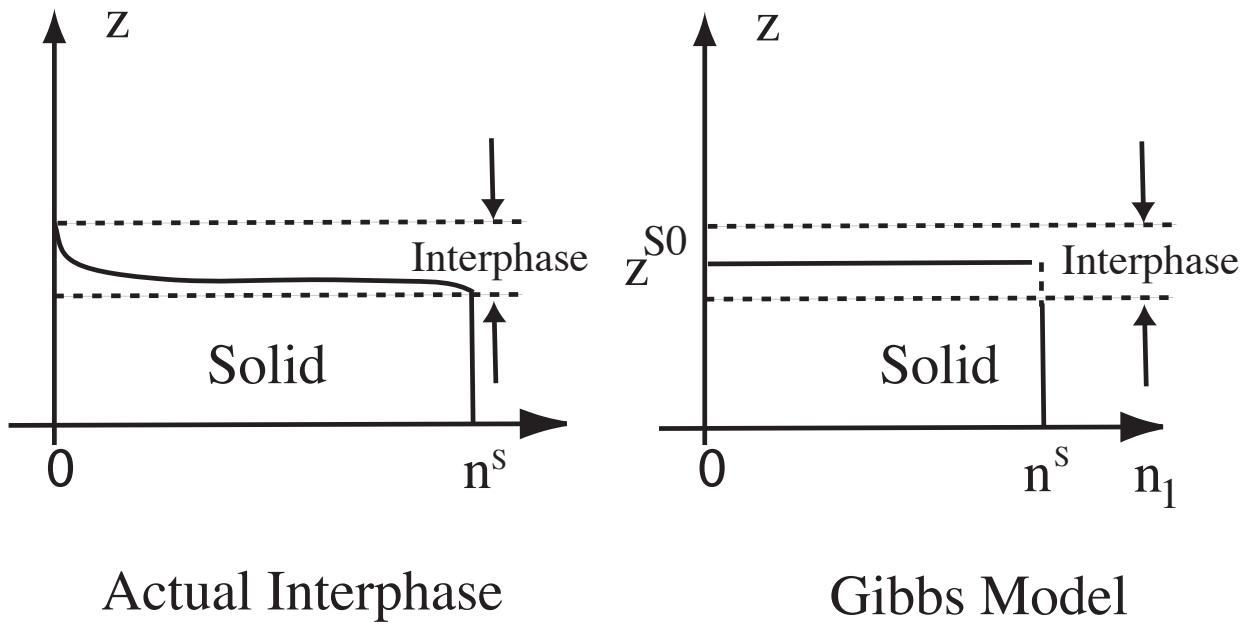


Figure 2.15: The interphase of a solid exposed to a vacuum is depicted.

a vacuum may be expressed

$$U_c = u^S V^S + U^{S0} \quad (2.105)$$

but the total volume of the solid, V^S , cannot be known because of the interphase. If we suppose the properties of the bulk-phase solid are known such as the number of moles per unit volume, n^S , then a Gibbs dividing surface approximation gives

$$N_c = n^S V^S + N^{S0} \quad (2.106)$$

This equation contains two unknowns, V^S and N^{S0} . Thus, even in this simple case, a deductive method of defining the position of the Gibbs dividing surface is not available. We shall take the position of the dividing surface to be such that N^{S0} vanishes. This defines the volume of the solid in terms of the bulk phase properties

$$V^S = \frac{N^S}{n^S}. \quad (2.107)$$

Then the internal energy of the solid surface may be expressed

$$U^{S0} = U^{S0}(S^{S0}, A^{S0}) \quad (2.108)$$

and the surface tension of this interface, γ^{S0} , is given by

$$\gamma^{S0} = \left(\frac{\partial U^{S0}}{\partial A^{S0}} \right)_{S^{S0}} \quad (2.109)$$

We now have a definition of the surface tension of a solid, but we need ask whether we have defined a physical quantity. We address this question after we consider the interaction of a fluid with an ideal solid surface.

2.3.1 Surface tension of an ideal solid-vapor interface

An important circumstance is depicted in Fig. 2.16: a solid surface is exposed to a vapor phase. Note that the interphase now contains molecular clusters, but we suppose there is no absorption of the vapor by the solid. Since the position of the dividing surface has already been defined, conservation of vapor molecules gives

$$N_1 = N_1^V + N_1^{LV}, \quad (2.110)$$

where N_1^{LV} is total amount of vapor adsorbed. Note that when these clusters adsorb, they tend to return the surface atoms of the solid to their initial lattice position. Thus, we might expect the adsorption of the vapor will reduce the surface tension of the solid from γ^{S0} to γ^{SV} .

When a solid surface is exposed to a vapor that consists of r chemical species, the modes of energy storage may be identified, as has been done for a simple material system and for a liquid-vapor interface. For a solid-vapor interface, one could reasonable hypothesis that the modes of energy storage are heating, S^{SV} , the extent of the surface phase, A^{SV} ,

and by adsorption, $N_1^{SV}, N_2^{SV} \dots N_r^{SV}$. These modes of energy storage then would be the independent variables of the internal energy:

$$U^{SV} = U^{SV}(S^{SV}, A^{SV}, N_1^{SV}, N_2^{SV} \dots N_r^{SV}). \quad (2.111)$$

We now define the intensive properties of a solid-vapor interface by the total differential of the U^{SV}

$$dU^{SV} = T^{SV} dS^{SV} + \gamma^{SV} dA^{SV} + \sum_{i=1}^r \mu_i^{SV} dN_i^{SV}. \quad (2.112)$$

Note that dN^{SV} does not appear. This is because we have taken the position of the Gibbs dividing surface to be such that there is no adsorption of the solid component. The solid is assumed to be uniform in composition right up to the dividing surface.

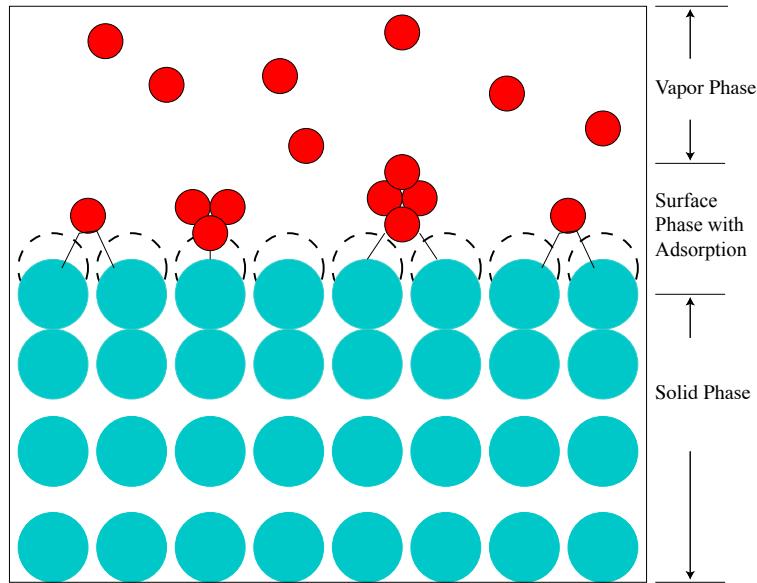


Figure 2.16: The interphase of a solid exposed to a vapor is depicted. The vapor can form adsorbed molecular clusters. The original lattice positions of the substrate atoms is indicated by the dashed lines; thus the effect of adsorption is to move the atoms toward positions in the uncleaved solid.

We require U^{SV} to be a first-order homogeneous function of its independent variables:

$$\lambda U^{SV} = U^{SV}(\lambda S^{SV}, \lambda A^{SV}, \lambda N_1^{SV}, \lambda N_2^{SV} \dots \lambda N_r^{SV}). \quad (2.113)$$

If the partial differential of Eq. (2.113) with respect to λ is taken, then in view of Eq. (2.112)

$$U^{SV} = T^{SV} S^{SV} + \gamma^{SV} A^{SV} + \sum_{i=1}^r \mu_i^{SV} N_i^{SV}. \quad (2.114)$$

This equation is the Euler equation for a solid-vapor surface phase.

If the expression for dU^{SV} is obtained from this equation and set equal to the expression for dU^{SV} given in Eq. (2.112), one finds equation for a solid-vapor surface phase:

$$\sum_i^r N_i^{SV} \mu_i^{SV} = -S^{SV} dT^{SV} - A^{SV} d\gamma^{SV},$$

and if the surface properties are expressed on a per unit area basis, this equation may simplified to the **Gibbs adsorption** equation

$$d\gamma^{SV} = -s^{SV} dT^{SV} - \sum_i^r n_i^{SV} d\mu_i^{SV}. \quad (2.115)$$

The independent variables of γ^{SV} may be identified from this equation:

$$\gamma^{SV} = \gamma^{SV}(T^{SV}, \mu_1^{SV}, \mu_2^{SV} \dots \mu_r^{SV}). \quad (2.116)$$

and if the vapor phase considered consists of only one component, the Gibbs adsorption equation gives

$$\left(\frac{\partial \gamma^{SV}}{\partial \mu^{SV}} \right)_{T^{SV}} = -n^{SV}. \quad (2.117)$$

Thus, if increasing n^{SV} increases μ^{SV} , then increasing n^{SV} has the effect of decreasing γ^{SV} . A possible explanation for this prediction is indicated by the model shown in Fig. 2.16.

Suppose there is only one component in the vapor phase of the three-phase, isolated system shown schematically in Fig. 2.16. The entropy would be given by

$$S_c = S^V + S^{SV} + S^S \quad (2.118)$$

and the constraints would be

$$\begin{aligned} U_c &= U^V + U^{SV} + U^S \\ V_c &= V^S + V^V \\ N_1 &= N_1^V + N_1^{SV} \end{aligned} \quad (2.119)$$

By requiring S_c to be an extremum, one finds the conditions for equilibrium to be

$$\begin{aligned} T^V &= T^{SV} = T^S \\ P^V &= P^S \\ \mu_1^V &= \mu_1^{SV} \end{aligned} \quad (2.120)$$

Note then that one of the conditions for equilibrium requires the chemical potential of the adsorbed molecules to be equal to the chemical potential of the molecules in the vapor phase.

2.3.2 Surface tension of an ideal solid-liquid interface

Suppose a liquid phase contacts an ideal solid surface as indicated in Fig. 2.17. An ideal solid surface is smooth, homogeneous non-dissolving and non-absorbing. An ideal solid substrate is non-deformable.

The interface is defined as being such that there is no adsorption of the ideal solid. Thus, the number of moles of the solid may be expressed:

$$N^S = V^S n^S \quad (2.121)$$

Then conservation of liquid component gives

$$N_1 = N_1^L + N_1^{SL} \quad (2.122)$$

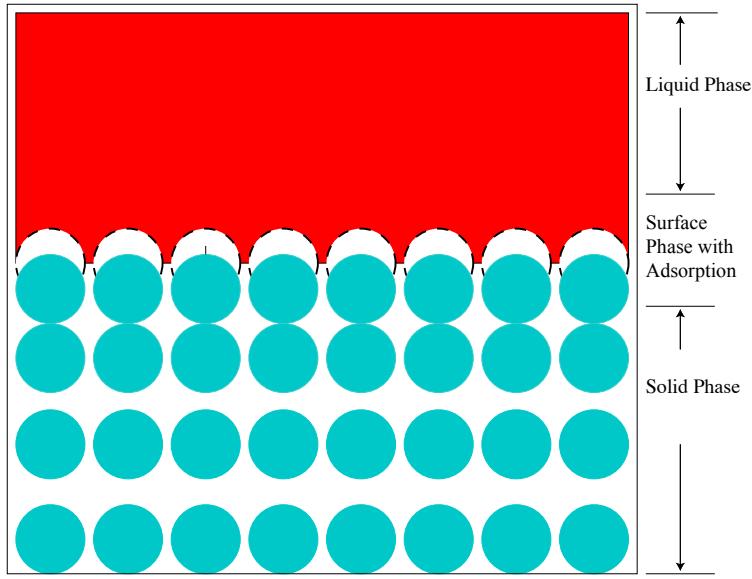


Figure 2.17: A solid-liquid interphase is depicted. The liquid forms adsorbed layer. The original lattice positions of the substrate atoms is indicated by the dashed lines.

The thermodynamic description of the solid-liquid interface will be established using the same procedure as that used for the solid-vapor interface. We first hypothesize the energy storage modes:

$$U^{SL} = U^{SL}(S^{SL}, A^{SL}, N_1^{SL}, N_2^{SL}, \dots, N_r^{SL}). \quad (2.123)$$

We define the intensive variables of this interface:

$$dU^{SL} = T^{SL}dS^{SL} + \gamma^{SL}dA^{SL} + \sum_{i=1}^r \mu_i^{SL}dN_i^{SL}. \quad (2.124)$$

We also require U^{SL} to be a first-order homogeneous function of its independent variables. These operations lead to an Euler type relation for this interface

$$U^{SL} = T^{SL}S^{SL} + \gamma^{SL}A^{SL} + \sum_{i=1}^r \mu_i^{SL}N_i^{SL} \quad (2.125)$$

Differentiating Eq. (2.125) and equating it to Eq. 2.124 leads to the Gibbs adsorption equation for the solid-interface:

$$d\gamma^{SL} = -s^{SL}dT^{SL} - \sum_i^r n_i^{SL} d\mu_i^{SL}. \quad (2.126)$$

It follows from this relation that the surface tension of the solid-liquid interface may be expressed

$$\gamma^{SL} = \gamma^{SL}(T^{SL}, \mu_1^{SL}, \mu_2^{SL} \dots \mu_r^{SL}) \quad (2.127)$$

2.4 Conditions for thermodynamic equilibrium of a sessile droplet

When a droplet of a liquid is placed on a ideal solid surface one of two possibilities occurs: either the sessile droplet spreads or it forms a non-zero contact angle, θ , as indicated in Fig. 2.18. If the contact angle approaches zero, the liquid is said to wet the solid.

We consider the case of incomplete wetting. The droplet forms a non-zero contact angle and the droplet shape can be both predicted and measured. This allows the definitions of the surface tensions that have been introduced to be examined experimentally. We suppose both the solid surface and the substrate are ideal.

Since we are not yet considering gravity, we assume the droplet spherical. Then it is characterized geometrically by its radius and the contact angle. The height of the droplet on its center line is given by

$$z_0 = R - R \cos \theta \quad (2.128)$$

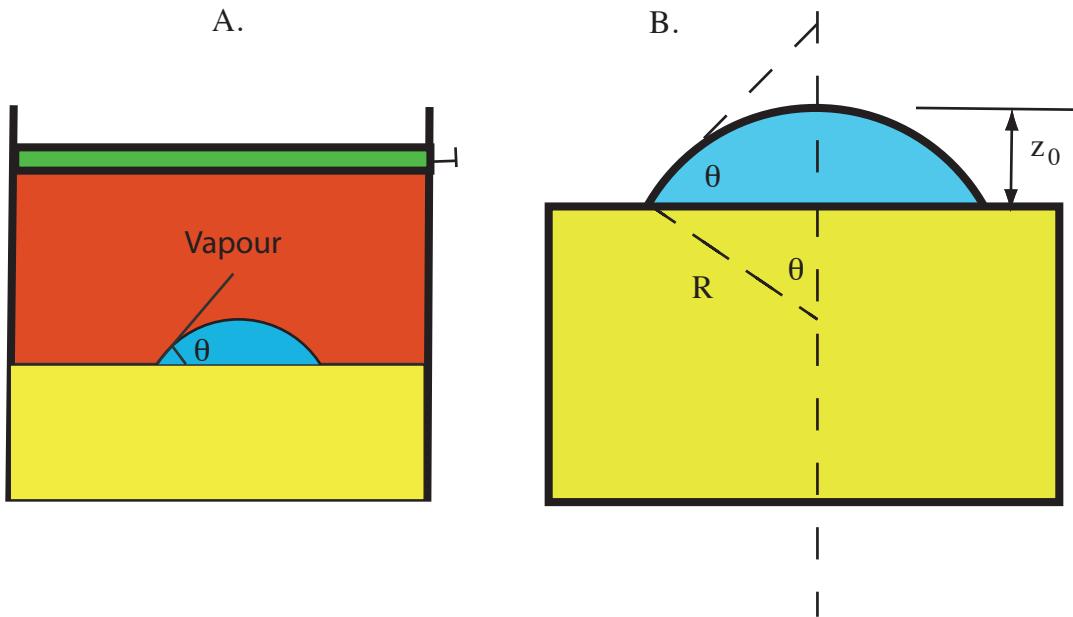


Figure 2.18: A. A sessile droplet is shown in an isolated system and the droplet forms a contact angle of θ with the solid surface. The spherical droplet is characterized its radius, R , its contact angle, and its height on its center line.

The volume of the liquid phase, V^L , is given by

$$V^L = \frac{\pi z_0^2 (3R - z_0)}{3}$$

or

$$V^L = \frac{\pi (R - R \cos \theta)^2 (2R + R \cos \theta)}{3} \quad (2.129)$$

The area of the liquid-vapor interface is given by

$$A^{LV} = 2\pi R^2 (1 - \cos \theta) \quad (2.130)$$

and the area of the solid-liquid interface by

$$A^{SL} = \pi (R \sin \theta)^2 \quad (2.131)$$

The constraints on the isolated system, Fig. 2.18, are:

1. The total energy of the composite system, U_c is constant:

$$U_c = U^S + U^L + U^V + U^{LV} + U^{SL} + U^{SV}. \quad (2.132)$$

2. The total volume of the system is constant:

$$V_c = V^L + V^V. \quad (2.133)$$

3. The total number of fluid moles is constant:

$$N_c = N^L + N^V + N^{LV} + N^{SV} + N^{SL}. \quad (2.134)$$

4. The total surface area is constant:

$$A_c = A^{SV} + A^{SL} \quad (2.135)$$

The total entropy of the system may be expressed

$$S_c = S^S + S^L + S^V + U^{SL} + U^{SV} \quad (2.136)$$

After taking the total differential of the entropy, making use of the definitions of the intensive properties for each of the surface and bulk phases and differentiating the constraints, one finds by requiring that for the virtual displacement about the equilibrium state dS_c must vanish that

$$T^j = \lambda_T \quad j = L, V, LV, SV, SL \quad (2.137)$$

where λ_T is a constant. The chemical potential of the fluid component must have the same value in every surface and bulk phase, except the solid. The solid has been assumed to be non-absorbing, but there is adsorption on its surface.

$$\mu^j = \lambda_\mu \quad j = L, V, LV, SV, SL \quad (2.138)$$

where λ_μ is also a constant. Along the liquid-vapor interface, the Laplace equation is again found to be a necessary condition for equilibrium:

$$P^L - P^V = \frac{2\gamma^{LV}}{R_\epsilon} \quad (2.139)$$

$$(2.140)$$

Since the solid was assumed to be rigid, no condition on its pressure is found. The new necessary condition for equilibrium is the Young equation. It applies at the three-phase line around the base of the droplet.

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \cos \theta \quad (2.141)$$

As indicated in Fig. 2.19, this equation may be interpreted as a force balance in the horizontal direction at the three-phase line. The forces are not required to balance in the vertical direction because we assumed the solid substrate to be rigid. Physically, this assumption means that the surface tension forces cannot deform the solid substrate.

2.4.1 The independent variables of the contact angle

We have previously seen that the surface tension of the liquid-vapor interface may be approximated as depending only on temperature, $\gamma^{LV}(T)$ (Section 2.1.4), the surface tension of the solid-vapor interface has been seen to depend on the temperature and the chemical potentials of the components in the vapor phase, $\gamma^{SV}(T, \mu^V)$ (Section 2.3.1). Similarly, the surface tension of the solid-liquid interface has been seen to depend on the temperature and the chemical potentials of the components in the liquid phase $\gamma^{SL}(T, \mu^{SL})$ (Section 2.3.2). If these relations were put into the Young equation

$$\cos \theta = \frac{\gamma^{SV}(T, \mu) - \gamma^{SL}(T, \mu)}{\gamma^{LV}(T)}, \quad (2.142)$$

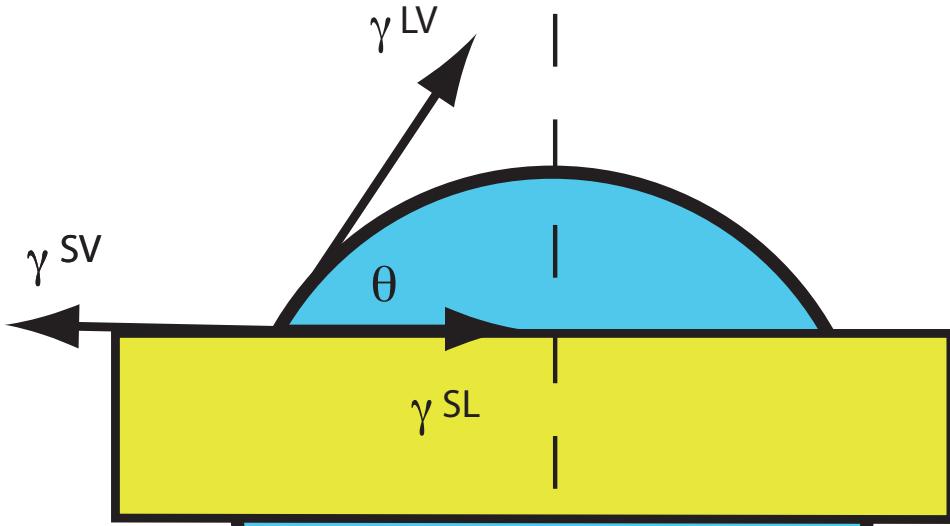


Figure 2.19: The necessary conditions for equilibrium may be interpreted as requiring a force balance at the three-phase line, a balance of forces at the liquid-vapor interface and no net molecular transport at any interface.

one might conclude that $\theta = \theta(T, \mu)$ but that would not be true because not all of the conditions for equilibrium condition have been accounted for. In particular, the Laplace equation has not been accounted for.

In the previous section, a single component liquid and vapor phase were assumed to be present, the liquid phase to form spherical liquid cap and a contact angle θ with an ideal solid interface.

$$\mu^j = \lambda \quad j = L, V, LV, SV, SL \quad (2.143)$$

where λ is a constant. If the ratios of P^L and P^V to P_s are denoted x^L and x^V respectively, the Laplace equation may be written

$$x^L(z_I) - x^V(z_I) = \frac{\gamma^{LV} C_0^{LV}}{P_s(T)}, \quad (2.144)$$

where C_0 is the curvature of liquid-vapor interface: $C_0^{LV} = R_0^{-1}$.

(2.145)

If we approximate the liquid as incompressible and the vapor as ideal, then the equality of the chemical potentials relates the pressure in the liquid to the pressure in the vapor:

$$x^V = \exp \left[\frac{v_f}{v_g} (x^L - 1) \right] \quad (2.146)$$

and if C_{slv} denotes the curvature of the three-phase line, then from geometry

$$\sin \theta = \frac{C_0^{LV}}{C_{slv}} \quad (2.147)$$

After combining Eqs. (2.144) and (2.146) with the geometrical relation, one finds

$$\sin \theta = \frac{P_s}{2C_{slv}\gamma^{LV}} \left\{ x^L - \exp \left[\frac{v_f}{v_g} (x^L - 1) \right] \right\}. \quad (2.148)$$

Thus, the contact angle may be expressed

$$\theta = \arcsin \left(\sqrt{\frac{P_s}{2C_{slv}\gamma^{LV}} \left\{ x^L - \exp \left[\frac{v_f}{v_g} (x^L - 1) \right] \right\}} \right). \quad (2.149)$$

$\cos \theta$ is given by

$$\cos \theta = \left[1 - \frac{P_s^2 \left(x^L - \exp \left[\frac{v_f(x^L-1)}{v_g} \right] \right)^2}{(2C_{slv}\gamma^{LV})^2} \right]^{1/2}. \quad (2.150)$$

As may be seen in Eq. (2.150), for an isothermal system, the independent variables of the contact angle are the curvature of three-phase line, C_{slv} , and the pressure in the liquid phase, x^L . Note that all the conditions for equilibrium were used to draw this conclusion, but we have not yet determined what properties the solid must have in order x^L, C_{slv} to be observed.

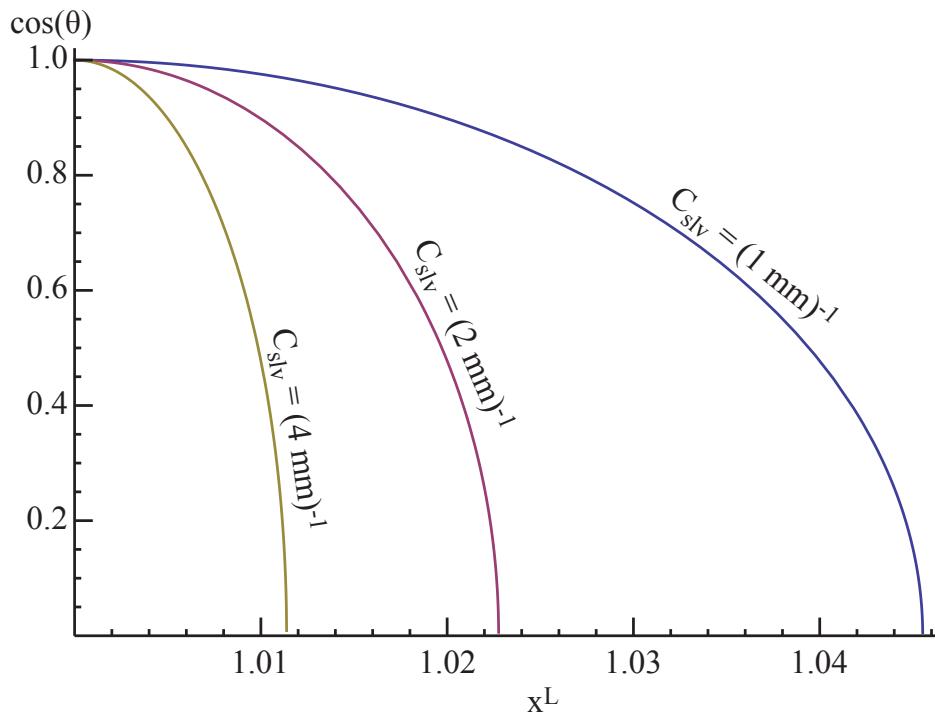


Figure 2.20: For a water droplet at 25 °C, the dependence of $\cos \theta$ on x^L and C_{slv} is shown.

2.4.2 Adsorption at solid-liquid and solid-vapor interfaces

The plot shown in Fig. 2.20 is based only on the properties of the fluid. This could be mis-interpreted as indicating the contact angle is independent of the properties of the solid, but recall that every point, x^L, C_{slv} , in the plot was **assumed** to be an equilibrium state. We now ask what properties the solid must have in order for an assumed value of x^L, C_{slv} .

When the Gibbs adsorption equations, Eqs. (2.115) and (2.126), are applied in the system shown in Fig. 2.18 they reduce to

$$d\gamma^{SV} = -n^{SV} d\mu^{SV}. \quad (2.151)$$

$$d\gamma^{SL} = -n^{SL} d\mu^{SL}. \quad (2.152)$$

and since the chemical potentials all have the same value

$$\mu^j = \lambda \quad j = L, V, LV, SV, SL; \quad (2.153)$$

we may require the chemical potentials to be equal to that of the liquid:

$$\mu^L = \mu^L(P_s) + P_s v_f (x^L - 1). \quad (2.154)$$

The Gibbs adsorption equations then reduces to

$$d\gamma^{SV} = -n^{SV} v_f P_s dx^L. \quad (2.155)$$

$$d\gamma^{SL} = -n^{SL} P_s v_f dx^L. \quad (2.156)$$

If we take the partial differential of the Young equation with respect to x^L while holding C_{slv} and T constant

$$\left(\frac{\partial \gamma^{SV}}{\partial x^L} \right)_{C_{slv}} - \left(\frac{\partial \gamma^{SV}}{\partial x^L} \right)_{C_{slv}} = \gamma^{LV} \left(\frac{\partial \cos \theta}{\partial x^L} \right)_{C_{slv}} \quad (2.157)$$

from Eqs. (2.115) and (2.126)

$$(n^{SL} - n^{SV}) = \frac{\gamma^{LV}}{v_f P_s} \left(\frac{\partial \cos \theta}{\partial x^L} \right)_{C_{slv}} \quad (2.158)$$

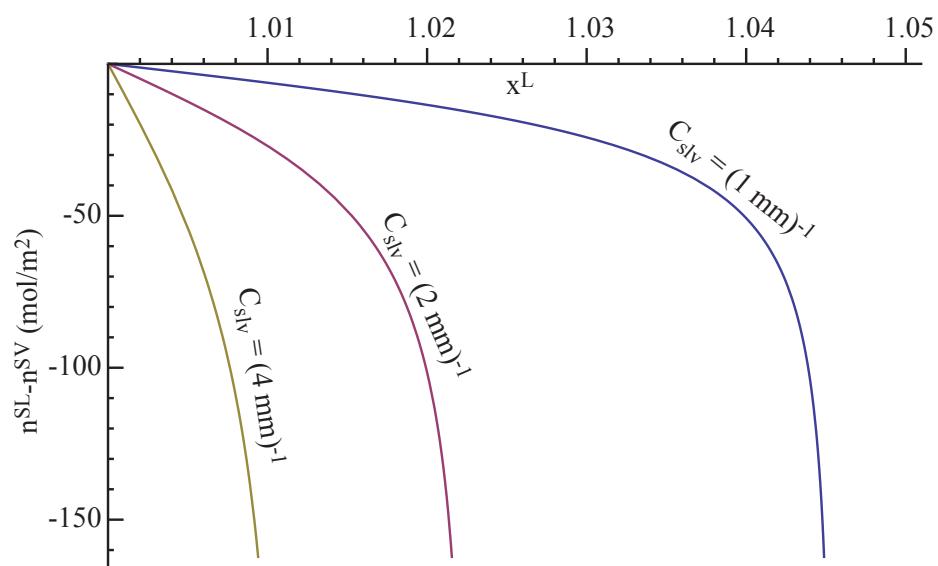


Figure 2.21: Difference in the adsorption at the solid-liquid and solid-vapor interface.

2.5 Chapter 2 Problems

1. If in the apparatus shown schematically on the left in Fig. 2.22, a droplet of water is surrounded by its vapor phase, and the reservoir temperature is 25 °C:
 - A. State explicitly the assumptions you make and give the expression for the radius of a droplet for which the droplet would be in equilibrium with its surroundings. This radius is denoted R_δ ,
 - B. Show a plot of R_δ as a function of the reservoir pressure and indicate pressure range for which equilibrium is possible.
 - C. Suppose the vapor phase is replaced by an ideal gas mixture. Give the expression for the radius of the droplet that could be in equilibrium with its surroundings. Give your answer in terms of properties in the gas-vapor mixture and the reservoir.
 - D. If the gas is N₂, and the mole fraction of N₂ is measured to be 0.1, for what total-pressure range could the droplet be in equilibrium? The Henry constant for a N₂-water solution is 8.65×10^9 Pa at 25 °C.
2. The piston-cylinder arrangement shown schematically in Fig. 2.23 contains three phases, is closed by a freely-moving-rigid piston. Both the piston and the cylinder are diathermal and impermeable. One phase is a weak liquid solution that consists of a solvent, N₁, and a solute, N₂, and surrounds a spherical droplet of pure solute.
 - A. Denote properties of the weak solution with a subscript S, properties of the pure liquid phase with a superscript L, properties of the liquid-solution interface with a superscript LS, and define the function that acts as the thermodynamic potential for the system in the piston-cylinder arrangement. Denote it as D .
 - B. Using the thermodynamic potential that you define, determine the conditions that the intensive properties of the system in the piston-cylinder arrangement must satisfy in order for the total system to be in equilibrium.

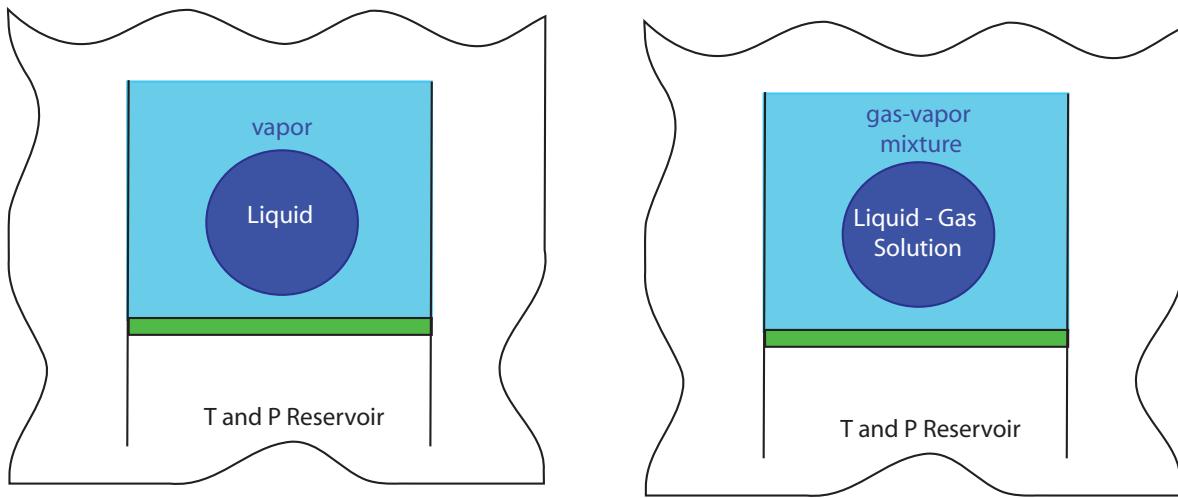
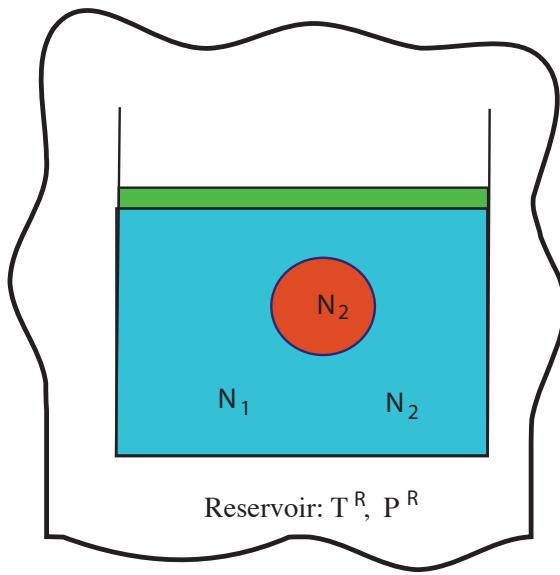


Figure 2.22: In the apparatus on the left a droplet that is surrounded by its vapor is interacting with a reservoir. The piston is freely moving and the system walls and the piston are nonporous. In the system on the right, the droplet is surrounded by a gas-vapor mixture.

C. If the isothermal compressibility of pure component 2 in the liquid phase, κ_T^{0L} , is only a function of temperature, give the expression for the chemical potential of this component when it is at pressure P^L , with P^R as the reference pressure. And give the expression for the chemical potential of this component in the weak liquid solution, $\mu_2(T, P^S, N_1^S, N_2^S)$. Denote the saturation concentration of component 2 in a saturated solution as N_{2sat}^S .

D. If $|\kappa_T^{0L}(P^R - P^L)| \ll 1$, $N_{2sat}^S = N_1^S P^S / K_h(T^S)$, where $K_h(T)$ is a parameter that depends only on T , and adsorption in the surface phase may be neglected, give the expression for the radius of an equilibrium-sized droplet, R_δ , in terms of the physical radius of the droplet, R , the constrained properties (T^R, P^R, N_1, N_2) and the symbols for the material properties listed in Table 2.3.

E. Give the numerical value of the droplet radius in each of the possible equilibrium states that you identify, and show a plot of $\log R_\delta$ versus $\log R$ to illustrate your

**Figure 2.23**

answer.

- F. With the same assumption as in Part E, give the expression for $D(R) - D_0$ as a function of the R , the constrained properties and the symbols for the material properties, where D_0 is the potential for the homogeneous solution. State the stability of each of the equilibrium states you identify, and show plots of $D(R) - D_0$ versus $\text{Log}(R)$ to illustrate the reason for your answer.
3. The system shown in Fig. 2.24 is diathermal, constant volume, multicomponent, contains gas-vapor phase and has impermeable walls.
- A. Define a transform of the intensive (per unit area) Helmholtz function for a surface phase, and show that the function you define, denoted ζ^{GV} , has as its independent variables T^{GV} and $\mu_j^{GV} j = 1, 2 \dots r$.
- B. Define the Helmholtz function for the composite system and show that the function you define acts as the thermodynamic potential for the system.
- C. If the system shown is reduced to only a single component, remain diathermal,

Table 2.3: Material properties

Material Property	value
Reservoir temperature, T^R	25 °C
Reservoir pressure, P^R	709,275 Pa
Number of moles of solvent in the piston, N_1	5.47991×10^{-6} mol
Number of moles of solute in the piston, N_2	3.25473×10^{-9} mol
Specific volume of solvent, v_2^{0L} , at 25 °C	1.8066×10^{-5} m ³ /mol
Specific volume of solute, v_2^{0L} , at 25 °C	9.21366×10^{-5} m ³ /mol
Saturation-vapor pressure of solvent, P_{s1} , at 25 °C	3,170 Pa
Saturation-vapor pressure of solute, P_{s2} , at 25 °C	6.52×10^5 Pa
Surface tension of solute-solution interface, γ^{LS} at 25 °C	0.063 N/m
Solubility parameter, K_h , at 25 °C	2.43×10^9 Pa

constant volume and contains a vapor bubble that may be approximated as spherical, determine the condition that the intensive properties must satisfy in order for equilibrium to exist in the system.

- D. Give the expression for the radius of the bubble in terms of properties that could be measured in the liquid phase.
4. In the system shown in Fig. 2.25A, a single component vapor phase is enclosed in a piston-cylinder arrangement; the cylinder walls are diathermal and impermeable, and the piston moves freely. The reservoir surrounding the piston-cylinder arrangement consists of the same vapor.
- A. If the pressure in the reservoir is greater than the saturation-vapor pressure, show that the vapor phase is not stable. State clearly the reason for your answer.
- B. Suppose a small, spherical droplet is present in the system, Fig. 2.25B. Define the thermodynamic potential for the system. Denote the function you define as D_δ .

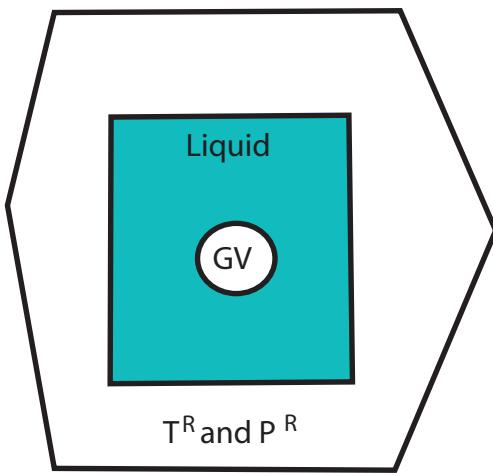


Figure 2.24

- C. If the state of the system is such that D_δ is an extremum and the liquid phase may be approximated as incompressible, the vapor as an ideal gas, give the expression for droplet radius, R_δ , in the extremum state. If the droplet is water, the temperature of the reservoir is 100 °C, the pressure 1.4 P_s , give the value of R_δ .
- D. If $P^V > P_s(T)$ or if $P^V < P_s(T)$, show plots of $D_\delta - D_0$ and state the satiability of the vapor phase in the two cases.
5. For the system shown in Fig. 2.26, what is the minimum number of moles of nitrogen that must be present in the system in order for a spherical gas-vapor mixture to be in equilibrium with the surrounding liquid-gas solution. The reservoir pressure is 1.01325×10^5 Pa and the temperature is 30 °C. There are a total 0.0553 moles of water in the system. You may approximate the parameter η as unity and neglect any dependence of γ^{LV} on gas adsorption.
6. Suppose a pure liquid is held in a piston-cylinder arrangement such as that shown schematically in Fig. 2.26, and a vapor phase forms homogeneously (i.e., not on the

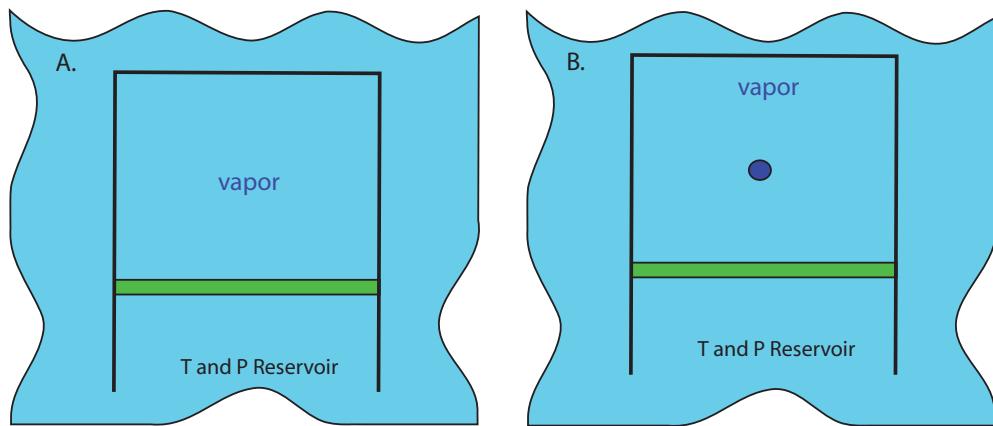


Figure 2.25: A droplet nucleates homogeneously in a vapor-phase.

walls).

- A. If the nucleate bubble is in equilibrium with the surrounding liquid, give the expression for the radius of the vapor phase in terms of the constrained and material properties.
- B. If the liquid is water, and the reservoir temperature is 30 °C, show a plot of η as a function of R_e for reservoir pressures in the range 0 to 0.99 $\text{Ps}(T^R)$.
- C. If the liquid is water, and the reservoir temperature is 100 °C, show a plot of η as a function of R_e for reservoir pressures in the range 0 to 0.99 $\text{Ps}(T^R)$. The surface tension of water at 100 °C is 0.0589 m Pa.
7. Suppose a pure liquid is held in a diathermal piston-cylinder arrangement with the piston fixed in position. The arrangement is surrounded by a temperature and pressure reservoir.
- A. If the liquid is water, the temperature is 100 °C, the volume is 1 ml, and there are 0.053 moles present, how many equilibrium states are available to spherical vapor phases in the system. Give the radius of each.

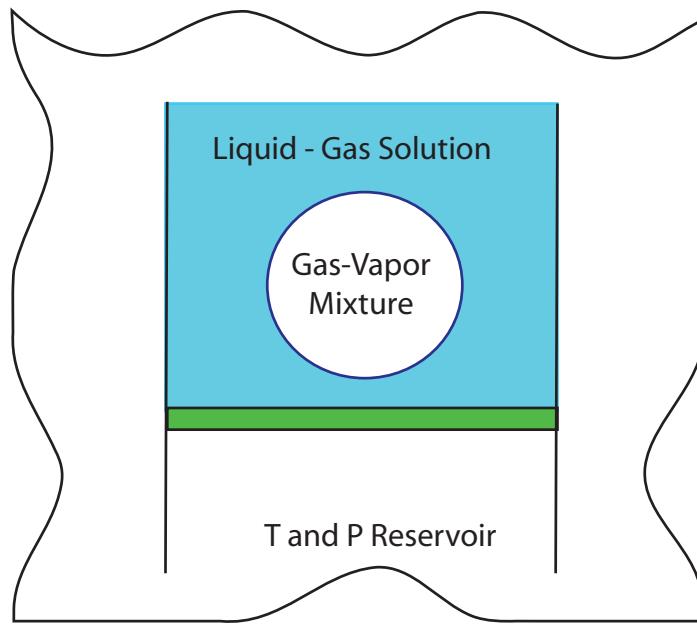


Figure 2.26: A gas-vapor bubble in equilibrium with the surrounding liquid-gas solution, and the gas concentration is the minimum possible.

- B. State the stability of each equilibrium state that you identify, and give the reason for your statement.
- 8. As indicated in Fig. 2.27, a single component, spherical, sessile droplet rest on a smooth, homogeneous surface, and is enclosed in a constant volume chamber that is surrounded by a reservoir with which the system interacts thermally.
 - A. What function acts as the thermodynamic potential for the system. Show the reason for your answer.
 - B. If the height of the droplet on its center line is denoted h and the radius of the liquid-vapor interface is denoted r , give the expressions for the volume of the liquid phase, V^L , the area of the liquid-vapor interface, A^{LV} , the area of the solid-liquid interface, A^{SL} , and the contact angle θ in terms of h and r .

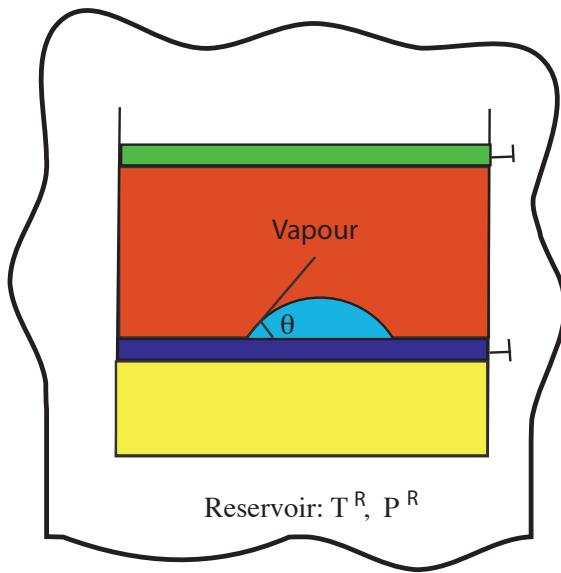


Figure 2.27: A sessile droplet on a smooth homogeneous surface.

- C. Using the thermodynamic potential that you define, determine the necessary conditions for equilibrium for the system.
- D. Show the necessary conditions for equilibrium are equivalent to the Laplace and the Young equations, among other conditions.

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