# THERMODYNAMICS

## 1. Introduction

Thermodynamics has its origins in the industrial age and the desire to develop more efficient steam and other engines. Today, the realm of thermodynamics includes the analysis of chemical and phase equilibria, of different types of devices including fuel cells, and even biochemical and physiological processes. Classical thermodynamics is a theory of very broad applicability built on a small number of empirical observations. Indeed, Albert Einstein is reputed to have said that "Classical thermodynamics. . .is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, will never be overthrown" (1). Classical thermodynamics deals with systems containing a very large number of molecules and uses only overall properties of systems such as internal, kinetic and potential energies, heat capacities, and equations of state (all to be discussed in this article). This is different from statistical thermodynamics that starts with information about individual molecules, such as their structure, bond lengths, vibrational frequencies, and interactions and attempts to predict heat capacities, equations of state, and other properties of a collection of molecules.

Classical thermodynamics, henceforth referred to as thermodynamics here, deals with changes that occur, generally from one equilibrium state to another as a result of a change of constraint (for example, a pressure change) and/or an energy flow in the form of work or heat entering or leaving the system. Here by equilibrium state is meant a time-invariant state in which temperature and pressure are spatially uniform, and the composition is uniform in each phase (ie, vapor, liquid, or solid), although as we shall see, in a multiphase phase system (ie, vapor + liquid), the equilibrium compositions can be different in each phase. The state of an equilibrium system is characterized by only a few bulk properties usually temperature, pressure, density, and composition. Also, the properties that describe an equilibrium thermodynamic state are properties of that state only and not of the history of the system. This is different from a metastable state of, for example, a polymer fiber or film whose properties depend on the way the polymer was processed.

A problem not considered in thermodynamics is the rate at which such changes in state occur. To be specific, if several chemicals that can react are placed in a reactor, thermodynamics can be used to predict the maximum extent of reaction that can occur; however, the rate at which such changes occur is the realm of reaction kinetics and/or reactor design, not thermodynamics. Nonetheless, it is useful to include time in the development of thermodynamics, because there is an arrow or direction of time in that many processes progress in only one direction. For example, if a hot body and a cold body are brought into contact, as time progresses, the temperature of the hot body decreases and that of the cold body increases. This is most easily described mathematically by stating that the derivative of the temperature of the hot body with time is negative and that of the cold body is positive. Consequently, although we do not want to predict how fast these temperature changes occur, it is useful to include time in the equations so that we can determine the allowable directions of changes.

We present here an overview of chemical and chemical engineering thermodynamics. References 2 to 6 have much more thorough presentations of this very important subject.

## 2. Basis of Thermodynamics

Thermodynamics is built on four very general experimental observations. The first is that relatively few properties are required to completely specify the equilibrium state of a system. The second is that in any process (except a nuclear reaction, which is not of interest to us here), mass is neither created nor destroyed; that is, mass is conserved. The third observation is that total energy, which consists of the sum of potential energy, kinetic energy, and the internal energy of the molecules are conserved. [There is a third conserved property, momentum; however, because rates and velocities are not of general interest in thermodynamics, it is not used.] The final basis is not a conservation principle, but the experimental observation that natural processes occur in a direction that eliminates gradients in a system, and not the reverse. For example, an isolated system, that is, a system that is not affected by changes (such as of temperature or pressure) of its environment and closed to flows of mass and flows of energy (ie, heat and work flows), will eventually reach an equilibrium state of uniformity in temperature, pressure, and density (if it consists of a single phase) or of subregions of uniform temperature and pressure, but of different densities if it consists of more than one phase (for example, a mixture of ice and water, or of water and steam) and, in the case of mixtures, also of different compositions.

The equations of thermodynamics are written for a system, which may be either a fixed mass or a fixed volume (for example, a steam engine); everything external to the system is referred to as environment. The general form of the equations for the differential change in some property $\theta$ of the system, in words, is

Rate of change of $\theta$ in the system =
net flow rate of $\theta$ into the system across the system boundaries +
net rate at which is $\theta$ generated within the system

and as an equation

$$\frac{d\theta}{dt} = \sum_j \dot{\theta}_j + \dot{\theta}_{\text{gen}} \tag{1}$$

where $d\theta/dt$ is the infinitesimal change in $\theta$ in the system, $\dot{\theta}_j$ is the rate at which $\theta$ enters the system at entry port $j$, and $\dot{\theta}_{\text{gen}}$ is the rate at which $\theta$ is generated within the system. This last term is zero for a conserved property such as total mass or total energy, but it is nonzero for any nonconserved property. For example, in a multicomponent system, $\dot{\theta}_{\text{gen}}$ is positive for a species generated by a chemical reaction and negative for a reactant species. In writing these, and all future, equations, a flow of mass or of energy as heat or work into the system is considered a positive quantity and a flow out of the system is negative. For a closed system, such as a block of metal or the contents of a sealed flask, each of the $\dot{\theta}_j$ is equal to zero. For a finite change in the system,

$$\Delta\theta = \sum_j \Delta\theta_j + \theta_{\text{gen}}, \tag{2}$$

where $\Delta\theta$ indicates the change in property $\theta$, $\Delta\theta_j$ is the net inflow of $\theta$ into the system at entry point $j$, and $\theta_{\text{gen}}$ is the amount of $\theta$ that has been generated within the system.

## 3. Thermodynamics of Pure Fluids

### 3.1. Thermodynamic Description of a System.

The size and equilibrium state of a thermodynamic system is completely specified by only a few properties. Most commonly the thermodynamic state (but not the size) of a single-component system is completely specified by its temperature ($T$) and pressure ($P$). That is, if $T$ and $P$ are specified, other properties such as the density or molar volume ($\underline{V}$), refractive index, internal energy per mole ($\underline{U}$), and other molar properties such as enthalpy ($\underline{H}$), entropy ($\underline{S}$), Gibbs ($\underline{G}$) and Helmholtz ($\underline{A}$) energies, all of which are defined later, are fixed. Indeed, any combination of a thermal property (such as temperature) and a mechanical property (such as pressure or volume) completely fix the state of a one-component system. In addition to fix the total size or amount of the system, the total mass or number of moles $N$ would need to be specified either directly or by specifying information from which this could be determined, for example, specifying the total volume of the system $V$ and $\underline{V}$, so that $N = V/\underline{V}$.

The interrelationships between easily measurable properties such as temperature and pressure and thermodynamic state variables ($\underline{V}$, $\underline{H}$, $\underline{U}$, $\underline{G}$, $\underline{S}$ and $\underline{A}$) may be available in one or more of several forms. For steam, oxygen, nitrogen, methane, refrigerants, light hydrocarbons, and some other fluids of engineering interest, there are specially prepared graphs and tables of properties. Also, for many fluids either specific or generalized volumetric equations of state, that is equations that interrelate $P$, $\underline{V}$, and $T$, are available that together with heat capacity data can be used to compute the change in thermodynamic properties between any two states. The National Institute of Standards and Technology (NIST; see Ref. 7) and others have prepared very detailed tables and equations of state for some pure fluids and mixtures.

In thermodynamics, our interest is in the changes in internal energy, enthalpy, entropy, and Gibbs and Helmholtz energies between two (equilibrium) states. If there is no chemical reaction, the absolute values of these properties in any state are not needed, only the change between states. There are two conventional methods for choosing reference states for tables of thermodynamic data. The first is to choose a temperature of absolute zero as the state at which the energy and (by the third law of thermodynamics) the entropy in a pure, perfectly ordered state are equal to zero. This choice has the disadvantage that to calculate the properties at temperatures commonly of interest, heat capacity and other data are needed from absolute zero to those temperatures. The second choice is to (somewhat arbitrarily) choose for each substance a temperature and pressure at which one energy-related property (typically the enthalpy or internal energy) and one entropy-related property (the entropy or Gibbs or Helmholtz energies) are set equal to zero. The disadvantage of this choice is that when chemical reactions are considered, a different choice of reference state is needed so that correct heats of reaction will be obtained. Some thermodynamic property tables, such as those from NIST mentioned above, are based on the first reference state, whereas many tables used in engineering are based on the second choice. For example, in the Steam Tables, liquid water at its vapor pressure at 0.01°C has been chosen as the reference state.

## 4. Mass Balance Equation

The balance equation for total mass of the one-component system shown in Fig. 1 in which there is no chemical reaction is

$$\frac{dM}{dt} = \sum_j \dot{M}_j \tag{3}$$

where $M$ is total mass in the system and $\dot{M}_j$ is the net rate at which mass enters the system at $j$. As total mass is a conserved property, there is no internal

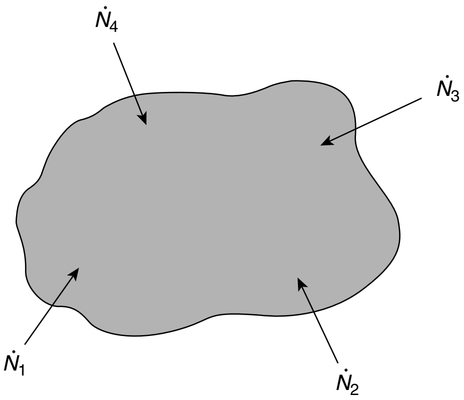

**Fig. 1.** General open system with several inlet and outlet streams. Adapted from Ref. 2, with permission.

generation term in this equation. The mass balance for any change (for example, over the time interval from $t_1$ to $t_2$) is

$$\Delta M = \sum_j M_j \tag{4}$$

where $\Delta M$ is the change of mass in the system and $M_j$ is the net flow of mass into the system over the time interval. By dividing by the molecular weight of the substance, these equations can be written on a molar basis:

$$\frac{dN}{dt} = \sum_j \dot{N}_j \quad \text{and} \quad \Delta N = \sum_j N_j \tag{5}$$

As some thermodynamic properties data are given on a molar basis, and as chemical reaction stoichiometry (which we consider later in this chapter) is written in terms of mole numbers, for economy of presentation, all balance equations hereafter will be written only on a molar basis.

## 5. The Energy Balance Equation: The First Law of Thermodynamics

The energy of a substance consists of three parts: the potential energy as a result of its location in a gravitational, electric, or magnetic field; the kinetic energy as a result of the translational velocity of its center-of mass and its rotational velocity; and the internal energy that arises from its chemical structure, the interactions among its molecules, and the internal molecular rotations, vibrations, and translations. Of these, the changes in overall kinetic and potential energies are generally much smaller than the change in internal energy (except for isothermal, that is, constant temperature, systems) and will generally be neglected here.

Changes in the energy of a system result from heat flows into ($\dot{Q} > 0$) or out of ($\dot{Q} < 0$) the system, the rate at which work being done on the system by its surroundings ($\dot{W} > 0$) or by the system on its surroundings ($\dot{W} < 0$), and as a result of each element of fluid that enters the system bringing with it its internal energy, and that work is done in pushing the mass into or out of the system, as will be clarified shortly. The rate-of-change form of the energy balance is

$$\frac{d(U)}{dt} = \frac{d(N\underline{U})}{dt} = \sum_j \dot{N}_j(\underline{U} + P\underline{V})_j + \dot{Q} + \dot{W} - P\frac{dV}{dt} = \sum_j (\dot{N}\underline{H})_j + \dot{Q} + \dot{W} - P\frac{dV}{dt} \tag{6}$$

where $H = U + PV$ is the enthalpy. In this equation, $\underline{U}$ and $\underline{V}$ are the molar internal energy and volume, respectively; the first term on the right-hand side of the equation is the energy input to the system as a result of mass flows, the second is the result of the heat flow, and the third term is the result of work flows across the system boundary, for example, the flow of electricity or work being supplied or extracted by a shaft or push rod that crosses the system boundaries. The last term is the energy change resulting from movement of the system boundaries. If the system expands against a constant external pressure $P$, the rate at which mechanical work is done by the system on its surroundings is $P\frac{dV}{dt}$ (this is the three-dimensional analog of $F\frac{dL}{dt}$, where $F$ is force and $L$ is length), with the negative sign indicating that if the system is expanding $\frac{dV}{dt} > 0$, it is doing work on its surroundings, so the contribution of this term to the system energy is negative. Note that as energy is conserved, there is no internal generation term. Finally, for those systems in which there are high flow velocities and/or significant differences in the heights at which the flow streams enter and leave, the external kinetic and potential energy terms may be important. In those cases, $\underline{H}$ is replaced with $\underline{H} + m(\frac{v^2}{2} + gh)$, where $m$ is the molecular weight, $v$ is the velocity, $g$ is the gravitational constant, and $h$ is the height with respect to some reference.

For a change from state 1 to state 2, this equation becomes

$$\Delta(N\underline{U}) = \sum_j \int_1^2 \dot{N}_j\underline{H}_j dt + Q + W - \int_1^2 PdV \tag{7}$$

Note that if the thermodynamic properties of each flow stream are constant (even though the flow rates may vary), then each integral $\int_1^2 \dot{N}_j\underline{H}_j dt$ can be replaced by $(\Delta N)_j\underline{H}_j$. However, if the thermodynamic properties in the process vary with time, this integral can be very difficult to evaluate, and it is generally best to make a different choice of system such that the integral does not appear. Also, if the pressure on a surface undergoing expansion or contraction is constant, $\int_1^2 PdV$ can be replaced by $P\Delta V$. With both of these simplifications, the open system energy balance is

$$\Delta(N\underline{U}) = \sum_j (\Delta N)_j\underline{H}_j + Q + W - P\Delta V \tag{8}$$

and the energy balance for a closed system (ie, no mass flows) is

$$N\Delta\underline{U} = Q + W - P\Delta V \tag{9}$$

The energy flow accompanying mass flow needs further discussion. To do this, consider the adiabatic pressure-reducing valve operating in steady state that receives fluid at $P_{\text{in}}$ and $T_{\text{in}}$ and exhausts it at $P_{\text{out}}$ and $T_{\text{out}}$. This system can described either as an open system with the boundaries as shown in Fig. 2a for which the mass and energy balance equations are

$$\begin{aligned}
&0 = \dot{N}_{\text{in}} - \dot{N}_{\text{out}} \quad \text{so that} \quad \dot{N}_{\text{out}} = \dot{N}_{\text{in}} : \\
&0 = \dot{N}_{\text{in}}\underline{H}(T_{\text{in}}, P_{\text{in}}) - \dot{N}_{\text{out}}\underline{H}(T_{\text{out}}, P_{\text{out}}) \quad \text{or that} \quad \underline{H}(T_{\text{out}}, P_{\text{out}}) = \underline{H}(T_{\text{in}}, P_{\text{in}})
\end{aligned} \tag{10}$$

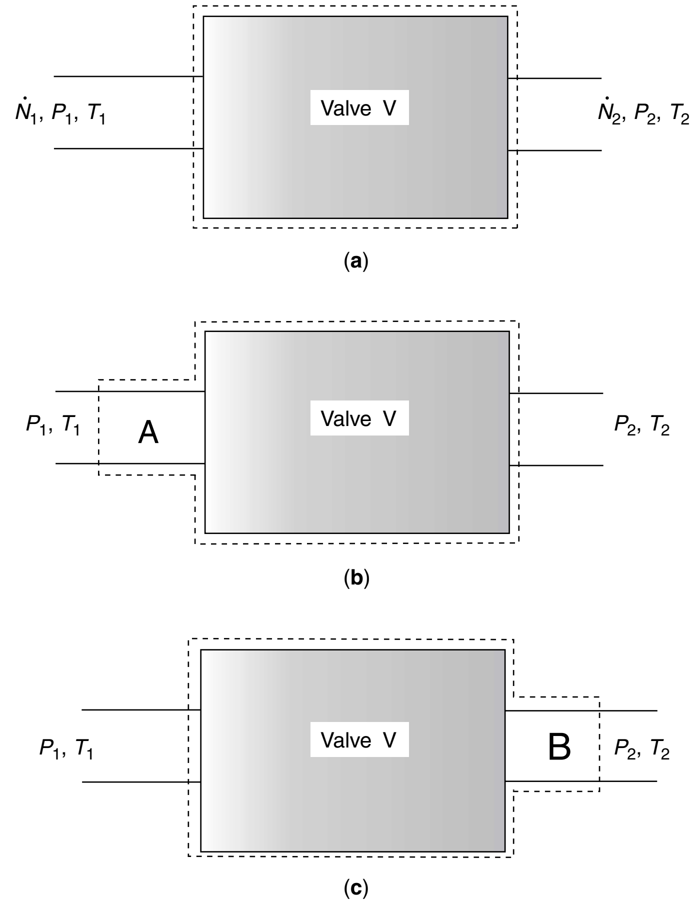

**Fig. 2.** Adiabatic valve or other pressure reducing device (Joule–Thomson expansion). (**a**) Treated as an open system. (**b**) Initial state when treated as a closed system. (**c**) Final state when treated as a closed system. Adapted from Ref. 2, with permission.

An alternative way is to consider a fixed mass as the system, which as shown in Fig. 2b initially consists of the fluid in the valve (denoted by $V$) and in the section of the entry pipe enclosed by the dashed line and designated by the letter $A$, and later is the fluid in the valve and that region $B$ of the exit enclosed by the dashed line in Fig. 2c. The mass balance for this system over the time it has taken for the fluid in $A$ to enter the valve and for the equal amount of fluid in $B$ to leave is

$$N_{\text{final}} = N_{\text{initial}} \quad \text{or} \quad N_{\text{B}} + N_{\text{V}} = N_{\text{A}} + N_{\text{V}} \quad \text{so that} \quad N_{\text{B}} = N_{\text{A}} \tag{11}$$

because the valve is operating in steady state. The energy balance for this system is

$$N_{\text{B}}\underline{U}_{\text{out}} + N_{\text{V}}\underline{U}_{\text{V}} - N_{\text{A}}\underline{U}_{\text{in}} - N_{\text{V}}\underline{U}_{\text{V}} = N_{\text{B}}\underline{U}_{\text{out}} - N_{\text{A}}\underline{U}_{\text{in}} = P_{\text{in}}N_{\text{A}}\underline{V}_{\text{in}} - P_{\text{out}}N_{\text{B}}\underline{V}_{\text{out}} \tag{12}$$

where the first term on the right is the work done by the upstream fluid in moving the system boundary so as to push the fluid in $A$ into the valve, and the second term is the work the fluid does leaving the compressor by moving its boundary (and pushing the fluid ahead of it out of the way). Using that $N_{\text{B}} = N_{\text{A}}$ gives

$$(\underline{U}_{\text{out}} + P_{\text{out}}\underline{V}_{\text{out}}) - (\underline{U}_{\text{in}} + P_{\text{in}}\underline{V}_{\text{in}}) = 0 \quad \text{or} \quad \underline{H}(T_{\text{out}}, P_{\text{out}}) = \underline{H}(T_{\text{in}}, P_{\text{in}}) \tag{13}$$

This result is the same as in equation 10, which is as it should be, because a process takes place independent of how we choose to describe it (i.e., as an open system or as a closed system). Therefore, if correct, different descriptions should lead to the same result, as is the case here. Also, examining the two descriptions, it becomes evident that the reason the enthalpy appears in the flow terms of the energy balance is that not only does a flow stream carry its internal energy, but there is $P$–$V$ work as a result of the fluid being pushed by the surrounding fluid into the system, or by pushing other fluid out of its way as it leaves the system. The adiabatic expansion here is referred to as a Joule–Thomson expansion. Typically in a Joule–Thomson expansion, the inlet temperature and pressure are known, as is the outlet pressure (for example, atmospheric pressure), but the outlet temperature is not known. It can be found from the known pressure and enthalpy if a thermodynamic data table or chart is available.

In this example, common sense tells us that the upstream pressure $P_1$ must be greater than the downstream pressure $P_2$ for the fluid to flow through the valve in the direction indicated. However, there is nothing in the mass balance or the energy balance that requires this. That is, the mass and energy balance equations would still have a solution if one specified that the direction of fluid flow should be in the unphysical direction from low pressure to high pressure. This difficulty is resolved with the introduction of the next balance equation, the second law of thermodynamics.

## 6. Entropy and the Second Law of Thermodynamics

Although the mass and energy balances are very useful, they do not provide the information needed to solve all problems of interest. Furthermore, there is the missing element in that the mass and energy balance equations apply equally well to any process and to the reverse of the process, and make no distinction between them as shown in the example above. However, an important observation is that natural processes proceed in only one direction, toward an equilibrium state, not away from such a state (ie, gradients spontaneously disappear rather than appear, a fluid flow only occurs from a region of high pressure to low pressure, and heat flows only occur from a high-temperature region to a low-temperature region).

To bring into thermodynamics the concept that spontaneous processes occur in one direction and not in reverse, a new thermodynamic function is needed. Equation 1 for a closed, isolated system without mass, work or heat flows, is

$$\frac{d\theta}{dt} = \dot{\theta}_{\text{gen}} \tag{14}$$

Now a property that is not conserved, that is, a property for which $\dot{\theta}_{\text{gen}}$ is not zero as the process evolves, must be considered as there are no remaining conserved properties. What is needed to describe the unidirectional nature of natural processes is a property whose rate of generation is either always positive (so that the function $\theta$ can only increase for a spontaneous process in an isolated system) or is always negative (so it decreases). By convention, a property that increases has been chosen, and that property is the entropy.

The entropy is not a directly measurable property (unlike temperature and pressure), and it is defined by its equation of change. The rate of change of entropy in an open system with a single heat flow is

$$\frac{dS}{dt} = \frac{d(N\underline{S})}{dt} = \sum_j \dot{N}_j \underline{S}_j + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \tag{15}$$

where $T$ is the absolute temperature (degrees Kelvin in the SI system). Defined in this way, the rate of entropy generation $\dot{S}_{\text{gen}}$ is always greater than or equal to zero. For a closed system, $\frac{d(N\underline{S})}{dt}$ becomes $N\frac{d\underline{S}}{dt}$, and each $\dot{N} = 0$ so that $\sum_j \dot{N}_j \underline{S}_j = 0$ and

$$\frac{dS}{dt} = N\frac{d\underline{S}}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \tag{16}$$

and further for an adiabatic system: $\dot{Q} = 0$.

The change in entropy between two states at $t_1$ and $t_2$ is

$$\Delta(N\underline{S}) = \int_1^2 \sum_j \dot{N}_j \underline{S}_j dt + \int_1^2 \frac{\dot{Q}}{T} dt + S_{\text{gen}} \tag{17}$$

The entropy balance contains an integral of the product of a mass flow rate and the entropy per unit mass of each flow stream. This can be difficult to evaluate unless the entropy per unit mass of the each flow stream is constant; in which case,

$$\int_1^2 \sum_j \dot{N}_j \underline{S}_j dt = \sum_j (\Delta N)_j \underline{S}_j$$

The following are other simplifications can be made in the entropy balance.

For a closed system, $\Delta(N\underline{S})$ becomes $N\Delta\underline{S}$, and each $\dot{N} = 0$ so that $\int_1^2 \sum_j \dot{N}_j \underline{S}_j dt = 0$.

For an isothermal system,

$$\int_1^2 \frac{\dot{Q}}{T} dt = \frac{1}{T} \int_1^2 \dot{Q} dt = \frac{Q}{T}$$

For an adiabatic system, $Q = 0$.

At equilibrium, when there are no longer any changes in a system, and the values of all state properties are constant, the entropy generation term $S_{\text{gen}}$ must equal zero (otherwise the state property entropy would continue to increase, whereas the state of the system is unchanged). The analysis here has only considered the overall system. If a microscopic approach is used to examine the gradients within the system, the rate of entropy generation can be shown to be proportional to the second power of the temperature gradients $(\nabla T)^2$, with the proportionality constant being related to the thermal conductivity of the substance for internal flows or the heat transfer coefficient at the surface of the system, and the second power of the velocity gradients $(\nabla v)^2$ or the stress tensor with the proportionality constant being related to the viscosity.

As the entropy generation rate depends on the square of the system gradients, one can imagine a change of state that occurs so slowly that the gradients in temperature $\nabla T$ and velocity $\nabla v$ are so small that the square of those terms can be neglected. Such a process, called a reversible process, is characterized by a zero rate of entropy generation; that is, $\dot{S}_{\text{gen}} = S_{\text{gen}} = 0$. Although no process is truly reversible, it is useful to consider such processes in two limiting cases. The first is a process that occurs so slowly (compared with the internal relaxation times of the substance) that the process may be considered to pass through a succession of equilibrium states, so that there is no entropy generation. The second is a process that is not reversible, but it is useful to consider a reversible path between the initial and the final states to obtain upper or lower bounds on the heat and work flows.

Returning to the Joule–Thomson expansion, the entropy balance on the steady-state adiabatic valve is

$$0 = \dot{N}_{\text{in}} \underline{S}_{\text{in}} - \dot{N}_{\text{out}} \underline{S}_{\text{out}} + \dot{S}_{\text{gen}} \quad \text{or that} \quad \underline{S}_{\text{out}} \geq \underline{S}_{\text{in}} \tag{18}$$

because $\dot{S}_{\text{gen}} \geq 0$ as there are significant temperature and pressure gradients within the valve. Using that the enthalpy of the inlet and outlet streams of the valve are equal, but that the entropy of the exit stream is greater than that of the inlet stream and thermodynamic property charts (or even assuming ideal gas behavior), leads to the conclusion that the pressure of the outlet stream must always be lower than that of the inlet stream.

## 7. Interrelationships Between Thermodynamic Properties

As thermodynamic state variables ($T$, $P$, $\underline{V}$, $\underline{H}$, $\underline{U}$, $\underline{G}$, $\underline{S}$ and $\underline{A}$) depend only the state of the system, and not the path to that state, to compute changes in thermodynamic properties between states, it is useful to consider a reversible path. In particular, for a closed system with a single heat flow and no work flow, we have from the energy and entropy balances that

$$N\frac{d\underline{U}}{dt} = \dot{Q} - P\frac{dV}{dt} \quad \text{and} \quad N\frac{d\underline{S}}{dt} = \frac{\dot{Q}}{T} \tag{19}$$

which when combined leads to

$$N\frac{d\underline{U}}{dt} = NT\frac{d\underline{S}}{dt} - P\frac{dV}{dt} = NT\frac{d\underline{S}}{dt} - NP\frac{d\underline{V}}{dt} \tag{20}$$

or as commonly written in thermodynamics (omitting the bottom half of the derivative) as

$$d\underline{U} = Td\underline{S} - Pd\underline{V} \tag{21}$$

Treating $\underline{U}$ as a function of $\underline{S}$ and $\underline{V}$, using the chain rule of partial differentiation

$$d\underline{U} = \left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} d\underline{S} + \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} d\underline{V} \tag{22}$$

and comparing these two equations gives

$$\left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} = T \quad \text{and} \quad \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} = -P \tag{23}$$

Using the definition of enthalpy $\underline{H} = \underline{U} + P\underline{V}$ in equation 21 yields

$$d\underline{H} = Td\underline{S} + \underline{V}dP = \left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P} d\underline{S} + \left(\frac{\partial \underline{H}}{\partial P}\right)_{\underline{S}} dP \tag{24}$$

so that

$$\left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P} = T \quad \text{and} \quad \left(\frac{\partial \underline{H}}{\partial P}\right)_{\underline{S}} = \underline{V} \tag{25}$$

Also, by simple rearrangement

$$d\underline{S} = \frac{1}{T}d\underline{U} + \frac{P}{T}d\underline{V} \quad \text{so that} \quad \left(\frac{\partial \underline{S}}{\partial \underline{U}}\right)_{\underline{V}} = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_{\underline{U}} = \frac{P}{T} \qquad (26)$$

and

$$d\underline{S} = \frac{1}{T}d\underline{H} - \frac{\underline{V}}{T}dP \quad \text{so that} \quad \left(\frac{\partial \underline{S}}{\partial \underline{H}}\right)_{P} = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial \underline{S}}{\partial P}\right)_{\underline{H}} = -\frac{\underline{V}}{T} \qquad (27)$$

Similarly, for the Gibbs energy using that $\underline{G} = \underline{H} - T\underline{S}$, we obtain

$$d\underline{G} = d\underline{H} - Td\underline{S} - \underline{S}dT = Td\underline{S} + \underline{V}dP - Td\underline{S} - \underline{S}dT = \underline{V}dP - \underline{S}dT$$

so that

$$\left(\frac{\partial \underline{G}}{\partial P}\right)_{T} = \underline{V} \quad \text{and} \quad \left(\frac{\partial \underline{G}}{\partial T}\right)_{P} = -\underline{S} \qquad (28)$$

and for the Helmholtz $\underline{A} = \underline{U} - T\underline{S}$,

$$d\underline{A} = d\underline{U} - Td\underline{S} - \underline{S}dT = Td\underline{S} - Pd\underline{V} - Td\underline{S} - \underline{S}dT = -Pd\underline{V} - \underline{V}dT$$

$$\left(\frac{\partial \underline{A}}{\partial \underline{V}}\right)_{T} = -P \quad \text{and} \quad \left(\frac{\partial \underline{A}}{\partial T}\right)_{\underline{V}} = -\underline{S} \qquad (29)$$

Two important relations come from the Maxwell equations, which are the result of mixed second derivatives being equal regardless of the order in which the derivatives are taken. For example,

$$\left.\frac{\partial}{\partial T}\right|_{\underline{V}} \left(\frac{\partial \underline{A}}{\partial \underline{V}}\right)_{T} = -\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \left.\frac{\partial}{\partial \underline{V}}\right|_{T} \left(\frac{\partial \underline{A}}{\partial T}\right)_{\underline{V}} = -\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_{T} \qquad (30)$$

and

$$\left.\frac{\partial}{\partial T}\right|_{P} \left(\frac{\partial \underline{G}}{\partial P}\right)_{T} = \left(\frac{\partial \underline{V}}{\partial T}\right)_{P} = -\left(\frac{\partial \underline{S}}{\partial P}\right)_{T} = \left.\frac{\partial}{\partial P}\right|_{T} \left(\frac{\partial \underline{G}}{\partial T}\right)_{P} \qquad (31)$$

For a reversible change of state in an isothermal open system with only a single flow stream of the same temperature as the system

$$\frac{dU}{dt} = T\frac{dS}{dt} - P\frac{dV}{dt} + \frac{dN}{dt}(\underline{H} - T\underline{S}) = T\frac{dS}{dt} - P\frac{dV}{dt} + \underline{G}\frac{dN}{dt} \qquad (32)$$

or

$$dU = TdS - PdV + \underline{G}dN \tag{33}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_{N,S} = \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}} = -P,\ \left(\frac{\partial U}{\partial S}\right)_{N,V} = \left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \underline{G} \tag{34}$$

Adding $d(PV)$ to both sides of equation 33

$$dU + d(PV) = dH = \underline{G}dN - PdV + TdS + d(PV) = \underline{G}dN + VdP + TdS$$

so that

$$\left(\frac{\partial H}{\partial P}\right)_{N,S} = V,\ \left(\frac{\partial H}{\partial S}\right)_{N,P} = \left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P} = T, \quad \text{and} \quad \left(\frac{\partial H}{\partial N}\right)_{S,P} = \underline{G} \tag{35}$$

In a similar fashion

$$\begin{aligned} dS &= \frac{1}{T}dU + \frac{P}{T}dV - \frac{\underline{G}}{T}dN, \\ dA &= -SdT - PdV + \underline{G}dN, \quad \text{and} \quad dG = -SdT + VdP + \underline{G}dN \end{aligned} \tag{36}$$

from which we find

$$\underline{G} = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{P,S} = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = -T\left(\frac{\partial S}{\partial N}\right)_{H,P} = \mu \tag{37}$$

suggesting that the Gibbs energy is an especially important variable in thermodynamics. Indeed, it appears so often that it is commonly designated by the symbol $\mu$ and referred to as the chemical potential of a species. Also,

$$\left(\frac{\partial \underline{G}}{\partial T}\right)_{P} = -\underline{S} \quad \text{and} \quad \left(\frac{\partial(\underline{G}/T)}{\partial T}\right)_{P} = -\frac{\underline{G}}{T^2} + \frac{1}{T}\left(\frac{\partial \underline{G}}{\partial T}\right)_{P} = -\frac{\underline{H} - T\underline{S}}{T^2} - \frac{\underline{S}}{T} = -\frac{\underline{H}}{T^2} \tag{38}$$

## 8. Heat Engines, Heat Pumps, and Turbines

Consider the engine schematically shown in Fig. 3, either operating in steady state or over one complete cycle of a cyclic engine. The energy and entropy balances relating the amount of work the engine can deliver to the surroundings ($-W$) from a flow of heat $Q_{\mathrm{H}}$ from a heat source ($T_{\mathrm{H}}$) into the engine and assuming there is also a flow of heat $Q_{\mathrm{L}}$ at a lower temperature ($T_{\mathrm{L}}$) are

$$0 = Q_{\mathrm{H}} + Q_{\mathrm{L}} + W, \quad 0 = \frac{Q_{\mathrm{H}}}{T_{\mathrm{H}}} + \frac{Q_{\mathrm{L}}}{T_{\mathrm{L}}} + S_{\mathrm{gen}}, \quad \text{and} \quad Q_{\mathrm{L}} = -Q_{\mathrm{H}}\frac{T_{\mathrm{L}}}{T_{\mathrm{H}}} - T_{\mathrm{L}}S_{\mathrm{gen}} \tag{39}$$

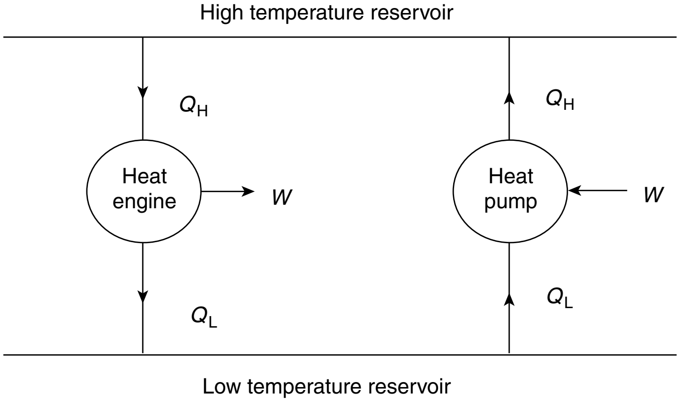

**Fig. 3.** Heat engine and heat pump.

so that

$$-W = Q_H + Q_L = Q_H\left(1 - \frac{T_L}{T_H}\right) - T_L S_{gen} \tag{40}$$

It can be shown that the maximum work attainable from a system for a given change of state (or that the minimum work required to produce a given change of state) occurs when the process occurs reversibly. Therefore, the largest positive value of $-W$ is obtained when $S_{gen} = 0$, because if $S_{gen} > 0$ and a lesser value of $-W$ is obtained. When the process is carried out reversibly, the engine efficiency is

$$\text{maximum efficiency} = \frac{\text{work produced}}{\text{heat supplied}} = \frac{-W}{Q_H} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H} \tag{41}$$

which is the well-known Carnot efficiency of heat engines. This equation sets the upper bound for the conversion of heat to work. It is important to note that thermodynamics is able to set this upper bound without any information about the detailed workings of the heat engine. Also note from equation 41 that unless the heat sink temperature $T_L$ is absolute zero, $Q_L$ will be negative. That is, there must be a heat flow out of the engine so that it cannot convert all the heat it receives into work. This is the Kelvin–Planck statement of the Second Law of Thermodynamics.

The heat engine does work on its surroundings by receiving heat at a high temperature and rejecting it at a lower temperature, while the heat pump in Fig. 3, of which a refrigerator and an air conditioner are examples, operates in reverse by using work (frequently electrical energy) to accept heat at a low temperature and reject it at a higher temperature. The efficiency of a heat pump is measured by its coefficient of performance:

$$\begin{matrix}\text{coefficient}\\ \text{of performance}\end{matrix} = \text{C.O.P.} = \frac{\text{low temperature heat accepted}}{\text{work required}} = \frac{Q_L}{W} \tag{42}$$

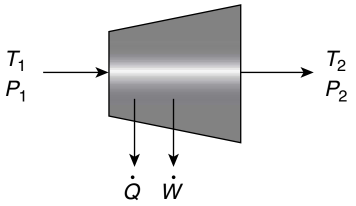

**Fig. 4.** Turbine or other type of flow engine. Adapted from Ref. 2, with permission.

For a Carnot cycle heat pump, the coefficient of performance is

$$\text{Carnot C.O.P.} = \frac{Q_\text{L}}{W} = \frac{T_\text{L}}{T_\text{H} - T_\text{L}} \tag{43}$$

Next consider the work that can be obtained in a steady-state flow process, for example, from the turbine in Fig. 4 with an inlet stream of high-pressure steam and an outlet stream that is low-pressure steam or a steam–water mixture. The mass (mole), energy, and entropy balances for this process are as follows:

$$\begin{aligned} 0 &= \dot{N}_\text{in} - \dot{N}_\text{out} \quad \text{so that} \quad \dot{N}_\text{out} = \dot{N}_\text{in} \\ 0 &= \dot{N}_\text{in}\underline{H}(T_\text{in}, P_\text{in}) - \dot{N}_\text{out}\underline{H}(T_\text{out}, P_\text{out}) + \dot{W} + \dot{Q} \quad \text{and} \\ 0 &= \dot{N}_\text{in}\underline{S}(T_\text{in}, P_\text{in}) - \dot{N}_\text{out}\underline{S}(T_\text{out}, P_\text{out}) + \frac{\dot{Q}}{T_q} + \dot{S}_\text{gen} \end{aligned} \tag{44}$$

or

$$\begin{aligned} \dot{Q} &= \dot{N}_\text{in}[T_q\underline{S}(T_\text{out}, P_\text{out}) - T_q\underline{S}(T_\text{in}, P_\text{in})] - T_q\dot{S}_\text{gen} \quad \text{and} \\ -\dot{W} &= \dot{N}_\text{in}\{[\underline{H}(T_\text{in}, P_\text{in}) - T_q\underline{S}(T_\text{in}, P_\text{in})] - [\underline{H}(T_\text{out}, P_\text{out}) \\ &\quad - T_q\underline{S}(T_\text{out}, P_\text{out})]\} - T_q\dot{S}_\text{gen} \end{aligned} \tag{45}$$

where $T_q$ is the temperature at which heat transfer occurs.

To obtain the maximum work possible from a given feed, any heat flow from the device to the environment should be the ambient environmental temperature $T_\text{amb}$ (if not, a heat engine could be used to extract additional work from this high-temperature heat), and for the same reason, the temperature of the exiting stream should be ambient. The pressure of the exit stream should be the ambient pressure as well; otherwise, a turbine could be used to extract additional work from this flow stream. Finally, the process should be reversible so that $\dot{S}_\text{gen} = 0$. Therefore, the maximum work that can be obtained from the initial flow stream is

$$-\dot{W}^\text{max} = \dot{N}_\text{in}[\underline{\mathbf{G}}(T_\text{in}, P_\text{in}, T_\text{amb}) - \underline{G}(T_\text{out}, P_\text{out})] \tag{46}$$

where $\underline{G}(T_{\mathrm{in}}, P_{\mathrm{in}}, T_{\mathrm{amb}}) = \underline{H}(T_{\mathrm{in}}, P_{\mathrm{in}}) - T_{\mathrm{amb}}\underline{S}(T_{\mathrm{in}}, P_{\mathrm{in}})$ is known as the availability function. Note that it is not a Gibbs energy, and its value depends on two different temperatures.

## 9. Calculation of Changes in Thermodynamic Properties on a Change of State

The energy and entropy balances are in terms of internal energy, enthalpy, and entropy, whereas the directly measured properties are temperature and pressure or temperature and volume. Therefore, it is necessary to interrelate these two types of properties. Values of the

$$\begin{aligned} &\text{constant volume heat capacity } C_{\mathrm{V}} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} \\ &\text{or the constant pressure heat capacity } C_{\mathrm{P}} = \left(\frac{\partial \underline{H}}{\partial T}\right)_{P} \end{aligned} \tag{47}$$

are available for many substances in the ideal gas state or for others as an incompressible liquid or solid. In both cases, $C_{\mathrm{V}}$ and $C_{\mathrm{P}}$ are only functions of temperature:

$$\begin{aligned} &C_{\mathrm{P}}(T) = C_{\mathrm{V}}(T) + R = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2 + \mathrm{d}T^3 + \ldots \quad \text{for ideal gases and} \\ &C_{\mathrm{P}}(T) = C_{\mathrm{V}}(T) = \mathrm{a} + \mathrm{b}T + \mathrm{c}T^2 + \mathrm{d}T^3 + \ldots \quad \text{for liquids and solids} \end{aligned} \tag{48}$$

where $R = 8.314\,\mathrm{J/(mol\,K)} = 8.314 \times 10^{-3}\,\mathrm{kPa\,m^3/(mol\,K)}$ is the gas constant.

For nonideal gases the heat capacities are also a fuction of temperature or density.

An equation of state relating pressure, volume, and temperature, that is, a $P{-}V{-}T$ relation, may be available for the substance of interest or estimated from a generalized correlation. Examples include

The simple ideal gas equation of state

$$P = \frac{RT}{\underline{V}} \tag{49}$$

The commonly used Peng–Robinson equation of state (8)

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \tag{50}$$

in which the temperature-dependent parameter $a(T)$ and the constant $b$ are specific to each fluid. These parameters may be obtained by correlating vapor pressure and density data, or more commonly by using generalized equations and the critical properties of the fluid as described later. This equation can be used for both gases and liquids of nonpolar compounds.

The virial equation of state

$$\frac{P\underline{V}}{RT} = Z(T,P) = 1 + \frac{B(T)}{\underline{V}} + \frac{C(T)}{\underline{V}^2} + \ldots \tag{51}$$

where $B(T)$, $C(T)$, …, etc are the temperature-dependent second, third, …, etc virial coefficients. This equation can only be used for gases with the pressure/density range depending on the number of terms kept in the expansion.

Extended virial equations such as the Benedict–Webb–Rubin equation (9):

$$\begin{aligned}\frac{P\underline{V}}{RT} = Z(T,P) = 1 + \left[B - \frac{A}{RT} - \frac{C}{RT^2}\right]\frac{1}{\underline{V}} + \left(b - \frac{a}{RT}\right)\frac{1}{\underline{V}^2}\\ + \frac{a\alpha}{RT\underline{V}^5} + \frac{\beta}{RT^3\underline{V}}\left(1 + \frac{\gamma}{\underline{V}^2}\right)\exp\left(-\frac{\gamma}{\underline{V}^2}\right)\end{aligned} \tag{52}$$

and others in this family can be used for both vapors and liquids; however, parameters are available for only a few substances. Information about these and other equations of state and pure fluid and mixture properties can be found in Refs. 10 and 11.

To compute how the entropy changes as a function of temperature and volume, one starts with

$$\begin{aligned}d\underline{S} &= \left(\frac{\partial \underline{S}}{\partial T}\right)_{\underline{V}} dT + \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T d\underline{V} = \left(\frac{\partial \underline{S}}{\partial \underline{U}}\right)_{\underline{V}}\left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V}\\ &= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V}\end{aligned} \tag{53}$$

Similarly, as a function of $T$ and $P$

$$d\underline{S} = \left(\frac{\partial \underline{S}}{\partial T}\right)_P dT + \left(\frac{\partial \underline{S}}{\partial P}\right)_T dP = \frac{C_P}{T} dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP \tag{54}$$

Therefore,

$$d\underline{U} = Td\underline{S} - Pd\underline{V} = T\left[\frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V}\right] - Pd\underline{V} = C_V dT + \left[\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] d\underline{V} \tag{55}$$

and

$$d\underline{H} = Td\underline{S} + \underline{V}dP = T\left[\frac{C_P}{T}dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP\right] + \underline{V}dP = C_P dT + \left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right] dP \tag{56}$$

These equations provide the relations needed to compute the change in thermodynamic properties ($\underline{S}$, $\underline{U}$ and $\underline{H}$, and from those $\underline{G}$ and $\underline{A}$) as a result of changes in temperature and pressure or temperature and volume knowing only heat capacities and a volumetric equation of state. By using these equations, thermodynamic tables (for example, the steam tables) and thermodynamic property diagrams (ie, the Mollier diagram, which is an entropy versus enthalpy diagram for steam) have been developed.

As heat capacity data for fluids are generally available only at very low pressures (the ideal gas state), and because thermodynamic state variables ($T$, $P$, $\underline{V}$, $\underline{H}$, $\underline{U}$, $\underline{G}$, $\underline{S}$ and $\underline{A}$) only depend on the state, and not the path to get to that state, to calculate the change in a thermodynamic variable between two states, the path used for the calculation is to first expand the fluid at the constant initial temperature from the initial pressure to the ideal gas state (zero pressure or infinite volume), heat or cool the fluid as necessary to the final temperature, and then compress the fluid at constant final temperature to the final pressure. That is,

$$\begin{aligned}\underline{H}(T_2,P_2)-\underline{H}(T_1,P_1) &= \int_{T_1,P_1}^{T_1,P=0}\left[\underline{V}-T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]dP \\ &\quad + \int_{T_1,P=0}^{T_2,P=0} C_{\mathrm{P}}dT + \int_{T_2,P=0}^{T_2,P_2}\left[\underline{V}-T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]dP\end{aligned} \tag{57}$$

$$\underline{S}(T_2,P_2)-\underline{S}(T_1,P_1) = -\int_{T_1,P_1}^{T_1,P=0}\left(\frac{\partial \underline{V}}{\partial T}\right)_P dP + \int_{T_1,P=0}^{T_2,P=0}\frac{C_{\mathrm{P}}}{T}dT - \int_{T_2,P=0}^{T_2,P_2}\left(\frac{\partial \underline{V}}{\partial T}\right)_P dP \tag{58}$$

$$\underline{S}(T_2,\underline{V}_2)-\underline{S}(T_1,\underline{V}_1) = \int_{T_1,\underline{V}_1}^{T_1,\underline{V}=\infty}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V} + \int_{T_1,\underline{V}=\infty}^{T_2,\underline{V}=\infty}\frac{C_{\mathrm{V}}}{T}dT + \int_{T_2,\underline{V}=\infty}^{T_2,\underline{V}_2}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V} \tag{59}$$

and

$$\begin{aligned}\underline{U}(T_2,\underline{V}_2)-\underline{U}(T_1,\underline{V}_1) &= \int_{T_1,\underline{V}_1}^{T_1,\underline{V}=\infty}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P\right]d\underline{V} + \int_{T_1,\underline{V}=\infty}^{T_2,\underline{V}=\infty} C_{\mathrm{V}}dT \\ &\quad + \int_{T_2,\underline{V}=\infty}^{T_2,\underline{V}_2}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P\right]d\underline{V}\end{aligned} \tag{60}$$

Thus, with heat capacity data at low pressure (the ideal gas state) and a volumetric equation of state (ie, a relation between $P$, $\underline{V}$ and $T$), the change in thermodynamic properties of a fluid between two states can be computed.

For the case of an ideal gas, these equations reduce to

$$\underline{H}^{\mathrm{IG}}(T_2,P_2) - \underline{H}^{\mathrm{IG}}(T_1,P_1) = \int_{T_1}^{T_2} C_{\mathrm{P}} dT \tag{61}$$

$$\underline{S}^{\mathrm{IG}}(T_2,P_2) - \underline{S}^{\mathrm{IG}}(T_1,P_1) = -\int_{P_1}^{P_2} \frac{R}{P} dP + \int_{T_1,P=0}^{T_2,P=0} \frac{C_{\mathrm{P}}}{T} dT = -R \ln \frac{P_2}{P_1} + \int_{T_1,P=0}^{T_2,P=0} \frac{C_{\mathrm{P}}}{T} dT \tag{62}$$

$$\underline{S}^{\mathrm{IG}}(T_2,\underline{V}_2) - \underline{S}^{\mathrm{IG}}(T_1,\underline{V}_1) = R \ln \frac{\underline{V}_2}{\underline{V}_1} + \int_{T_1,\underline{V}=\infty}^{T_2,\underline{V}=\infty} \frac{C_{\mathrm{V}}}{T} dT \tag{63}$$

and

$$\underline{U}^{\mathrm{IG}}(T_2,\underline{V}_2) - \underline{U}^{\mathrm{IG}}(T_1,\underline{V}_1) = \int_{T_1}^{T_2} C_{\mathrm{V}} dT \tag{64}$$

For other equations of state, such as the virial and Peng–Robinson equations mentioned earlier, the appropriate equations are found in Ref. 2 and elsewhere.

For a liquid or solid, which is considered incompressible (ie, $(\frac{\partial \underline{V}}{\partial P})_T = 0$),

$$\underline{H}(T_2,P_2) - \underline{H}(T_1,P_1) = \int_{P_1}^{P_2} \underline{V} dP + \int_{T_1}^{T_2} C_{\mathrm{P}} dT \tag{65}$$

$$\underline{S}(T_2,P_2) - \underline{S}(T_1,P_1) = \int_{T_1}^{T_2} \frac{C_{\mathrm{P}}}{T} dT \tag{66}$$

$$\underline{S}(T_2,\underline{V}_2) - \underline{S}(T_1,\underline{V}_1) = \int_{T_1}^{T_2} \frac{C_{\mathrm{V}}}{T} dT \tag{67}$$

and

$$\underline{U}(T_2,\underline{V}_2) - \underline{U}(T_1,\underline{V}_1) = \int_{T_1}^{T_2} C_{\mathrm{V}} dT \tag{68}$$

A residual property $\underline{\theta}^{\mathrm{res}}$ is defined as the difference between the property of a real fluid and an ideal gas at the same temperature and pressure; ie,

$$\underline{\theta}^{\mathrm{res}}(T,P) = \underline{\theta}(T,P) - \underline{\theta}^{\mathrm{IG}}(T,P) \tag{69}$$

Each residual property is easily derived from the equations above.

Finally, as we will see in the following and later sections, the Gibbs energy is of special importance in equilibrium calculations. As a prelude to computing changes in Gibbs energy between states, note that from equations 61 and 62, the change in the molar Gibbs energy of an ideal gas between states of different pressure but at the same temperature is

$$\underline{G}^{\mathrm{IG}}(P_2, T) - \underline{G}^{\mathrm{IG}}(P_1, T) = RT \ln \frac{P_2}{P_1} \tag{70}$$

Common terminology is to write this as

$$\underline{G}^{\mathrm{IG}}(P, T) = \underline{G}^{\mathrm{IG}}(P^o, T) + RT \ln \frac{P}{P^o} = \underline{G}^o(T) + RT \ln \frac{P}{P^o} \tag{71}$$

where $P^o$ is some fixed reference pressure (frequently 1 bar) and $\underline{G}^o(T)$, which is only a function of temperature at the fixed reference pressure. In a pure fluid, the chemical potential of a species designated by the symbol $\mu$ is just equal to the molar Gibbs energy, so that an alternative way of writing the equations above is

$$\mu^{\mathrm{IG}}(P_2, T) - \mu^{\mathrm{IG}}(P_1, T) = RT \ln \frac{P_2}{P_1} \quad \text{and} \quad \mu^{\mathrm{IG}}(P, T) = \mu^o(T) + RT \ln \frac{P}{P^o} \tag{72}$$

## 10. Equilibrium

As

$$\dot{S}_{\mathrm{gen}} \geq 0 \,\text{away from equilibrium}, \quad \text{and} \quad \dot{S}_{\mathrm{gen}} = 0 \,\text{at equilibrium} \tag{73}$$

the condition for equilibrium in an isolated system is that

$$\frac{dS}{dt} \geq 0 \,\text{away from equilibrium}, \quad \text{and} \quad \frac{dS}{dt} = 0 \,\text{at equilibrium} \tag{74}$$

Therefore, the mathematical criterion for equilibrium in an isolated system is that the entropy of the system must be a maximum subject to the isolated system constraints of no heat, work, or mass flows.

Other system constraints result in different equilibrium conditions. For example, for a closed system at constant temperature and pressure,

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} \quad \text{and} \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\mathrm{gen}} \tag{75}$$

Combining these two equations by eliminating the heat flow $\dot{Q}$, and recognizing that because the temperature is constant $\frac{dT}{dt} = 0$ and the pressure is constant $\frac{dP}{dt} = 0$ gives

$$\frac{dU}{dt} = -P\frac{dV}{dt} + T\frac{dS}{dt} - T\dot{S}_{\mathrm{gen}} \quad \text{or} \quad \frac{d(U + PV - TS)}{dt} = \frac{dG}{dt} = -T\dot{S}_{\mathrm{gen}} \leq 0 \tag{76}$$

leading to the conclusion that the Gibbs energy is a minimum at equilibrium subject to the constraints of constant mass (ie, a closed system), constant temperature, and constant pressure. For a closed system at constant temperature and constant volume, following the analysis above, now with $\frac{dT}{dt}=0$ and $\frac{dV}{dt}=0$ gives

$$\frac{dU}{dt}=T\frac{dS}{dt}-T\dot{S}_{\text{gen}} \quad \text{or} \quad \frac{d(U-TS)}{dt}=\frac{dA}{dt}=-T\dot{S}_{\text{gen}}\leq 0 \tag{77}$$

leading to the conclusion that the Helmholtz energy is a minimum at equilibrium subject to the constraints of constant mass (ie, a closed system), constant temperature, and constant volume.

As equilibrium states are of central importance in thermodynamics, equations 74, 76, and 77, which provide the path to computationally determining the equilibrium state under various constraints, are exceptionally important in thermodynamics.

## 11. Phase Equilibrium in a One-Component System

Consider a closed, one-component system at constant temperature and pressure in which two phases, I and II, coexist at equilibrium. The distribution of mass between the two phases is

$$N=N^{\text{I}}+N^{\text{II}} \tag{78}$$

where $N$ is the total number of moles in the system and $N^{\text{I}}$ and $N^{\text{II}}$ are the number of moles in each phase. The total Gibbs energy of this two-phase system is

$$N\underline{G}=N^{\text{I}}\underline{G}^{\text{I}}+N^{\text{II}}\underline{G}^{\text{II}} \tag{79}$$

The condition for equilibrium for a closed system at constant temperature and constant pressure is that the Gibbs energy should be a minimum, or that $d(N\underline{G})=0$ for all possible system variations, which here is for all variations of the number of moles in each phase, subject to the constraints of fixed temperature, fixed pressure, and fixed total number of moles that is

$$dN=0=dN^{\text{I}}+dN^{\text{II}}, \quad \text{or} \quad dN^{\text{II}}=-dN^{\text{I}} \tag{80}$$

Therefore, using

$$dG=d(N\underline{G})=-SdT+VdP+\underline{G}dN$$

results in

$$d(N\underline{G})=\underline{G}^{\text{I}}dN^{\text{I}}+\underline{G}^{\text{II}}dN^{\text{II}}=(\underline{G}^{\text{I}}-\underline{G}^{\text{II}})dN^{\text{I}}=0 \tag{81}$$

for all changes in the number of moles in phase I, that is, for all values of $dN^{\mathrm{I}}$. (Note that $\underline{G}^{\mathrm{I}}$ and $\underline{G}^{\mathrm{II}}$ cannot change because temperature and pressure are constant.) The only way this can be true is for

$$\underline{G}^{\mathrm{I}}(T,P) = \underline{G}^{\mathrm{II}}(T,P) \tag{82}$$

So the temperature must be the same in both phases, and the pressure must be the same in both phases, which are obvious, but also the molar Gibbs energy must be the same in both phases, which is not an obvious result. In terms of the chemical potential, these equations are

$$dG = d(N\underline{G}) = -SdT + VdP + \mu dN \quad \text{and} \quad \mu^{\mathrm{I}}(T,P) = \mu^{\mathrm{II}}(T,P) \tag{83}$$

Next consider two-phase equilibrium in a closed system constrained to be at constant temperature and constant volume. For this case, it was shown earlier that the Helmholtz energy $A$ is a minimum. So that

$$\begin{aligned} dA &= d(N\underline{A}) = -SdT - PdV + \underline{G}dN \\ dA &= dA^{\mathrm{I}} + dA^{\mathrm{II}} = \underline{G}^{\mathrm{I}}dN^{\mathrm{I}} + \underline{G}^{\mathrm{II}}dN^{\mathrm{II}} = (\underline{G}^{\mathrm{I}} - \underline{G}^{\mathrm{II}})dN^{\mathrm{I}} \end{aligned} \tag{84}$$

and again that $\underline{G}^{\mathrm{I}}(T,P) = \underline{G}^{\mathrm{II}}(T,P)$ or equivalently in terms of the chemical potential $\mu^{\mathrm{I}}(T,P) = \mu^{\mathrm{II}}(T,P)$. Indeed, the equality of temperature, equality of pressure, and equality of Gibbs energies (or chemical potential) in the two phases are obtained as the conditions for phase equilibrium independent of the constraints.

As at each temperature at which two phases are in equilibrium, along the phase boundary, we have $\underline{G}^{\mathrm{I}}(T,P) = \underline{G}^{\mathrm{II}}(T,P)$ and

$$d\underline{G}^{\mathrm{I}}(T,P)|_{\sigma} = [-\underline{S}^{\mathrm{I}}dT + \underline{V}^{\mathrm{I}}dP]_{\sigma} = d\underline{G}^{\mathrm{II}}(T,P)|_{\sigma} = [-\underline{S}^{\mathrm{II}}dT + \underline{V}^{\mathrm{II}}dP]_{\sigma} \tag{85}$$

or

$$\left.\frac{dP}{dT}\right|_{\sigma} = \left.\frac{\underline{S}^{\mathrm{I}} - \underline{S}^{\mathrm{II}}}{\underline{V}^{\mathrm{I}} - \underline{V}^{\mathrm{II}}}\right|_{\sigma}$$

where the symbol $\sigma$ indicates changes following the equilibrium temperature-pressure line. However, by the equality of Gibbs energies,

$$\begin{aligned} \underline{G}^{\mathrm{I}}(T,P) = \underline{H}^{\mathrm{I}}(T,P) - T\underline{S}^{\mathrm{I}}(T,P) = \underline{G}^{\mathrm{II}}(T,P) = \underline{H}^{\mathrm{II}}(T,P) - T\underline{S}^{\mathrm{II}}(T,P) \\ \underline{S}^{\mathrm{I}}(T,P) - \underline{S}^{\mathrm{II}}(T,P) = \frac{\underline{H}^{\mathrm{I}}(T,P) - \underline{H}^{\mathrm{II}}(T,P)}{T} \end{aligned} \tag{86}$$

so that

$$\left.\frac{dP}{dT}\right|_{\sigma} = \left.\frac{\underline{H}^{\mathrm{I}} - \underline{H}^{\mathrm{II}}}{T(\underline{V}^{\mathrm{I}} - \underline{V}^{\mathrm{II}})}\right|_{\sigma} = \frac{\Delta\underline{H}}{T\Delta\underline{V}} \tag{87}$$

which is the Clapeyron equation relating the change in equilibrium pressure with temperature along a phase boundary to the enthalpy and volume differences on the phase change. This equation is applicable to liquid–vapor phase changes giving the temperature variation of the vapor pressure, to solid–vapor phase changes giving the temperature variation of the sublimation pressure, and to solid–liquid phase changes giving the variation of the melting temperature with pressure.

For the case of vapor–liquid equilibrium at low pressure, for which $\underline{V}^{\mathrm{V}} \gg \underline{V}^{\mathrm{L}}$, $\underline{V}^{\mathrm{V}} = \frac{RT}{P}$, and

$$\frac{dP^{\mathrm{vap}}}{dT} = \frac{\Delta_{\mathrm{L}\to\mathrm{V}}\underline{H}}{T\Delta\underline{V}} = \frac{P^{\mathrm{vap}}\Delta_{\mathrm{L}\to\mathrm{V}}\underline{H}}{RT^2} \quad \text{or} \quad \frac{d\ln P^{\mathrm{vap}}}{dT} = \frac{\Delta_{\mathrm{L}\to\mathrm{V}}\underline{H}}{RT^2} \tag{88}$$

which is the Clausius–Clapeyron equation. If the enthalpy (heat) of vaporization is not a function of temperature, integrating this equation gives

$$\ln P^{\mathrm{vap}}(T) = -\frac{\Delta_{\mathrm{L}\to\mathrm{V}}\underline{H}}{RT} + A \quad \text{or} \quad \ln P^{\mathrm{vap}}(T) = A - \frac{B}{T} \tag{89}$$

where $A$ is an integration constant. To account for the variation of the heat of vaporization with temperature, as the temperature (and, therefore, vapor pressure) increases so that the vapor becomes progressively nonideal, equations such as

$$\ln P^{\mathrm{vap}}(T) = A - \frac{B}{T+C} \quad \text{or} \quad \ln P^{\mathrm{vap}}(T) = A - \frac{B}{T} + C\ln T + DT^6 \tag{90}$$

are used to describe the temperature variation of the vapor pressure from the melting point to the near critical point of a fluid. Other equations are given in Ref. 10.

Figure 5 is an example of a phase diagram showing the vapor, liquid, and solid phases as a function of temperature and pressure (Fig. 5a) and temperature and volume (Fig. 5b). At low temperatures, a solid is in equilibrium with a vapor; this coexistence pressure is referred to as the sublimation pressure, and because

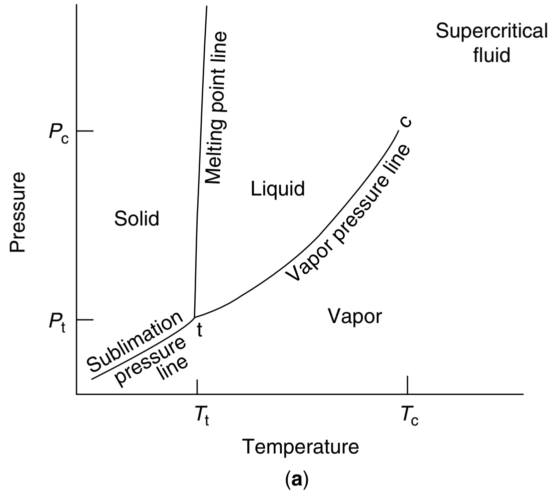

**Fig. 5.** Phase behavior of a pure substance. (**a**) $P$ - $T$ plot showing the solid, liquid, vapor, and supercritical fluid regions; the phase transition boundaries; and the critical and triple points. (**b**) $P$ - $V$ plot for the same substance. The dashed lines are three representative lines of constant temperature (isotherms), one below, one at, and one above the critical temperature $T_c$. Note the inflection point along the critical isotherm at the critical point.

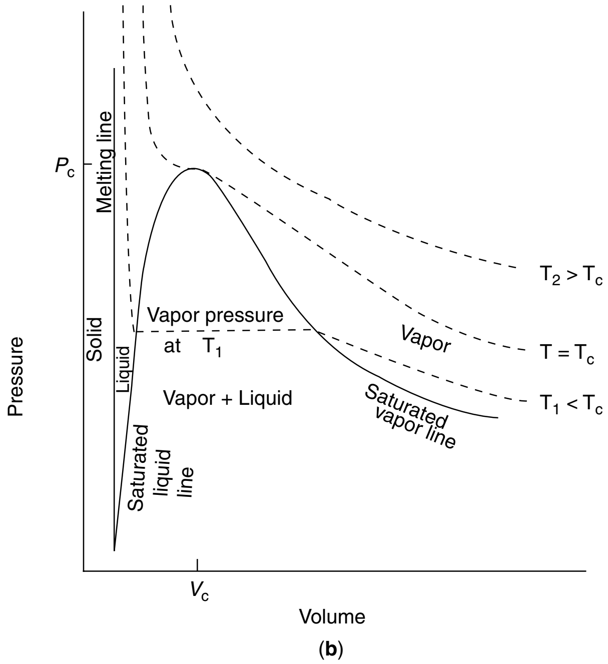

**Fig. 5.** (*Continued*)

the heat of sublimation $\Delta_{S\rightarrow V}\underline{H}$ is positive and the molar volume of the vapor is greater than that of the solid $\Delta_{S\rightarrow V}\underline{V} > 0$, the sublimation pressure increases with increasing temperature. At low temperature and higher pressure, solid–liquid equilibrium occurs. As $\Delta_{S\rightarrow L}\underline{H}$ is positive and the molar volume of the liquid is generally greater than that of the solid $\Delta_{S\rightarrow L}\underline{V} > 0$, the melting pressure increases with increasing temperature, or equivalently, the melting temperature increases with increasing pressure. Note, however, that for water, $\Delta_{S\rightarrow L}\underline{V} < 0$ so that the melting temperature decreases with increasing pressure. Finally, at temperatures above the melting temperature, vapor–liquid equilibrium occurs, and because $\Delta_{L\rightarrow V}\underline{H} > 0$ and $\Delta_{V\rightarrow L}\underline{V} > 0$, the vapor pressure of a liquid $P^{\text{vap}}$ increases with increasing temperature.

As temperature increases, the increased molecular motion in the liquid causes its molar volume to increase, whereas the increasing vapor pressure results in a compression (decrease in molar volume) of the highly compressible vapor. Along the vapor–liquid equilibrium line, a temperature-pressure point is reached at which the densities or molar volumes of the vapor and liquid phases become equal, and the two phases are indistinguishable. This is referred to as the critical point of the fluid, where $T_C$ is the critical temperature and $P_C$ is the critical pressure. At all higher temperatures, only a single fluid phase exists, which is referred to as a supercritical fluid.

At the critical point,

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_{T_c} = 0 \qquad (91)$$

These relations are used to determine values of the temperature-independent part of the parameters in a generalized equation of state. For example, using these conditions with the Peng–Robinson equation (8) gives

$$b = 0.07780\frac{RT_\mathrm{c}}{P_\mathrm{c}} \quad \text{and} \quad a(T) = 0.45724\frac{R^2T_\mathrm{c}^2}{P_\mathrm{c}}\left[1+\kappa\left(1-\sqrt{\frac{T}{T_\mathrm{c}}}\right)\right]^2,$$

$$\text{with} \quad \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

The empirical temperature dependence of the $a(T)$ term has been introduced to provide a good representation of the vapor pressure as a function of temperature using the acentric factor

$$\omega = -1.0 - \log_{10}\left(\frac{P^\mathrm{vap}(T=0.7T_\mathrm{c})}{P_\mathrm{c}}\right) \tag{93}$$

## 12. Fugacity

For real fluids, in analogy with ideal gases, the fugacity of a species is defined as

$$\underline{G}(P,T) = \underline{G}^o(T) + RT\ln\frac{f(T,P)}{P^o} \quad \text{or} \quad \mu(P,T) = \mu^o(T) + RT\ln\frac{f(T,P)}{P^o} \tag{94}$$

and equivalently as

$$\underline{G}(P,T) = \underline{G}^\mathrm{IG}(P,T) + RT\ln\frac{f(T,P)}{P} \quad \text{or} \quad \mu(P,T) = \mu^\mathrm{IG}(P,T) + RT\ln\frac{f(T,P)}{P} \tag{95}$$

In fact, using the Gibbs energy or chemical potential directly in calculations is generally not convenient since, as can be seen from equations 70 and 94, this function goes to negative infinity as the pressure becomes very low (for example, the low sublimation pressure of a solid). It is more convenient to use the fugacity in such calculations, which can be calculated from

$$f(T,P) = P\exp\left[\frac{\underline{G}(T,P)-\underline{G}^\mathrm{IG}(T,P)}{RT}\right] = P\exp\left[\frac{1}{RT}\int_{P=0}^{P}\left(\underline{V}-\frac{RT}{P}\right)dP\right] \tag{96}$$

Note that mathematically the fugacity is better behaved in that as $P \to 0$, so that the fluid becomes an ideal gas, $f(T,P) \to P$. Substituting the fugacity into equation 82 gives as the condition for phase equilibrium:

$$f^\mathrm{I}(T,P) = f^\mathrm{II}(T,P) \tag{97}$$

The fugacity can be computed in several ways, depending on the data available.

1. If an equation of state is available, it may be used directly to compute the fugacity. For example, if the fluid is an ideal gas, one obtains $f(T,P) = P$. If

more complicated equations of state, for example, the van der Waals or Peng–Robinson equations are used, as these are more easily solved for $P$ as a function of $\underline{V}$ than for $\underline{V}$ as a function of $P$, it is best to use the equivalent transformed equation

$$\ln\frac{f(T,P)}{P} = \ln\phi(T,P) = \frac{1}{RT}\int\limits_{\underline{V}=\infty}^{\underline{V}(T,P)}\left[\frac{RT}{\underline{V}} - P\right]d\underline{V} - \ln Z + (Z-1) \qquad (98)$$

where $Z(T,P) = \frac{P\underline{V}(T,P)}{RT}$ is the compressibility factor and $\phi$ is the fugacity coefficient. This equation can be used for both gases and liquids, if an equation of state is available.

2. If an equation of state is not available, which is likely to be the case for a liquid (or solid), but data are available on the molar volume as a function of temperature and pressure, equation 96 can be integrated directly

$$\begin{aligned}\ln\frac{f(T,P)}{P} &= \frac{1}{RT}\int\limits_{P=0}^{P^{\mathrm{vap}}(T)}\left(\underline{V}^{\mathrm{V}} - \frac{RT}{P}\right)dP + \frac{1}{RT}\int\limits_{P^{\mathrm{vap}}(T)}^{P}\left(\underline{V}^{\mathrm{L}} - \frac{RT}{P}\right)dP \\ &= \ln\frac{f(T,P)}{P}\bigg|_{P^{\mathrm{vap}}} + \ln\frac{P^{\mathrm{vap}}(T)}{P} + \frac{1}{RT}\int\limits_{P^{\mathrm{vap}}(T)}^{P}\underline{V}^{\mathrm{L}}dP\end{aligned}$$

or

$$\begin{aligned}f(T,P) &= P^{\mathrm{vap}}(T)\frac{f(T,P)}{P}\bigg|_{P^{\mathrm{vap}}}\exp\left[\int\limits_{P^{\mathrm{vap}}(T)}^{P}\frac{\underline{V}^{\mathrm{L}}}{RT}dP\right] \\ &\approx P^{\mathrm{vap}}(T)\frac{f(T,P)}{P}\bigg|_{P^{\mathrm{vap}}}\exp\left[\frac{\underline{V}^{\mathrm{L}}(P - P^{\mathrm{vap}}(T))}{RT}\right]\end{aligned} \qquad (99)$$

In the last integral term, which is referred to as the Poynting correction, we have used the fact that most liquids are not very compressible; that is, the volume does not change much with pressure and can be taken out of the integral. Several approximations can be made to this equation. If the total pressure is low, and the temperature is such that the vapor pressure of the liquid (or sublimation pressure of a solid) is low, then for a liquid or solid

$$f(T,P) = P^{\mathrm{vap}}(T). \qquad (100)$$

If the pressure on the liquid is much above the vapor pressure, and the vapor pressure is low,

$$f(T,P) = P^{\mathrm{vap}}(T)\exp\left[\frac{\underline{V}^{\mathrm{L}}(P - P^{\mathrm{vap}}(T))}{RT}\right] \qquad (101)$$

## 13. Thermodynamics of Mixtures

**13.1. Partial Molar Properties.** The thermodynamics of mixtures is complicated by the fact that there is an additional variable, the composition of the mixture, and all thermodynamic properties depend on composition. That is, $\theta(N_1, N_2, \ldots N_C, T, P) = N\underline{\theta}(N_1, N_2, \ldots N_C, T, P)$, where $\underline{\theta}$ is any molar state property, $N_i$ is the number of moles of species $i$, and $N$ is the total number of moles in the system. Then,

$$\begin{aligned} dN\underline{\theta}(N_1, N_2, \ldots, N_C, T, P) = {} & \left(\frac{\partial N\underline{\theta}}{\partial T}\right)_{P, N_1, N_2 ..} dT \\ & + \left(\frac{\partial N\underline{\theta}}{\partial P}\right)_{T, N_1, N_2 ..} dP + \sum_{i=1}^{C} \left(\frac{\partial N\underline{\theta}}{\partial N_i}\right)_{T, P, N_{j \neq i}} dN_i \end{aligned} \tag{102}$$

where the subscript $N_{j \neq i}$ signifies that all mole numbers other than $i$ are held constant in taking the partial derivative. Defining a partial molar property as

$$\bar{\theta}_i(T, P, x_1, x_2, \ldots) = \left(\frac{\partial N\underline{\theta}}{\partial N_i}\right)_{T, P, N_{j \neq i}} \tag{103}$$

gives

$$dN\underline{\theta}(N_1, N_2, \ldots, N_C, T, P) = \left(\frac{\partial N\underline{\theta}}{\partial T}\right)_{P, N_1, N_2 ..} dT + \left(\frac{\partial N\underline{\theta}}{\partial P}\right)_{T, N_1, N_2 ..} dP + \sum_{i=1}^{C} \bar{\theta}_i(T, P, \underline{x}) dN_i \tag{104}$$

where we have used that any molar or partial property of a mixture depends on the mole fractions $x_i = N_i / \sum_{j=1}^{C} N_j$ rather than on the number of moles of each species. That is, increasing or decreasing the number of moles of each species by the same factor so that the mole ratios (and mole fractions) remain the same leaves the molar property of a mixture unchanged. It is then easily shown that (2)

$$N\underline{\theta}(x_1, x_2, \ldots, x_C, T, P) = \sum_{j=1}^{C} N_j \bar{\theta}_j(x_1, x_2, \ldots, x_C, T, P) \tag{105}$$

or

$$\underline{\theta}(x_1, x_2, \ldots, x_C, T, P) = \sum_{j=1}^{C} x_j \bar{\theta}_j(x_1, x_2, \ldots, x_C, T, P) \tag{106}$$

Note that because all mole fractions must sum to one, there are only C-1 independent mole fractions in a C-component system.

Thermodynamic state properties are then obtained as the mole fraction weighted sum of the partial molar properties of the system; ie,

$$\begin{aligned}\underline{V}(x_1, x_2, \ldots, x_C, T, P) &= \sum_{j=1}^{C} x_j \bar{V}_j(x_1, x_2, \ldots, x_C, T, P),\\ \underline{H}(x_1, x_2, \ldots, x_C, T, P) &= \sum_{j=1}^{C} x_j \bar{H}_j(x_1, x_2, \ldots, x_C, T, P), \text{ etc.}\end{aligned} \tag{107}$$

The physical interpretation of a partial molar property can be seen by considering, for example, how the total volume of a mixture changes as a result of adding a very small amount of species 1, $\Delta N_1$, to a mixture. The volume change is

$$\begin{aligned}&V(N_1 + \Delta N_1, N_2, \ldots N_C, T, P) - V(N_1, N_2, \ldots N_C, T, P) = \Delta V\\ &\quad = [(N_1 + \Delta N_1)\bar{V}_1 + N_2\bar{V}_2 + N_3\bar{V}_3 \ldots\ldots] - [N_1\bar{V}_1 + N_2\bar{V}_2 + N_3\bar{V}_3 \ldots\ldots]\end{aligned} \tag{108}$$

Now in the limit of $\Delta N_1$ going to zero, the partial molar properties before and after the addition of $\Delta N_1$ can be considered to be identical, so that

$$\lim_{\Delta N_1 \to 0} \Delta V = \Delta N_1 \times \bar{V}_1 \quad \text{or} \quad \lim_{\Delta N_1 \to 0} \frac{\Delta V}{\Delta N_1} = \bar{V}_1 \tag{109}$$

That is, the volume change of the mixture resulting from the addition of a very small number of moles of a species is proportional to the partial molar volume of that component, not to its pure component molar volume. The pure component and partial molar volumes are different. For example, the partial molar volume of a small amount of electrolyte added to an aqueous solution may be negative due to electrostriction.

## 14. Notation for Chemical Reactions and the Balance Equations for a Mixture

A general chemical reaction can be written as

$$\alpha A + \beta B + \ldots \rightleftarrows \rho R + \sigma S + \ldots$$

which will be written as

$$\rho R + \sigma S + \ldots - \alpha A - \beta B - \ldots = 0 \quad \text{or} \quad \sum_{i=1}^{C} \nu_i I_i = 0 \tag{110}$$

where $I$ is the chemical formula of species $i$ and $\nu_i$ is its stoichiometric coefficient (positive for reaction products and negative for reactants). Using this notation, the number of moles of species $i$ present at any time if $N_{i,\text{initial}}$ moles of species $i$ were initially in a system in which only a single reaction occurs is

$$N_i = N_{i,\text{initial}} + \nu_i X \quad \text{where} \quad X = \frac{N_i - N_{i,\text{initial}}}{\nu_i} \tag{111}$$

is the molar extent of reaction and has the important property that it has the same value for each species in the mixture.

The general form of the mass (mole) balance for a species $i$ in a reacting mixture is

$$\frac{dN_i}{dt} = \sum_j \dot{N}_{i,j} + \left(\frac{dN_i}{dt}\right)_{\text{rxn}} \tag{112}$$

where $\dot{N}_{i,j}$ is the flowrate of species $i$ and entry point $j$ and the last term is the rate at which species $i$ is produced (+ value) or consumed (− value) by the chemical reaction. This last term is the rate of internal generation (or destruction) of the species, because the number of moles of a species in a chemically reacting system is not a conserved species (although total mass is). The change in the number of moles of species $i$ over a time interval is

$$\Delta N_i = \sum_j N_{i,j} + (\Delta N_i)_{\text{rxn}} \tag{113}$$

Using the molar extent of reaction, these balances become

$$\frac{dN_i}{dt} = \sum_j \dot{N}_{i,j} + \nu_i \frac{dX}{dt} \quad \text{and} \quad \Delta N_i = \sum_j N_{i,j} + \nu_i \Delta X \tag{114}$$

The energy balance is

$$\frac{d(N\underline{U})}{dt} = \sum_j (\dot{N}\underline{H})_j + \dot{Q} + \dot{W} - P\frac{dV}{dt} \tag{115}$$

which is the same as the pure component energy balance, as we have previously identified all energy flows into and out of the system. However, in using this balance equation, the internal energy, enthalpy, and volume need to be computed from their partial molar properties; that is,

$$U = N\underline{U} = \sum_{i=1}^{\mathrm{C}} N_i \bar{U}_i, \quad (\dot{N}\underline{H})_j = \left(\sum_{i=1}^{\mathrm{C}} \dot{N}_i \bar{H}_i\right)_j, \quad \text{and} \quad V = N\underline{V} = \sum_{i=1}^{\mathrm{C}} N_i \bar{V}_i \tag{116}$$

The energy balance for the change between states 1 and 2 is

$$\Delta U = \Delta(N\underline{U}) = \sum_j \int_1^2 (\dot{N}\underline{H})_j dt + Q + W - \int_1^2 P dV \tag{117}$$

Similarly, the entropy balances are

$$\frac{dS}{dt} = \frac{d(N\underline{S})}{dt} = \sum_j (\dot{N}\underline{S})_j + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}} \tag{118}$$

and

$$\Delta S = \Delta(N\underline{S}) = \int_1^2 \sum_j (\dot{N}\underline{S})_j dt + \int_1^2 \frac{\dot{Q}}{T} dt + S_{\text{gen}} \tag{119}$$

where

$$S = N\underline{S} = \sum_{i=1}^{C} N_i \bar{S}_i \quad \text{and} \quad (\dot{N}\underline{S})_j = \left( \sum_{i=1}^{C} \dot{N}_i \bar{S}_i \right)_j \tag{120}$$

Notice that the reaction term and the heat of reaction do not explicitly appear in the energy and entropy balances. However, they are contained therein, but implicitly. To see this, consider the isothermal continuous flow stirred tank reactor operating in steady state and schematically shown in Figure 6. The mass and energy balances for this reactor are

$$\frac{dN_i}{dt} = 0 = N_{i,\text{in}} - N_{i,\text{out}} + \nu_i \frac{dX}{dt} \quad \text{or} \quad N_{i,\text{out}} = N_{i,\text{in}} + \nu_i \frac{dX}{dt} \tag{121}$$

and

$$\frac{d(N\underline{U})}{dt} = 0 = \sum_{i=1}^{C} N_{i,\text{in}} \bar{H}_{i,\text{in}}(T, P, \underline{x}_{\text{in}}) - \sum_{i=1}^{C} N_{i,\text{out}} \bar{H}_{i,\text{out}}(T, P, \underline{x}_{\text{out}}) + \dot{Q} \tag{122}$$

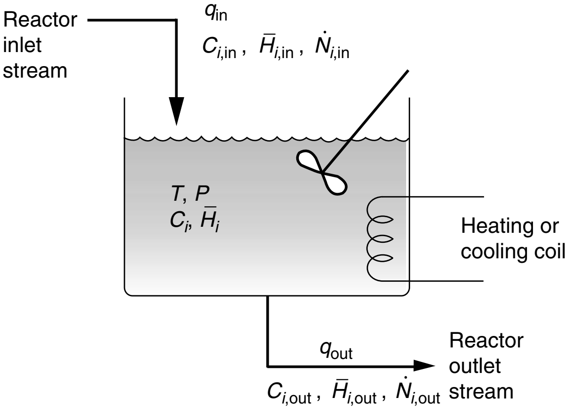

**Fig. 6.** Continuous flow stirred reactor. Adapted from Ref. 2, with permission.

$$\begin{aligned}
\dot{Q} &= \sum_{i=1}^{C} N_{i,\text{out}}\bar{H}_{i,\text{out}}(T,P,\underline{x}_{\text{out}}) - \sum_{i=1}^{C} N_{i,\text{in}}\bar{H}_{i,\text{in}}(T,P,\underline{x}_{\text{in}}) \\
&= \sum_{i=1}^{C} (N_{i,\text{in}} + \nu_i \frac{dX}{dt})\bar{H}_{i,\text{out}}(T,P,\underline{x}_{\text{out}}) - \sum_{i=1}^{C} N_{i,\text{in}}\bar{H}_{i,\text{in}}(T,P,\underline{x}_{\text{in}}) \\
&= \sum_{i=1}^{C} \nu_i \frac{dX}{dt}\bar{H}_{i,\text{out}}(T,P,\underline{x}_{\text{out}}) + \sum_{i=1}^{C} N_{i,\text{in}}[\bar{H}_{i,\text{out}}(T,P,\underline{x}_{\text{out}}) - \bar{H}_{i,\text{in}}(T,P,\underline{x}_{\text{in}})] \\
&= \Delta_{\text{rxn}}H(T,P,\underline{x}_{\text{out}})\frac{dX}{dt} + \sum_{i=1}^{C} N_{i,\text{in}}[\bar{H}_{i,\text{out}}(T,P,\underline{x}_{\text{out}}) - \bar{H}_{i,\text{in}}(T,P,\underline{x}_{\text{in}})]
\end{aligned} \tag{123}$$

The first term on the right is the product of the enthalpy change (heat) of reaction and rate of reaction, and the second term, which is generally very much smaller and usually neglected, depends on how the partial molar enthalpy changes with composition. We see from this equation that the heat flow (either in for an endothermic reaction or out for an exothermic reaction) to keep the reactor at constant temperature is directly proportional to the heat of the reaction. Thus, although the heat of the reaction does not explicitly appear in the energy balance of equation 115, it is contained implicitly through the change in the mole numbers of each species as a result of the chemical reaction.

## 15. State Properties of Mixtures and the Gibbs–Duhem Equation

Considering the Gibbs energy to be a function of temperature, pressure, and the number of moles of each species, using the chain rule of partial differentiation and the definition of a partial molar property, we have

$$\begin{aligned}
dG &= \left(\frac{\partial G}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N_i} dP + \sum_{i=1}^{C}\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i \\
&= -SdT + VdP + \sum_{i=1}^{C}\bar{G}_i dN_i
\end{aligned} \tag{124}$$

In analogy with the pure fluid, defining the chemical potential of a species in a mixture to be equal to the partial molar Gibbs energy, $\bar{\mu}_i = \bar{G}_i$, one obtains

$$dG = -SdT + VdP + \sum_{i=1}^{C}\bar{\mu}_i dN_i \tag{125}$$

Similarly, following the same procedure as used in the analysis of pure fluids, one obtains

$$dH = TdS + VdP + \sum_{i=1}^{C}\bar{G}_i dN_i = TdS + VdP + \sum_{i=1}^{C}\bar{\mu}_i dN_i \tag{126}$$

$$dU = TdS - PdV + \sum_{i=1}^{C}\bar{G}_i dN_i = TdS - PdV + \sum_{i=1}^{C}\bar{\mu}_i dN_i \tag{127}$$

and

$$dA = -SdT - PdV + \sum_{i=1}^{C}\bar{G}_i dN_i = -SdT - PdV + \sum_{i=1}^{C}\bar{\mu}_i dN_i \tag{128}$$

Note that one can also write

$$dG = d\left(\sum_{i=1}^{C}N_i\bar{G}_i\right) = \sum_{i=1}^{C}\bar{G}_i(dN_i) + \sum_{i=1}^{C}N_i d\bar{G}_i = \sum_{i=1}^{C}\bar{\mu}_i(dN_i) + \sum_{i=1}^{C}N_i d\bar{\mu}_i \tag{129}$$

Subtracting equation 129 from equation 124 gives the Gibbs–Duhem equation

$$0 = -SdT + VdP - \sum_{i=1}^{C}N_i d\bar{G}_i = -SdT + VdP - \sum_{i=1}^{C}N_i d\bar{\mu}_i \tag{130}$$

For systems at constant temperature and constant pressure, this equation becomes

$$\begin{aligned} &\sum_{i=1}^{C}N_i d\bar{G}_i = 0 \quad \text{and} \quad \sum_{i=1}^{C}x_i d\bar{G}_i = 0 \quad \text{or equivalently} \\ &\sum_{i=1}^{C}N_i d\bar{\mu}_i = 0 \quad \text{and} \quad \sum_{i=1}^{C}x_i d\bar{\mu}_i = 0 \end{aligned} \tag{131}$$

This equation is a constraint on how the partial molar Gibbs energy of each species in a mixture can change as a result of changes in composition. For a binary mixture, this equation is

$$x_1\left(\frac{\partial\bar{G}_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\bar{G}_2}{\partial x_1}\right)_{T,P} = 0 = x_1\left(\frac{\partial\bar{\mu}_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\bar{\mu}_2}{\partial x_1}\right)_{T,P} \tag{132}$$

It can be shown using similar arguments that for other partial molar properties, the analogous equation

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right)_{T,P} = 0 \tag{133}$$

applies. Equations 132 and 133 are useful in several ways, including in the experimental determination of partial molar properties and in testing the consistency of experimental data.

## 16. The Ideal Gas Mixture

An ideal gas mixture (IGM) is one in which at all temperatures, pressures, and compositions, the volumetric equation of state is

$$PV^{\mathrm{IGM}} = NRT = RT\sum_{i=1}^{\mathrm{C}} N_i \tag{134}$$

and the internal energy of the mixture is related to that of the pure components as ideal gases (IG) by

$$U^{\mathrm{IGM}}(T, P, \underline{N}) = \sum_{i=1}^{\mathrm{C}} N_i \underline{U}_i^{\mathrm{IG}}(T, P) \tag{135}$$

from which it follows that

$$\bar{V}_i^{\mathrm{IGM}}(T, P, \underline{x}) = \frac{RT}{P} = \underline{V}_i^{\mathrm{IG}}(T, P);\ \bar{U}_i^{\mathrm{IGM}}(T, P, \underline{x}) = \underline{U}_i^{\mathrm{IG}}(T, P);$$

and

$$\bar{H}_i^{\mathrm{IGM}}(T, P, \underline{x}) = \underline{H}_i^{\mathrm{IG}}(T, P) \tag{136}$$

The partial molar entropy of an ideal gas mixture is somewhat more complicated. Forming an ideal gas mixture from its pure components at constant temperature and constant pressure results in each component $i$ before mixing being contained in a volume

$$V_{i,\mathrm{initial}} = \frac{N_i RT}{P} \tag{137}$$

and after mixing being contained in the larger volume

$$V_{\mathrm{final}} = \frac{NRT}{P} = \frac{\sum_{i=1}^{\mathrm{C}} N_i RT}{P} \tag{138}$$

As was shown earlier

$$d\underline{S} = \frac{C_{\mathrm{V}}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V}$$

which at constant temperature for an ideal gas becomes

$$d\underline{S}^{\mathrm{IG}} = \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V} = \frac{R}{\underline{V}} d\underline{V} \tag{139}$$

In preparing an ideal gas mixture at constant temperature and constant pressure from its pure components at the same temperature and pressure, each species $i$ experiences the change in accessible volume above so that

$$\begin{aligned}\underline{S}_{i,\text{final}}(T,P,\underline{x}) - \underline{S}_{i,\text{initial}}(T,P) &= R\ln\frac{\underline{V}_{\text{final}}(T,P,\underline{x})}{\underline{V}_{i,\text{initial}}(T,P)} \\ &= R\ln\frac{RT\sum_{i=1}^{C}N_i/P}{RTN_i/P} = R\ln\frac{1}{x_i} = -R\ln x_i\end{aligned} \tag{140}$$

As the final state of the species is in a mixture, the final entropy is the partial molar entropy, so that the relation between the ideal gas mixture partial molar entropy and the pure component molar entropy at the same temperature and same pressure is

$$\bar{S}_i^{\text{IGM}}(T,P,\underline{x}) = \underline{S}_i^{\text{IG}}(T,P) - R\ln x_i \tag{141}$$

It then follows that

$$\bar{G}_i^{\text{IGM}}(T,P,\underline{x}) = \underline{G}_i^{\text{IG}}(T,P) + RT\ln x_i \quad \text{and} \quad \bar{A}_i^{\text{IGM}}(T,P,\underline{x}) = \underline{A}_i^{\text{IG}}(T,P) + RT\ln x_i \tag{142}$$

## 17. The Ideal Mixture and Excess Properties

An ideal mixture (IM) is one in which at all temperatures and pressures,

$$\bar{V}_i^{\text{IM}}(T,P,\underline{x}) = \underline{V}_i(T,P) \quad \text{and} \quad \bar{U}_i^{\text{IM}}(T,P,\underline{x}) = \underline{U}_i(T,P) \tag{143}$$

Although these look like the relations for an ideal gas mixture, they differ from those in the very important way that the pure component properties here are those of the real substance (in its gas, liquid, or solid state), and not those of an ideal gas. From these properties, one obtains

$$\begin{aligned}&\bar{H}_i^{\text{IM}}(T,P,\underline{x}) = \underline{H}_i(T,P);\ \bar{S}_i^{\text{IM}}(T,P,\underline{x}) = \underline{S}_i(T,P) - R\ln x_i; \\ &\bar{G}_i^{\text{IM}}(T,P,\underline{x}) = \underline{G}_i(T,P) + RT\ln x_i \quad \text{and} \quad \bar{A}_i^{\text{IM}}(T,P,\underline{x}) = \underline{A}_i(T,P) + RT\ln x_i\end{aligned} \tag{144}$$

Very few mixtures are ideal mixtures (and fewer still are ideal gas mixtures). One way to indicate the deviation from ideal mixture behavior is to use the difference between the properties of the real mixture and that of an ideal mixture of the same components at the same temperature, same pressure, and same state of aggregation (that is, the pure components should be in the same phase when pure as they are in the mixture). The excess properties are defined as

$$
\begin{aligned}
V^{\mathrm{ex}}(T,P,\underline{x}) = \sum_{i=1}^{\mathrm{C}} N_i \bar{V}_i(T,P,\underline{x}) - \sum_{i=1}^{\mathrm{C}} N_i \underline{V}_i(T,P) &= \sum_{i=1}^{\mathrm{C}} N_i [\bar{V}_i(T,P,\underline{x}) - \underline{V}_i(T,P)] \\
U^{\mathrm{ex}}(T,P,\underline{x}) &= \sum_{i=1}^{\mathrm{C}} N_i [\bar{U}_i(T,P,\underline{x}) - \underline{U}_i(T,P)] \\
H^{\mathrm{ex}}(T,P,\underline{x}) &= \sum_{i=1}^{\mathrm{C}} N_i [\bar{H}_i(T,P,\underline{x}) - \underline{H}_i(T,P)] \\
S^{\mathrm{ex}}(T,P,\underline{x}) &= \sum_{i=1}^{\mathrm{C}} N_i [\bar{S}_i(T,P,\underline{x}) - [\underline{S}_i(T,P) - R\ln x_i]] \\
G^{\mathrm{ex}}(T,P,\underline{x}) &= \sum_{i=1}^{\mathrm{C}} N_i [\bar{G}_i(T,P,\underline{x}) - [\underline{G}_i(T,P) + RT\ln x_i]]
\end{aligned}
\tag{145}
$$

and

$$
A^{\mathrm{ex}}(T,P,\underline{x}) = \sum_{i=1}^{\mathrm{C}} N_i [\bar{A}_i(T,P,\underline{x}) - [\underline{A}_i(T,P) + RT\ln x_i]]
$$

It then follows that for any partial molar property $\bar{\theta}_i(T,P,\underline{x})$,

$$
\bar{\theta}_i(T,P,\underline{x}) = \bar{\theta}_i^{\mathrm{IM}}(T,P,\underline{x}) + \bar{\theta}_i^{\mathrm{ex}}(T,P,\underline{x}) \tag{146}
$$

or

$$
\begin{aligned}
\bar{\theta}_i(T,P,\underline{x}) &= \underline{\theta}_i(T,P) + \bar{\theta}_i^{\mathrm{ex}}(T,P,\underline{x}), \quad \text{if} \quad \theta = V, U \,\text{or}\, H \\
\bar{\theta}_i(T,P,\underline{x}) &= \underline{\theta}_i(T,P) + \bar{\theta}_i^{\mathrm{ex}}(T,P,\underline{x}) - RT\ln x_i, \quad \text{if} \quad \theta = G \,\text{or}\, A
\end{aligned}
$$

and

$$
\bar{S}_i(T,P,\underline{x}) = \underline{S}_i(T,P) + \bar{S}_i^{\mathrm{ex}}(T,P,\underline{x}) + R\ln x_i \tag{147}
$$

One procedure for estimating the properties of mixtures is to calculate separately the pure component and excess properties, which leads to the activity coefficient description to be used shortly.

## 18. Criteria for Phase and Chemical Equilibrium in Multicomponent Mixtures

The energy and entropy balances for the multicomponent system considered above are identical in form to those for a pure component, and they differ only in that the

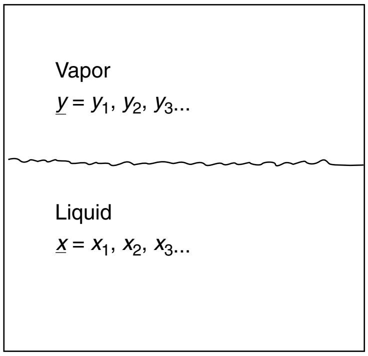

**Fig. 7.** Closed container containing a vapor and liquid in equilibrium.

properties are now calculated as a sum over all components of the mole fraction (or mole number) weighted partial molar properties. It therefore follows that the same general criteria equilibrium developed earlier apply here as well.

Entropy $S$ is a maximum for a closed system maintained at constant $U$ and $V$
Helmholtz energy $A$ is a minimum for a closed system
maintained at constant $T$ and $V$
Gibbs energy $G$ is a minimum for a closed system at constant $T$ and $P$.
(148)

Consider the closed container shown in Figure 7 that is held at fixed temperature and fixed pressure, in which there is no chemical reaction and within which two phases are at equilibrium, either a vapor and a liquid, two liquids, a solid and a liquid, or a solid and a vapor. We denote these two phases as I and II, and the number of moles of each species is

$$N_{i,\,\mathrm{total}} = N_i^{\mathrm{I}} + N_i^{\mathrm{II}} \tag{149}$$

As shown, the condition for equilibrium is that the total Gibbs energy should be a minimum, which here the sum of the Gibbs energies of the two phases

$$G = G^{\mathrm{I}} + G^{\mathrm{II}} = \sum_{i=1}^{\mathrm{C}} N_i^{\mathrm{I}} \bar{G}_i^{\mathrm{I}}(T, P, \underline{x}^{\mathrm{I}}) + \sum_{i=1}^{\mathrm{C}} N_i^{\mathrm{II}} \bar{G}_i^{\mathrm{II}}(T, P, \underline{x}^{\mathrm{II}}) \tag{150}$$

subject to the constraints of constant (and uniform) temperature, constant (and uniform) pressure, and constant total number of moles of each species (as there is no chemical reaction). To find the equilibrium state, $dG$ is set to zero subject to $dN_{i,\,\mathrm{total}} = 0 = dN_i^{\mathrm{I}} + dN_i^{\mathrm{II}}$ or $dN_i^{\mathrm{II}} = -dN_i^{\mathrm{I}}$. Thus,

$$\begin{aligned} dG = 0 = dG^{\mathrm{I}} + dG^{\mathrm{II}} &= \sum_{i=1}^{\mathrm{C}} \bar{G}_i^{\mathrm{I}}(T, P, \underline{x}^{\mathrm{I}}) dN_i^{\mathrm{I}} + \sum_{i=1}^{\mathrm{C}} \bar{G}_i^{\mathrm{II}}(T, P, \underline{x}^{\mathrm{II}}) dN_i^{\mathrm{II}} \\ &+ \sum_{i=1}^{\mathrm{C}} N_i^{\mathrm{I}} d\bar{G}_i^{\mathrm{I}}(T, P, \underline{x}^{\mathrm{I}}) + \sum_{i=1}^{\mathrm{C}} N_i^{\mathrm{II}} d\bar{G}_i^{\mathrm{II}}(T, P, \underline{x}^{\mathrm{II}}) \end{aligned} \tag{151}$$

Each of the last two terms is separately equal to zero by the Gibbs–Duhem equation (eq. 131) applied to each phase and using $dN_i^{\mathrm{II}} = -dN_i^{\mathrm{I}}$ gives

$$0 = \sum_{i=1}^{\mathrm{C}} [\bar{G}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) - \bar{G}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}})]dN_i^{\mathrm{I}} \tag{152}$$

As this must be true for all variations of the independent variables, that is, for all values of each $dN_i^{\mathrm{I}}$, the condition for phase equilibrium is

$$\bar{G}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{G}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \quad \text{or} \quad \bar{\mu}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{\mu}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \text{ for each species } i \tag{153}$$

To obtain the condition for chemical equilibrium of a single reaction in a closed single-phase system at constant temperature and constant pressure, the starting point is again that the Gibbs energy must be a minimum, so that

$$dG = 0 = \sum_{i=1}^{\mathrm{C}} \bar{G}_i(T,P,\underline{x})dN_i + \sum_{i=1}^{\mathrm{C}} N_i d\bar{G}_i(T,P,\underline{x}) \tag{154}$$

The second term on the right-hand side is zero by the Gibbs–Duhem equation. Here, however, each mole number is not independent, but interrelated to all others by stoichiometry through the molar extent of reaction variable. That is, $dN_i = \nu_i dX$, so that

$$0 = \sum_{i=1}^{\mathrm{C}} \nu_i \bar{G}_i(T,P,\underline{x})dX \quad \text{or} \quad 0 = \sum_{i=1}^{\mathrm{C}} \nu_i \bar{\mu}_i(T,P,\underline{x})dX \tag{155}$$

for all possible variations of $X$, that is, all values of $dX$ (consistent with the constraints, such as initial numbers of moles of each species). So the condition for chemical equilibrium in a single-reaction system is

$$\sum_{i=1}^{\mathrm{C}} \nu_i \bar{G}_i(T,P,\underline{x}) = \sum_{i=1}^{\mathrm{C}} \nu_i \bar{\mu}_i(T,P,\underline{x}) = 0 \tag{156}$$

The generalization to multireaction systems is

$$\sum_{i=1}^{\mathrm{C}} \nu_{ij} \bar{G}_i(T,P,\underline{x}) = \sum_{i=1}^{\mathrm{C}} \nu_{ij} \bar{\mu}_i(T,P,\underline{x}) = 0 \quad \text{for each reaction } j \tag{157}$$

where $\nu_{ij}$ is the stoichiometric coefficient for species $i$ in reaction $j$. To avoid redundancies and unnecessary complications in a multireaction system, it is only necessary to consider a set of independent reactions. That is, a set of reactions in which no reaction is a linear combination of the others. It is important to note that although there will not be a unique independent reaction set, that is, several independent reaction sets can be formed from a set of redundant reactions, all will have the same number of independent reactions, and any one of the sets can be used in thermodynamic calculations and will lead to the same result.

The further generalization to a multireaction, multiphase system is

$$\bar{G}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{G}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \text{ or } \bar{\mu}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{\mu}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \text{ for each species } i \tag{158}$$

and

$$\sum_{i=1}^{C} \nu_{ij}\bar{G}_i^P(T,P,\underline{x}^P) = 0 = \sum_{i=1}^{C} \nu_{ij}\bar{\mu}_i^P(T,P,\underline{x}^P) \text{ for each reaction } j \text{ in each phase } P$$

Note that by phase equilibrium condition (eq. 153), if the chemical equilibrium condition (eq. 147) is satisfied in one phase, it will be satisfied in all phases. However, the compositions that satisfy these equations will be different in each phase. In using these equations to solve multireaction problems, again only a set of independent reactions should be used.

It can also be shown that precisely the same conditions for chemical and phase equilibrium are obtained in a system subject to constraints other than constant temperature and pressure, for example, constant temperature and volume.

## 19. Fugacity of a Species in a Mixture

To compute the equilibrium compositions of the coexisting phases, it is necessary to replace the equality of partial molar Gibbs energies with relations among temperature, pressure, and composition. In fact, the partial molar Gibbs energy is not a convenient function to use because as a species becomes very dilute (ie, $x_i \to 0$), $\bar{G}_i \to -\infty$. A more well-behaved quantity is the fugacity of a species in a mixture, $\bar{f}_i(T,P,\underline{x})$, which in analogy with the pure fluid is defined as

$$\bar{G}_i(P,T,\underline{x}) = \bar{G}_i^{\mathrm{IGM}}(P,T,\underline{x}) + RT\ln\frac{\bar{f}_i(T,P,\underline{x})}{P}$$

or equivalently

$$\bar{\mu}_i(P,T,\underline{x}) = \bar{\mu}_i^{\mathrm{IGM}}(P,T,\underline{x}) + RT\ln\frac{\bar{f}_i(T,P,\underline{x})}{P} \tag{159}$$

The following expression can be used to compute the fugacity of a species in a mixture:

$$\begin{aligned}
\bar{f}_i(T,P,\underline{x}) &= x_i P \exp\left[\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IGM}}(T,P,\underline{x})}{RT}\right] \\
&= x_i P \exp\left[\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IM}}(T,P,\underline{x}) + \bar{G}_i^{\mathrm{IM}}(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IGM}}(T,P)}{RT}\right] \\
&= x_i P \exp\left[\frac{\bar{G}_i(T,P,\underline{x}) - \bar{G}_i^{\mathrm{IM}}(T,P,\underline{x}) + \underline{G}_i(T,P,\underline{x}) - \underline{G}_i^{\mathrm{IG}}(T,P)}{RT}\right] \\
&= x_i\, f_i(T,P) \exp\left[\frac{\bar{G}_i(T,P,\underline{x}) - \underline{G}_i^{\mathrm{IM}}(T,P)}{RT}\right] = x_i\, f_i(T,P) \exp\left[\frac{\bar{G}_i^{\mathrm{ex}}(T,P,\underline{x})}{RT}\right]
\end{aligned} \tag{160}$$

where $f_i(T,P)$ is the fugacity of pure species $i$ defined earlier. The activity coefficient of a species in a mixture $\gamma_i$ is defined to be

$$\gamma_i(T,P,\underline{x}) = \exp\left[\frac{\bar{G}_i^{\text{ex}}(T,P,\underline{x})}{RT}\right] \tag{161}$$

With this definition, the fugacity of a species in a liquid mixture is

$$\bar{f}_i^L(T,P,\underline{x}) = x_i\gamma_i(T,P,\underline{x})\, f_i(T,P) \tag{162}$$

The analogous expression for the partial molar Gibbs energy is

$$\bar{G}_i(T,P,\underline{x}) = \underline{G}_i(T,P) + RT\ln(x_i\gamma_i) \tag{163}$$

and more generally for any mixture (vapor or liquid)

$$\bar{G}_i(T,P,\underline{x}) = \underline{G}_i(T,P) + RT\ln\frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P)} = \underline{G}_i + RT\ln a_i(T,P,\underline{x}) \tag{164}$$

where

$$a_i(T,P,\underline{x}) = \frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P)} \tag{165}$$

is referred to as the activity of species $i$. If the vapor pressure of the pure liquid and the total pressure are not too high, the fugacity of a species in a liquid mixture is

$$\bar{f}_i^L(T,P,\underline{x}) = x_i\gamma_i(T,P,\underline{x})P_i^{\text{vap}}(T) \quad \text{and} \quad a_i^L(T,P,\underline{x}) = x_i\gamma_i(T,P,\underline{x}) \tag{166}$$

In the simple case of an ideal mixture,

$$\bar{f}_i^L(T,P,\underline{x}) = x_i\, f_i(T,P) \quad \text{and} \quad a_i(T,P,\underline{x}) = x_i \tag{167}$$

This is the Lewis–Randall rule.

An important property of the fugacity is that when used in equation 153, the condition for equilibrium becomes

$$\bar{f}_i^{\text{I}}(T,P,\underline{x}^{\text{I}}) = \bar{f}_i^{\text{II}}(T,P,\underline{x}^{\text{II}})\,\text{for each species}\,i \tag{168}$$

If a mixture equation of state is available, the fugacity of a species in a mixture can be computed from

$$\ln\frac{\bar{f}_i(T,P,\underline{x})}{x_iP} = \ln\bar{\phi}_i(T,P,\underline{x}) = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,\underline{V},N_{j\neq i}}\right]d\underline{V} - \ln Z(T,P,\underline{x}) \tag{169}$$

where $\bar{\phi}_i(T, P, \underline{x})$ is the fugacity coefficient for species $i$ in the mixture. If an equation of state is not available, then equation 162 is used with the partial molar excess Gibbs energy calculated from a model with parameters that have been fitted to some experimental data (see, for example, the models in Refs. 10 and 11), have been estimated, for example, using a group contribution model such as UNIFAC (12,13); or more recently have been estimated from quantum mechanics (14). A very simple excess Gibbs energy model for a binary mixture is $\underline{G}^{\mathrm{ex}}(T, P, \underline{x}) = \Gamma x_1 x_2$, which satisfies the boundary conditions that in the pure component limits (ie, $x_1 \to 1 \,\mathrm{or}\, x_2 \to 1$), the excess Gibbs energy is zero. With this model, we have

$$\begin{aligned}\bar{G}_1^{\mathrm{ex}}(T, P, \underline{x}) &= \left(\frac{\partial(N\underline{G}^{\mathrm{ex}})}{\partial N_1}\right)_{T,P,N_2} = \Gamma\left(\frac{\partial N x_1 x_2}{\partial N_1}\right)_{T,P,N_2} = \Gamma\left(\frac{\partial}{\partial N_1}\frac{N_1 N_2}{N_1 + N_2}\right)_{T,P,N_2} \\ &= \Gamma\frac{N_2^2}{(N_1 + N_2)^2} = \Gamma x_2^2 = \Gamma(1 - x_1)^2\end{aligned} \tag{170}$$

So that

$$\ln \gamma_1(T, P, \underline{x}) = \frac{\Gamma x_2^2}{RT} = \frac{\Gamma(1 - x_1)^2}{RT}$$

and similarly

$$\ln \gamma_2(T, P, \underline{x}) = \frac{\Gamma x_1^2}{RT} = \frac{\Gamma(1 - x_2)^2}{RT} \tag{171}$$

There are many more complex and accurate models for the excess Gibbs energy and activity coefficients of mixtures discussed elsewhere (1,10,11). These include the Van Laar, Wilson, NRTL, UNIQUAC, and other models.

## 20. Types of Mixture Phase Equilibrium Calculations

Below is a list of the common types of phase equilibrium calculations.

1. *Bubble point calculation*: The composition of a liquid is fixed, and either the temperature is increased at fixed pressure or the pressure is decreased at fixed temperature until the first infinitesimal bubble of vapor is formed. In this case, one wants the composition of the equilibrium vapor and the bubble point temperature (if pressure is fixed) or bubble point pressure (if temperature is fixed).
2. *Dew point calculation*: The composition of a vapor is fixed, and either the temperature is decreased at fixed pressure or the pressure is increased at fixed temperature until the first infinitesimal drop of liquid (dew) is formed. Here one wants the composition of the equilibrium liquid and the dew point temperature (if pressure is fixed) or dew point pressure (if temperature is fixed).

3. *Flash calculation*: A liquid of known initial composition undergoes a change in pressure and/or temperature, so a significant amount of vapor is formed, but the liquid is not completely vaporized. Here one wants to know the amounts of vapor and liquid present, and the compositions of vapor and liquid phases at a specified temperature and pressure.
4. *Adiabatic flash calculation*: A liquid of known initial composition, temperature, and pressure undergoes an adiabatic change in pressure, for example, as a result of a Joule–Thomson expansion through a pressure-reducing valve, to a specified final pressure, so that a significant amount of vapor is formed, but the liquid is not completely vaporized. Here one wants to know the final temperature, the amounts of vapor and liquid formed, and the compositions of vapor and liquid phases.
5. *Liquid–liquid equilibrium*: Two liquids of limited mutual solubility are mixed. Here one wants to know the amounts and equilibrium compositions of the two liquid phases at a specified temperature.
6. *Vapor–liquid–liquid equilibrium*: Two liquids of limited mutual solubility are mixed and the temperature and/or pressure varied to result in the formation of some vapor. Here one wants to know the amounts and equilibrium compositions of the two liquid phases and the vapor at a specified temperature and pressure.

Other types of phase equilibrium calculations include the solubility of a gas in a liquid, solid–liquid and solid–liquid–liquid equilibrium, and the freezing point depression of a liquid due to the presence of a solute. The important point is that these phase equilibrium calculations are based on equation 142, the equality of the partial molar Gibbs energies (or chemical potentials) of each species in each phase, or equivalently (and more conveniently), on equation 156, the equality of the fugacities of each species in each phase.

## 21. The Gibbs Phase Rule

To fix the thermodynamic state of a single phase of a pure component, it has been found from experiments that two independent state variables, such as pressure and temperature, are needed. Then the values of all other properties, such as the molar volume, molar enthalpy, and molar entropy, are fixed. To fix the properties of a single phase of a C-component mixture, two independent state variables must be fixed, as well as C-1 mole fractions (the remaining mole fraction is not independent because the mole fractions must sum to unity). That is, to fix the thermodynamic state of a single-phase C component mixture, a total of $\mathrm{C}+1$ independent state variables must be specified.

For an equilibrium system of P phases and M independent chemical reactions, it might appear that $\mathrm{P}(\mathrm{C}+1)$ properties need to be specified to fix all its properties. However, the temperature must be equal in all phases, $T^{\mathrm{I}} = T^{\mathrm{II}} = \ldots = T^{\mathrm{P}}$, so that fixing the temperature in one phase fixes the temperature in the remaining $\mathrm{P}-1$ phases and reduces the number of variables that must be specified, or the number of degrees of freedom, by $\mathrm{P}-1$. Similarly, that the pressure must be the same in all phases $P^{\mathrm{I}} = P^{\mathrm{II}} = \ldots = P^{\mathrm{P}}$ reduces the number of degrees of freedom by an additional $P-1$. As for each C species its fugacity must be the same in each phase, $\bar{f}_i^{\,\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{f}_i^{\,\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) = \ldots = \bar{f}_i^{\,\mathrm{P}}(T,P,\underline{x}^{\mathrm{P}})$ further reduces the number of degrees of freedom by $\mathrm{C(P-1)}$. Finally, if there are M independent chemical reactions, the condition for chemical equilibrium of equation 157 $\sum_{i=1}^{\mathrm{C}} \nu_{ij} \bar{G}_i(T,P,\underline{x}) = 0$ for each of the M independent reactions places additional M restrictions on the variables and reduces the degrees of freedom by that number. Therefore, in a C-component system of P phases in which M independent chemical reactions occur, the actual number of degrees of freedom is

$$\begin{aligned}\text{Degrees of freedom} &= \mathrm{P(C+1) - (P-1) - (P-1) - C(P-1) - M} \\ &= \mathrm{C - P - M + 2}\end{aligned} \tag{172}$$

This relation is known as the Gibbs phase rule. It is useful in determining how many state variables are needed to fix the properties of a mixture and, consequently, to determine whether enough information has been provided to solve a problem. For example, from the Gibbs phase rule, we find that to fix the properties of a single-phase, binary mixture in which there are no chemical reactions, $2 - 1 - 0 + 2 = 3$ properties are needed, such as temperature, pressure, and the mole fraction of one species. However, if two phases are present (for example, a vapor and a liquid), the system has only $2 - 2 - 0 + 2 = 2$ degrees of freedom. In this case, fixing the temperature and the mole fraction of one phase is sufficient to determine the equilibrium pressure and mole fraction of the remaining phase, or fixing the temperature and pressure fixes the mole fractions of both phases. How to determine these compositions is discussed below. If three phases (e.g., liquid–liquid–vapor) are present at equilibrium, the system has only $2 - 3 - 0 + 2 = 1$ degrees of freedom. That is, if the temperature, the pressure, or the mole fraction in one phase is specified, the values of all other state variables can, in principle, be determined.

## 22. Vapor–Liquid Equilibrium Calculations

In the chemical industry, the phase equilibrium calculations needed are frequently at low-to-moderate pressures for mixtures for which an equation of state is not available, for example, aqueous solutions and/or mixtures containing organic acids, alcohols, and other polar compounds. At low pressures, the vapor phase can frequently be considered an ideal gas mixture, so that denoting the vapor compositions by $y_i$,

$$\bar{f}_i^{V}(T,P,y) = y_i P \tag{173}$$

For the liquid phase at low pressure,

$$\bar{f}_i^{L}(T,P,\underline{x}) = x_i \gamma_i(T,P,\underline{x}) P_i^{\mathrm{vap}}(T) \tag{174}$$

so that at equilibrium

$$x_i \gamma_i(T,P,\underline{x}) P_i^{\mathrm{vap}}(T) = y_i P \tag{175}$$

where because the vapor-phase mole fraction must sum to one, the equilibrium pressure is

$$\sum_{i=1}^{C} x_i \gamma_i(T, P, \underline{x}) P_i^{\text{vap}}(T) = P \sum_{i=1}^{C} y_i = P \tag{176}$$

For the case of an ideal mixture ($G^{\text{ex}} = 0$ and therefore all $\gamma_i = 1$), these equations reduce to

$$y_i = \frac{x_i(T, P, \underline{x}) P_i^{\text{vap}}(T)}{P} \quad \text{and} \quad P = \sum_{i=1}^{C} x_i P_i^{\text{vap}}(T) \tag{177}$$

which indicates the equilibrium pressure in a linear function of a mole fraction. This is referred to as Raoult's law, and equation 176 is the modified Raoult's law. An example of the vapor–liquid equilibrium in a mixture that is almost ideal is shown in Figure 8, which shows the total pressure as a function of both the vapor and the liquid compositions at fixed temperature. Note that the total pressure is a linear function of liquid composition. Also one of many tie lines, that is, lines of constant pressure connecting the equilibrium vapor and liquid compositions, has been drawn.

Most mixtures are not ideal, so that the composition-dependent activity coefficients are not unity and the equilibrium pressure is not a linear function of liquid mole fraction; examples are shown in Figures 9 and 10. An interesting feature of Figure 10 is that the equilibrium pressure at fixed temperature has a maximum at a function of composition. It can easily be shown that at the composition at which this occurs, the vapor and liquid compositions are identical. These are referred to as the azeotropic point and

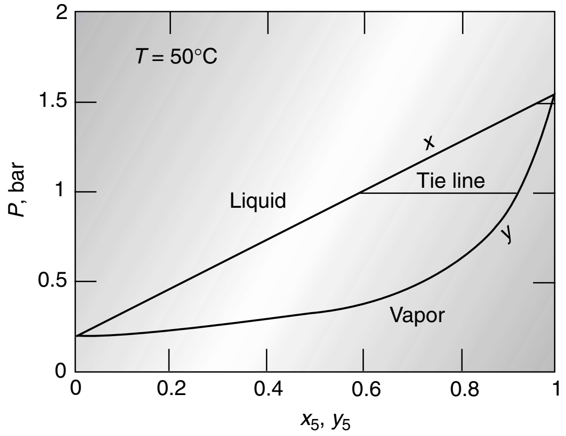

**Fig. 8.** $P$ - $x$ - $y$ vapor–liquid equilibrium diagram of an ideal mixture: *n*-pentane + *n*-heptane at 50°C. One tie line connecting the compositions of the coexisting vapor and liquid phases is shown. Adapted from Ref. 2, with permission.

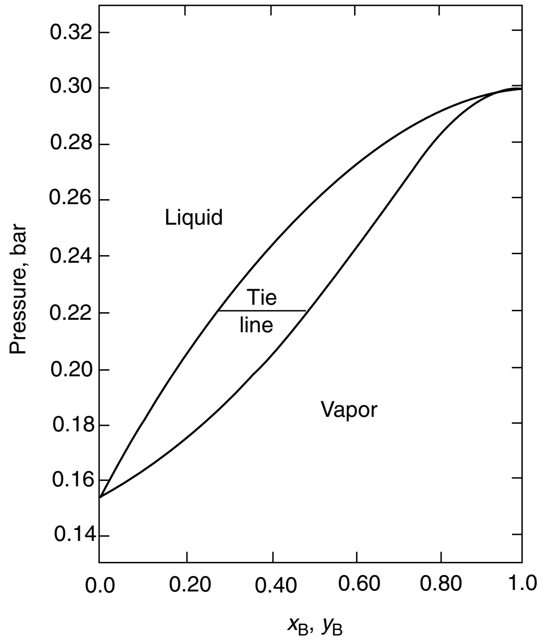

**Fig. 9.** $P$ - $x$ - $y$ vapor–liquid equilibrium diagram of a slightly nonideal mixture: benzene + $n$-heptane at 45°C. One tie line connecting the compositions of the coexisting vapor and liquid phases is shown. Adapted from Ref. 2, with permission.

the azeotropic composition. There are also azeotropes in which the equilibrium pressure at fixed temperature is a minimum, although those are somewhat less common. Data such as those in these figures are easily correlated using one of the excess Gibbs energy or activity coefficient models mentioned earlier.

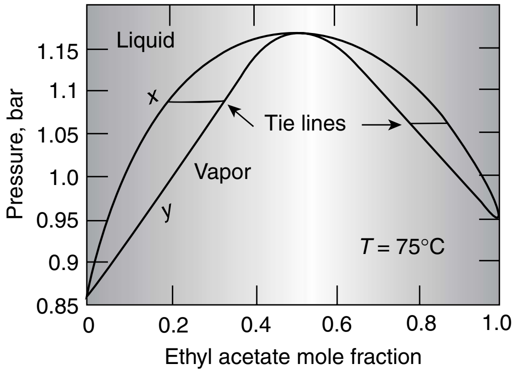

**Fig. 10.** $P$ - $x$ - $y$ vapor–liquid equilibrium diagram of nonideal mixture exhibiting a maximum pressure (minimum boiling) azeotropic mixture: ethyl acetate + benzene at 75°C. Two tie lines connecting the compositions of the coexisting vapor and liquid phases are shown. Adapted from Ref. 2, with permission.

In the fuels and petrochemical industries, processing at high pressures occurs, but generally it only involves hydrocarbons, inorganic gases (ie, oxygen, nitrogen, etc), and other relatively nonpolar species. In such cases, it is common to use an equation of state for mixtures that is applicable to both the vapor and the liquid phases, such as the Peng–Robinson equation:

$$P = \frac{RT}{\underline{V} - b_{\text{mix}}} - \frac{a_{\text{mix}}(T)}{\underline{V}(\underline{V} + b_{\text{mix}}) + b_{\text{mix}}(\underline{V} - b_{\text{mix}})} \tag{178}$$

The parameters in these (and related) equations of state for mixtures are generally obtained from the pure component equation-of-state parameters using the van der Waals one-fluid mixing rules:

$$a_{\text{mix}}(T, \underline{x}) = \sum_{i=1}^{C}\sum_{j=1}^{C} x_i x_j a_{ij}(T) \quad \text{and} \quad b_{\text{mix}}(\underline{x}) = \sum_{i=1}^{C}\sum_{j=1}^{C} x_i x_j b_{ij} \tag{179}$$

and the combining rules:

$$a_{ij}(T) = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \quad \text{and} \quad b_{ij} = \frac{1}{2}(b_{ii} + b_{jj}) \quad \text{so that}\, b(\underline{x}) = \sum_{i=1}^{C} x_i b_{ii} \tag{180}$$

In these equations, $a_{ii}$ and $b_{ii}$ are pure component properties and $k_{ij}$ is the binary interaction parameter chosen to best fit the experimental data. The resulting equations for the fugacity of each species can be found elsewhere.

When an equation of state is used for both the vapor and the liquid phases, the phase equilibrium calculation involves solving the equations

$$\bar{f}_i^L(T, P, \underline{x}) = \bar{f}_i^V(T, P, \underline{y}) \quad \text{usually in the form} \quad x_i \bar{\phi}_i^L(T, P, \underline{x}) = y_i \bar{\phi}_i^V(T, P, \underline{y}) \tag{181}$$

for each component in the mixture. This is done by iteration. As an example, a bubble point pressure calculation at fixed temperature using an equation of state proceeds as follows. The pressure is guessed, and the fugacity of each species in the liquid is computed using the known composition. Next, the composition of the vapor is guessed, and these guessed compositions are used to calculate the fugacity of each species in the vapor and compared with the liquid fugacities. An iterative procedure on both pressure and composition is then used to adjust the pressure and vapor compositions until the fugacity of each species is the same in both phases. Figure 11 is an example of the results of the correlation of high-pressure vapor–liquid equilibrium data obtained using the Peng–Robinson equation of state, the mixing rules above, and adjusting the binary interaction parameter $k_{ij}$ to fit the experimental data.

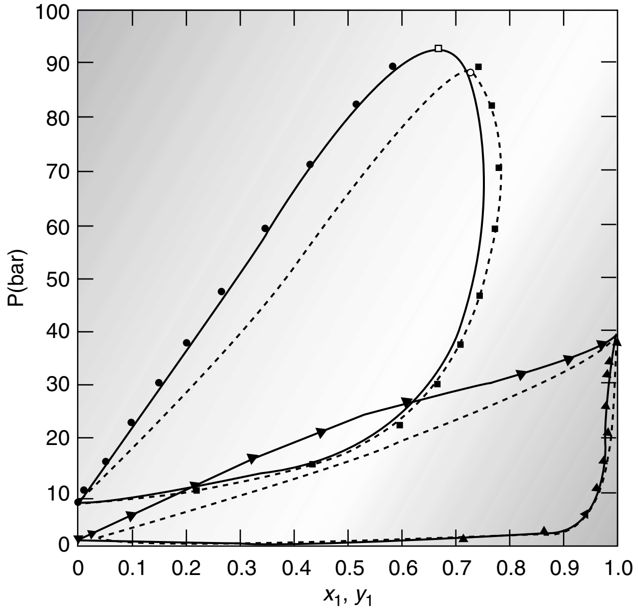

**Fig. 11.** Vapor–liquid equilibrium of the carbon dioxide (1)-isopentane (2) system. The experimental data of G. J. Besserer and D. B. Robinson [*J. Chem. Eng. Data* 20, 93 (1976)] are shown at 277.59 K (▼ liquid and ▲ vapor) and 377.65 K (● liquid and ■ vapor). The dashed curves are the predictions using the Peng–Robinson equation of state and the van der Waals mixing rule with $k_{12} = 0$, and the solid lines are the correlation using the same equation of state with $k_{12} = 0.121$. The points ○ and □ are the estimated mixture critical points at 377.65 K using the same equation of state with $k_{12} = 0$ and 0.121, respectively. Adapted from Ref. 2, with permission.

## 23. Liquid–Liquid Equilibrium and Vapor–Liquid–Liquid Equilibrium Calculations

Mixtures that form two liquids generally contain components that are best described by activity coefficients. In this case, the equations to be solved are

$$\bar{f}_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{f}_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \text{ for each species } i \tag{182}$$

which reduces to

$$x_i^{\mathrm{I}}\gamma_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = x_i^{\mathrm{II}}\gamma_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) \quad \text{for each species } i \tag{183}$$

because the pure component fugacities cancel from both sides of the equation. This equation together with the restrictions that

$$\sum_{i=1}^{\mathrm{C}} x_i^{\mathrm{I}} = 1 \quad \text{and} \quad \sum_{i=1}^{\mathrm{C}} x_i^{\mathrm{II}} = 1 \tag{184}$$

are solved by iteration based on some initial guesses.

The starting point for vapor–liquid–liquid calculations is

$$\bar{f}_i^{\,\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}}) = \bar{f}_i^{\,\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}}) = \bar{f}_i^{\,V}(T,P,\underline{y}) \text{ for each species } i \tag{185}$$

At low-to-moderate pressures, this becomes

$$x_i^{\mathrm{I}}\gamma_i^{\mathrm{I}}(T,P,\underline{x}^{\mathrm{I}})P_i^{\mathrm{vap}}(T) = x_i^{\mathrm{II}}\gamma_i^{\mathrm{II}}(T,P,\underline{x}^{\mathrm{II}})P_i^{\mathrm{vap}}(T) = y_iP \tag{186}$$

which is solved together with the constraints that

$$\sum_{i=1}^{\mathrm{C}} x_i^{\mathrm{I}} = 1,\ \sum_{i=1}^{\mathrm{C}} x_i^{\mathrm{II}} = 1 \quad \text{and} \quad \sum_{i=1}^{\mathrm{C}} y_i = 1 \tag{187}$$

One difficulty in all phase equilibrium calculations is determining how many phases, and which phases, are present at equilibrium. For example, in a mixture of water and an organic compound at a given temperature, pressure, and overall composition, the equilibrium state might be a vapor, a single liquid, a vapor–liquid mixture, two liquids, or a vapor–liquid–liquid mixture. It is only by testing for these possibilities and determining the state with the minimum total Gibbs energy that the true equilibrium state is determined. Not considering all possibilities can give an incorrect answer.

## 24. Chemical Equilibrium Calculations

For a pure substance, any convenient state can be chosen as the basis for preparing thermodynamic properties charts, and different states can be chosen for different substances. However, for reacting mixtures, the reference states for thermodynamic properties must be chosen with care. In particular, in the reactor analysis discussed, the enthalpy of each substance cannot be set arbitrarily, but it must be chosen relative to the others to give the correct heat of reaction and the correct equilibrium constant. Consequently, the reference states for all substances must be chosen in a consistent manner. This is accomplished by choosing a reference state for each type of atom, not for each molecule. The common choice is that both the enthalpy and the Gibbs energy for each atomic species is set to zero at 25°C and 1 bar in its simplest pure stable state. Thus, for oxygen, the stable state is as $O_2$ gas; for mercury, it is as a liquid; for carbon, it is solid graphite, and so on. The enthalpy of any other substance, referred to as its enthalpy or heat of formation and designated by the symbol $\Delta_f H$, is the heat of reaction to form that species for its constituent atoms in their reference states. Thus, the heat of formation of gaseous nitric acid is the heat of reaction for its formation from gaseous $N_2$, $O_2$, and $H_2$, and the heat of formation of gaseous carbon dioxide is the heat of reaction for burning solid graphite in $O_2$.

A standard state for each molecule is then chosen to be the pure component (for gases as an ideal gas, and as the pure liquid or solid for a condensed phase) at the reaction temperature $T$ and a standard state pressure $P^o$. However, in some cases, for example, an electrolyte or a dissolved gas, the standard state can be a (hypothetical) ideal aqueous solution of a fixed composition. Thermodynamic properties are then computed with respect to this standard state. Thus,

$$\bar{G}_i(T,P,\underline{x}) = \underline{G}_i^o(T,P^o) + RT\ln\frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P^o)} = \underline{G}_i^o(T,P^o) + RT\ln a_i(T,P,P^o,\underline{x}) \tag{188}$$

where $\underline{G}_i^o(T,P^o)$ is the Gibbs energy of species $i$ in its standard state, and the standard-state heat (enthalpy change) on reaction is computed from the heats of formation as

$$\Delta_{\mathrm{rxn}}H^o(T,P^o) = \sum_{i=1}^{\mathrm{C}} \nu_i \Delta_f \underline{H}_i^o(T,P^o) \tag{189}$$

The standard-state enthalpies and Gibbs energies of formation are reported in tables, at $P^o$ = 1 bar but only at 25°C. The standard-state heat of reaction at any other temperature is

$$\Delta_{\mathrm{rxn}}\underline{H}_i^o(T,P^o) = \Delta_{\mathrm{rxn}}\underline{H}_i^o(T = 25^\circ\mathrm{C},P^o) + \int_{25^\circ\mathrm{C}}^{T} \Delta_{\mathrm{rxn}}C_P^o(T)dT \tag{190}$$

where $\Delta_{\mathrm{rxn}}C_P^o$ is the difference in the heat capacities of the products and reactants in their standard states. If $\Delta_{\mathrm{rxn}}C_P^o$ is independent of temperature,

$$\Delta_{\mathrm{rxn}}\underline{H}^o(T,P^o) = \Delta_{\mathrm{rxn}}\underline{H}^o(T = 25^\circ\mathrm{C},P^o) + \Delta_{\mathrm{rxn}}C_P^o \times (T - 25^\circ\mathrm{C}) \tag{191}$$

For the Gibbs energy, using equation 38,

$$\left(\frac{\partial(\Delta_{\mathrm{rxn}}\underline{G}^o(T,P^o)/T)}{\partial T}\right)_P = -\frac{\Delta_{\mathrm{rxn}}\underline{H}^o(T,P^o)}{T^2} \tag{192}$$

For chemical equilibrium in a single-reaction system starting from the criterion of equation 156 and using equation 188:

$$\begin{aligned}\sum_{i=1}^{\mathrm{C}} \nu_i \underline{G}_i^o(T,P^o) &= \Delta_{\mathrm{rxn}}G^o(T,P^o) = -RT\sum_{i=1}^{\mathrm{C}} \nu_i \ln\left[\frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P^o)}\right] = -RT\sum_{i=1}^{\mathrm{C}} \ln\left[\frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P^o)}\right]^{\nu_i} \\ &= -RT\ln\prod_{i=1}^{\mathrm{C}}\left[\frac{\bar{f}_i(T,P,\underline{x})}{f_i(T,P^o)}\right]^{\nu_i} = -RT\ln\prod_{i=1}^{\mathrm{C}} a_i^{\nu_i}(T,P,P^o,\underline{x})\end{aligned} \tag{193}$$

or

$$K_{\mathrm{eq}}(T) = \exp\left[-\frac{\Delta_{\mathrm{rxn}}G^o(T,P^o)}{RT}\right] = \prod_{i=1}^{\mathrm{C}} a_i^{\nu_i}(T,P,P^o,\underline{x}) \tag{194}$$

where $K_{\mathrm{eq}}$ is the equilibrium constant. Its value depends on temperature and the difference between the molar Gibbs energies of the products and the reactants in their standard states, but not on pressure. The starting point for calculating the temperature dependence of an equilibrium constant is

$$\frac{d\ln K_{\mathrm{eq}}(T)}{dT} = \frac{d(\Delta_{\mathrm{rxn}}G^o(T,P^o)/RT^2)}{dT} = -\frac{\Delta_{\mathrm{rxn}}H^o(T,P^o)}{RT^2} \tag{195}$$

If $\Delta_{\mathrm{rxn}}H^o(T,P^o)$ is independent of temperature, then

$$\ln\frac{K_{\mathrm{eq}}(T)}{K_{\mathrm{eq}}(T = 25^\circ\mathrm{C})} = -\frac{\Delta_{\mathrm{rxn}}H^o}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right) \tag{196}$$

If it is not independent of temperature, then

$$\ln\frac{K_{\mathrm{eq}}(T)}{K_{\mathrm{eq}}(T = 25^\circ\mathrm{C})} = \int\limits_{T=298.15}^{T} \frac{\Delta_{\mathrm{rxn}}H^o(T,P^o)}{RT^2}\,dT \tag{197}$$

As an example, consider the reaction of hydrogen and oxygen to form water (perhaps in a fuel cell). The reaction is written as

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \rightleftarrows \mathrm{H_2O} \quad \text{so that} \quad \nu_{\mathrm{H_2}} = -1,\ \nu_{\mathrm{H_2}} = -\frac{1}{2}, \quad \text{and} \quad \nu_{\mathrm{H_2O}} = 1 \tag{198}$$

If the reaction pressure is not very high, and recognizing that the standard states are pure components at 1 bar so that

$$a_i(T,P,P^o,\underline{y}) = \frac{\bar{f}_i(T,P,\underline{y})}{f_i(T,P^o)} = \frac{y_iP}{P^o} \tag{199}$$

then

$$K_{\mathrm{eq}}(T) = \prod_{i=1}^{\mathrm{C}} a_i^{\nu_i}(T,P,P^o,\underline{y}) = \frac{y_{\mathrm{H_2O}}\left(\frac{P}{P^o}\right)}{y_{\mathrm{H_2}}\left(\frac{P}{P^o}\right)\left[y_{\mathrm{O_2}}\left(\frac{P}{P^o}\right)\right]^{\frac{1}{2}}} = \frac{y_{\mathrm{H_2O}}}{y_{\mathrm{H_2}}y_{\mathrm{O_2}}^{\frac{1}{2}}}\left(\frac{P^o}{P}\right)^{\frac{1}{2}} \tag{200}$$

where $y_i$ is a gas-phase mole fraction. Note that all mole fractions are also related to the stoichiometry of the chemical reaction, so finding for the equilibrium composition involves the simultaneous solution of the equilibrium relation and the mass balances.

Similarly for the reaction of burning carbon for carbon dioxide,

$$\mathrm{C} + \mathrm{O_2} \rightleftarrows \mathrm{CO_2} \quad \text{for which} \quad \nu_{\mathrm{C}} = -1,\ \nu_{\mathrm{O_2}} = -1, \quad \text{and} \quad \nu_{\mathrm{CO_2}} = 1$$

$$K_{\mathrm{eq}}(T) = \frac{a_{\mathrm{CO_2}}}{a_{\mathrm{C}}a_{\mathrm{O_2}}} = \frac{y_{\mathrm{CO_2}}\left(\frac{P}{P^o}\right)}{y_{\mathrm{O_2}}\left(\frac{P}{P^o}\right)} = \frac{y_{\mathrm{CO_2}}}{y_{\mathrm{O_2}}} \tag{201}$$

as the activity of solid carbon is unity, because it is pure and the fugacity of solids (and liquids) are very weak functions of pressure, which we neglect here (that is, we are assuming the pressure is not very high so that the Poynting correction can be neglected). The final example is the liquid-phase reaction:

$$\mathrm{CH_3COOH + CH_3OH \rightleftarrows CH_3COOC_2H_5 + H_2O}$$

for which

$$\begin{aligned} K_{\mathrm{eq}}(T) &= \frac{a_{\mathrm{CH_3COOCH_3}}a_{\mathrm{H_2O}}}{a_{\mathrm{CH_3COOH}}a_{\mathrm{CH_3OH}}} = \frac{x_{\mathrm{CH_3COOCH_3}}\gamma_{\mathrm{CH_3COOCH_3}}x_{\mathrm{H_2O}}\gamma_{\mathrm{H_2O}}}{x_{\mathrm{CH_3COOH}}\gamma_{\mathrm{CH_3COOH}}x_{\mathrm{CH_3OH}}\gamma_{\mathrm{CH_3OH}}} \\ &= \frac{x_{\mathrm{CH_3COOCH_3}}x_{\mathrm{H_2O}}}{x_{\mathrm{CH_3COOH}}x_{\mathrm{CH_3OH}}} \times \frac{\gamma_{\mathrm{CH_3COOCH_3}}\gamma_{\mathrm{H_2O}}}{\gamma_{\mathrm{CH_3COOH}}\gamma_{\mathrm{CH_3OH}}} = K_x \times K_\gamma \end{aligned} \tag{202}$$

where each activity coefficient is a function of the compositions of all species in the mixture.

Each of these chemical equilibrium relations must be solved together with the constraints on the compositions as a result of the mass balance for each species of equation 111 and the initial mole numbers. Also, if several chemical reactions occur, then the combination of all chemical equilibrium relations and the mass balances must be solved simultaneously.

## 25. Maximum Work Obtainable (or Minimum Work Required) for a Change of State Involving Mixtures

Consider the work-producing device based on chemical reaction schematically shown in Fig. 12. This device could be a fuel cell, a coal-fired steam power plant, or some other device. The steady-state mass (mole), energy, and entropy

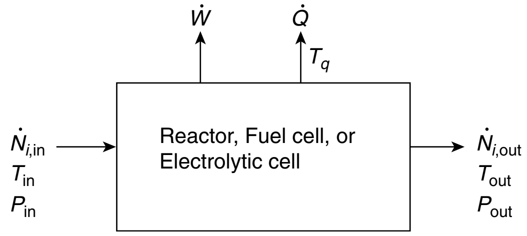

**Fig. 12.** Schematic diagram of a fuel cell, reactor, electrolytic cell, or other device. Fuel cells and reactors generally deliver work to the surroundings ($W < 0$), whereas for electrolytic cells $W < 0$ for a battery, while, work is required (in the form of electrical energy) $W > 0$ for an electrolysis cell.

balances for this system at constant temperature and constant volume are as follows:

$$\frac{dN_i}{dt} = 0 = N_{i,\mathrm{in}} - N_{i,\mathrm{out}} + \nu_i \frac{dX}{dt} \quad \text{or} \quad N_{i,\mathrm{out}} = N_{i,\mathrm{in}} + \nu_i \frac{dX}{dt} \tag{203}$$

$$\frac{d(N\underline{U})}{dt} = 0 = \sum_{i=1}^{\mathrm{C}} N_{i,\mathrm{in}} \bar{H}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}}) - \sum_{i=1}^{\mathrm{C}} N_{i,\mathrm{out}} \bar{H}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) + \dot{W} + \dot{Q} \tag{204}$$

and

$$\frac{d(N\underline{S})}{dt} = 0 = \sum_{i=1}^{\mathrm{C}} N_{i,\mathrm{in}} \bar{S}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}}) - \sum_{i=1}^{\mathrm{C}} N_{i,\mathrm{out}} \bar{S}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) + \frac{\dot{Q}}{T_q} + \dot{S}_{\mathrm{gen}} \tag{205}$$

Solving for the $\dot{Q}$ and combining the energy and entropy balances gives

$$\begin{aligned}
-\dot{W} &= \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{in}} [\bar{H}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}}) - T_q \bar{S}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}})] \\
&\quad - \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{out}} [\bar{H}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) - T_q \bar{S}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}})] - T_q \dot{S}_{\mathrm{gen}} \\
&= \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{in}} [\bar{H}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}}) - T_q \bar{S}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}})] \\
&\quad - \sum_{i=1}^{\mathrm{C}} (\dot{N}_{i,\mathrm{in}} + \nu_i \frac{dX}{dt}) [\bar{H}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) - T_q \bar{S}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}})] - T_q \dot{S}_{\mathrm{gen}} \\
&= \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{in}} \{[\bar{H}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}}) - T_q \bar{S}_i(T_{\mathrm{in}}, P_{\mathrm{in}}, \underline{x}_{\mathrm{in}})] - [\bar{H}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) \\
&\quad - T_q \bar{S}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}})]\} \\
&\quad - \frac{dX}{dt} \sum_{i=1}^{\mathrm{C}} \nu_i [\bar{H}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}}) - T_q \bar{S}_i(T_{\mathrm{out}}, P_{\mathrm{out}}, \underline{x}_{\mathrm{out}})] - T_q \dot{S}_{\mathrm{gen}}
\end{aligned} \tag{206}$$

Note that the terms in brackets are not partial molar Gibbs energies unless the temperature at which heat transfer occurs $T_q$ is also the temperature of the flow stream.

The maximum work attainable from the system for a given feed stream, or the minimum work required to produce a given change of state, occurs when the process occurs reversibly, that is, $\dot{S}_{\mathrm{gen}} = 0$, when the temperatures for heat transfer and of the exiting stream are both at the ambient temperature $T_{\mathrm{amb}}$, when the pressure of the exit stream is ambient (otherwise the potential to obtain useful work will be lost), and when the exiting stream is in chemical equilibrium so that the reaction term vanishes. In that case,

$$-\dot{W}^{\max} = \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{in}}\{[\bar{H}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}}) - T_{\mathrm{amb}}\bar{S}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}})] - \bar{G}_{i,\mathrm{out}}(T_{\mathrm{amb}},P_{\mathrm{amb}},\underline{x}_{\mathrm{out}})\}$$

$$= \sum_{i=1}^{\mathrm{C}} \dot{N}_{i,\mathrm{in}}\{[\bar{\mathbf{G}}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}},T_{\mathrm{amb}})] - \bar{G}_{i,\mathrm{out}}(T_{\mathrm{amb}},P_{\mathrm{amb}},\underline{x}_{\mathrm{out}})\} \tag{207}$$

where $\bar{\mathbf{G}}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}},T_{\mathrm{amb}}) = \bar{H}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}}) - T_{\mathrm{amb}}\bar{S}_{i,\mathrm{in}}(T_{\mathrm{in}},P_{\mathrm{in}},\underline{x}_{\mathrm{in}})$ is the partial molar availability of species $i$ in the inlet stream. Note that its value depends on both the temperature of the inlet stream and the ambient temperature (so it is not a partial molar Gibbs energy).

This equation is applicable to all work-producing devices that involve chemical reaction, including fuel cells. It is also applicable to biochemical processes and bioreactors, but there the complication that arises is determining the properties of the biochemical species.

## 26. Nomenclature

(Note that symbols that are only used once, for example, in an illustrative equation of state, are not shown.)

| Symbol | Definition | Units |
|---|---|---|
| a | parameter in heat capacity equation | J/(mol K) |
| $a$ | equation of state parameter | various |
| $a$ | activity (sections 19, 24, 25 ) | |
| $\underline{A}$ ($\underline{A}$) | Helmholtz energy (per mole) | J (J/mol) |
| $\bar{A}_i$ | partial molar Helmholtz energy of species $i$ in a mixture | J/mol |
| b | parameter in heat capacity equation | J/(mol $K^2$) |
| $b$ | equation of state parameter | $m^3$/mol |
| $B$ | second virial coefficient | $m^3$/mol |
| d | parameter in heat capacity equation | J/(mol $K^3$) |
| $C$ | third virial coefficient | $m^6$/mol |
| C | number of components in a mixture | |
| $C_P$ | constant pressure heat capacity | J/(mol K) |
| $C_V$ | constant volume hear capacity | J/(mol K) |
| C.O.P. | coefficient of performance | |
| d | parameter in heat capacity equation | J/(mol $K^4$) |
| D | fourth virial coefficient | $m^9$/mol |
| $\underline{f}$ | fugacity | kPa |
| $\bar{f}_i$ | fugacity of species $i$ in a mixture | kPa |
| $\underline{G}$ ($\underline{G}$) | Gibbs energy (per mole) | J (J/mol) |
| $\bar{G}_i$ | partial molar Gibbs energy of species $i$ in a mixture | J/mol |
| $\underline{\mathbf{G}}$ | flow availability per mole | J/mol |
| $\bar{H}$ ($\underline{H}$) | enthalpy (per mole) | J (J/mol) |
| $\bar{H}_i$ | partial molar enthalpy of species $i$ in a mixture | J/mol |
| I | stoichiometric chemical formula | |
| $K_{\mathrm{eq}}$ | equilibrium constant | |
| $K_x$ | mole fraction ratio at chemical equilibrium | |
| $K_\gamma$ | activity coefficient ratio at chemical equilibrium | |
| $k_{ij}$ | binary interaction parameter | |

| Symbol | Definition | Units |
|---|---|---|
| $m$ | molecular weight | g/mol |
| M | number of independent reactions | |
| $N_i$ | moles of species $i$ | mol |
| $\dot{N}_j$ | molar flow rate at entry point $j$ | mol/s |
| $\dot{N}_{i,j}$ | molar flow rate of species $i$ at entry point $j$ | mol/s |
| $P$ | absolute pressure | kPa |
| P | number of phases | |
| $P^{\mathrm{vap}}$ | vapor pressure | kPa |
| $P_{\mathrm{c}}$ | critical pressure | kPa |
| $Q$ | heat | J |
| $\dot{Q}$ | heat flow rate | J/s |
| $R$ | gas constant | J/(mol K) |
| $S$ ($\underline{S}$) | entropy (per mole) | J/mol (J/mol K) |
| $\bar{S}_i$ | partial molar entropy of species $i$ in a mixture | J/(mol K) |
| $t$ | time | s |
| $T$ | absolute temperature | K |
| $T_{\mathrm{c}}$ | critical temperature | K |
| $U$ ($\underline{U}$) | internal energy (per mole) | J (J/mol) |
| $U_i$ | partial molar internal energy of species $i$ in a mixture | J/mol |
| $v$ | velocity | m/s |
| $V$ ($\underline{V}$) | volume (per mole) | $m^3$ ($m^3$/mol) |
| $\bar{V}_i$ | partial molar volume of species $i$ in a mixture | $m^3$/mol |
| $W$ | work | J |
| $\dot{W}$ | rate at which work is done | J/s |
| $x_i$ | mole fraction of species $i$ in liquid | |
| $\underline{x}$ | set of mole fractions $x_1, x_2$, etc | |
| $y_i$ | mole fraction of species $i$ in vapor | |
| $\underline{y}$ | set of mole fractions $y_1, y_2$, etc | |
| $Z$ | compressibility factor | |
| *Superscripts* | | |
| ID | ideal mixture | |
| IG | ideal gas | |
| IGM | ideal gas mixture | |
| ex | excess property | |
| I, II | phase identifier | |
| *L* | liquid phase | |
| max | maximum attainable | |
| *o* | standard state | |
| *V* | vapor phase | |
| vap | vapor pressure | |
| *Subscripts* | | |
| *i* | species identifier | |
| in | inlet stream | |
| c | critical property | |
| H | high-temperature heat reservoir | |
| gen | indicating generation within the system | |
| L | low-temperature heat reservoir | |
| rxn | reaction | |
| out | outlet stream | |
| 1,2,C | species identifiers | |
| *Greek Letters* | | |
| $\alpha,\beta,\rho\ldots$ | reaction stoichiometric coefficients | |

| Symbol | Definition | Units |
|---|---|---|
| $\Delta_{L \to V}$ | change on a liquid-to-vapor phase change | |
| $\Delta_{S \to L}$ | change on a solid-to-liquid phase change | |
| $\Delta_{S \to V}$ | change on a solid-to-vapor phase change | |
| $\Delta_{\mathrm{rxn}}$ | change on chemical reaction | |
| $\gamma_i$ | activity coefficient of species $i$ in a mixture | |
| $\Gamma$ | coefficient in excess Gibbs energy expression | |
| $\theta$ | general variable | |
| $\kappa$ | equation of state parameter | |
| $\mu$ | chemical potential | |
| $\bar{\mu}_i$ | chemical potential of species $i$ in a mixture | |
| $\nu_i$ | stoichiometric coefficient of species $i$ in a reaction | |
| $\nu_{ij}$ | stoichiometric coefficient of species $i$ in reaction $j$ | |
| $\sigma$ | phase boundary | |
| $\phi$ | fugacity coefficient of a species | |
| $\bar{\phi}_i$ | fugacity coefficient of species $i$ in a mixture | |
| $\omega$ | acentric factor | |

## BIBLIOGRAPHY

"Thermodynamics" in *ECT* 1st ed., Vol. 14, pp. 1–37, by J. C. Chu, Polytechnic Institute of Brooklyn; in *ECT* 2nd ed., Vol. 20, pp. 118–146, by H. T. Chen, Newark College of Engineering, and D. F. Othmer, Polytechnic Institute of Brooklyn; in *ECT* 3rd ed., Vol. 22, pp. 868–899, by H. C. Van Ness and M. M. Abbott, Rensselaer Polytechnic Institute; in *ECT* 4th ed., Vol. 23, pp. 985–1027, by H. C. Van Ness and M. M. Abbott, Rensselaer Polytechnic Institute; in *ECT* (online), posting date: December 4, 2000, by H. C. Van Ness and M. M. Abbott, Rensselaer Polytechnic Institute.

## CITED PUBLICATIONS

1. P. A. Schilpp, ed., *Albert Einstein: Philosopher-Scientist*, Library of Living Philosophers, Evanston, Ill., 1949, p. 32 (in Autobiographical Notes).
2. S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed., John Wiley & Sons, Inc., New York, 2006.
3. J. M. Smith, H. C. Van Ness, and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 7th ed., McGraw-Hill Book Co., New York, 2005.
4. J. W. Tester and M. Modell, *Thermodynamics and its Applications*, 3rd ed., Prentice-Hall, Englewood Cliffs, N.J., 1996.
5. K. S. Pitzer, *Thermodynamics*, 3rd ed., McGraw-Hill Book Co., New York, 1995.
6. B. G. Kyle, *Chemical and Process Thermodynamics*, 3rd ed., Prentice-Hall PTR, Upper Saddle River, N.J., 1999.
7. *NIST Thermophysical Properties of Fluid Systems*. Available at: http://webbook.nist.gov/chemistry/fluid/ and the collections of tables and other data in the J. Phys. Chem. Ref. Data.
8. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**, 59 (1976).
9. M. Benedict, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.* **8**, 334 (1940).
10. E. B. Poling, J. M. Prausnitz, and L. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill Book Co., New York, 2000.
11. J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, 3rd ed., Prentice-Hall PTR, Upper Saddle River, N.J., 1999.

12. A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibrium Using UNIFAC*, Elsevier, Amsterdam, 1977.
13. R. Wittig, J. Lohmann, and J. Gmehling, *IEC Res.* **42**, 183–188 (2003).
14. A. Klamt, *COSMO-RS From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, Amsterdam, 2005.

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