

14.1: Dependence of the Internal Energy on the Composition of the System

We develop the thermodynamic criteria for change in a closed system without specifying the composition of the system. It is clear, therefore, that the validity of the results is not restricted in any way by the composition of the system. For the most part, our development proceeds as if the system is a single substance. However, the validity of the thermodynamic criteria for change is independent of whether the system comprises a single substance in a single phase or multiple substances in multiple phases. The criteria for reversible change are independent of whether the change involves interconversions among the substances comprising the system, so long as these interconversions occur reversibly.

While we develop these criteria without specifying the composition of the system undergoing change, we use them to make predictions about processes in which system compositions do change. In [Chapter 12](#), we apply the Gibbs free energy criterion for reversible change to equilibria between two phases of a pure substance. This application is successful because the thermodynamic properties of one pure phase are independent of how much of any other pure phase is present.

In [Chapter 13](#), we find a relationship between the standard Gibbs free energy change and the equilibrium constant for a reaction of ideal gases. We also use the equation for the Gibbs free energy of an ideal gas to find the value of the Gibbs free energy change for a spontaneous reaction of ideal gases at a constant temperature. This is a noteworthy result. Because we can find this value, we can predict the spontaneous transformation of one non-equilibrium state to a second non-equilibrium state. These applications are successful because ideal gas molecules do not interact with one another; the laws describing the behavior of an ideal gas do not depend on the properties of other substances that may be present.

In general, the behavior of a system depends on the molecular characteristics of all of the components and on their concentrations. For example, the pressure at which pure ice is in equilibrium with a salt solution depends not only on the temperature but also on the choice of salt and its concentration. When it is expressed as a function of reagent concentrations, the equilibrium constant for a reaction of real gases varies to some extent with the composition and with the total pressure of the system. Such observations are consistent with the idea that the thermodynamic properties of a system depend on the attractive and repulsive forces among its molecules. Such forces act between any pair of real molecules, whether they are molecules of the same substance or molecules of different substances.

Our treatment of ideal-gas reactions shows that, if we can model the effects of compositional changes on the values of a system's thermodynamic functions, we can use our thermodynamic theory to predict spontaneous changes in chemical composition. To extend to real substances the treatment that we develop for ideal gases in [Chapter 13](#), we must find general relationships between a system's thermodynamic properties and its chemical composition. These relationships must reflect the dependence of the thermodynamic properties of one substance on the molecular characteristics of the other substances present. To find them, we must introduce additional inferences and assumptions. Since we want to describe spontaneous processes, these ideas must apply to non-equilibrium systems.

To introduce these ideas, let us consider an open system that can undergo a spontaneous change. We begin by considering its energy. We want to model any change in the energy, dE , of this system as a function of a sufficient set of independent variables. Thus far, we have developed equalities that relate thermodynamic functions only for closed systems undergoing reversible change. Consequently, when we now seek an equation for dE that is valid for an open, spontaneously changing system, our task is one of scientific inference, not mathematical deduction from the reversible-process equations. Nevertheless, the reversible-process equations are our primary resource.

For a closed, reversible system, we interpret the fundamental equation to mean that dS determines the effect of thermal processes and that dV determines the effect of pressure–volume work on the energy of the system. We infer that entropy and volume changes will play these same roles in the description of open, spontaneously changing systems. If λ different kinds of non-pressure–volume work are possible, the energy of the system is also a function of λ generalized extensive thermodynamic variables, $\theta_1, \theta_2, \dots, \theta_k, \dots, \theta_\lambda$. If the system contains ω substances, adding or removing some amount of any of these substances changes the energy of the system. Evidently, the energy of the system is a function of the number of moles of each substance present. Let $n_1, n_2, \dots, n_\omega$, represent the number of moles of each component in the system. We can recognize these dependencies formally by writing

$$E = E(S, V, \theta_1, \theta_2, \dots, \theta_\lambda, n_1, n_2, \dots, n_\omega)$$

This formalism applies to both open and closed systems. If the system is open, all of these variables are independent; any one of them can be changed independently of the others. If the system is closed, changes in the n_j are not independent, because the mass

of the system is constant. (Letting \overline{M}_j be the molar mass of the j -th substance, we have $0 = \sum_1^\omega \overline{M}_j dn_j$.) If the energy is a continuous and differentiable function of each of these variables, the total differential becomes

$$dE = \left(\frac{\partial E}{\partial S} \right)_{V, \theta_m, n_j} dS + \left(\frac{\partial E}{\partial V} \right)_{S, \theta_m, n_j} dV + \sum_{k=1}^{\lambda} \left(\frac{\partial E}{\partial \theta_k} \right)_{S, V, \theta_{m \neq k}, n_j} d\theta_k + \sum_{j=1}^{\omega} \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}} dn_j$$

(Inclusion of “ $\theta_{m \neq k}$ ” and “ $n_{p \neq j}$ ” in the subscripted variable lists indicates that the partial taken with respect to any θ_k is taken with the other θ -values held constant, and the partial taken with respect to any of the n_j is taken with the other n -values held constant.)

We hypothesize that this total differential describes energy changes in any system whose energy, entropy, volume, work variables, θ_k , and composition variables, n_j , vary in a continuous manner. In particular, we hypothesize that it describes the energy change that results from any change in composition, specified by the dn_j , whether the system is open or closed. All of these partial derivatives are intensive variables. Each of them specifies how much the energy of the system changes when its associated extensive variable undergoes an incremental change. We find it convenient to refer to the partial derivatives as **potentials**. In this book, we restrict our attention to systems in which a given potential has the same value at every location within the system.

Since

$$\left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}}$$

is the energy change that occurs when the amount of the j -th chemical substance changes by dn_j , we call this partial derivative a **chemical potential**. We introduce the new symbol μ_j to denote the chemical potential of the j -th substance; that is,

$$\mu_j = \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}}$$

The value of μ_j depends exclusively on the properties of the system. When the amount of the j -th substance changes by dn_j , the contribution to the energy change is $dE = \mu_j dn_j$. When the system is open, the amount of the j -th substance can change either because of a process that occurs entirely within the system or because some of the substance moves across the system's boundary.

Reversible processes in closed systems

In [Section 9.14](#), we find, for a reversible process in a closed system, that $dE = TdS - PdV + dw_{NPV}$, where

$$dw_{NPV} = \sum_{k=1}^{\lambda} \Phi_k d\theta_k$$

In our hypothesized total differential, the contribution that composition changes make to dE is

$$\sum_{j=1}^{\omega} \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}} dn_j = \sum_{j=1}^{\omega} \mu_j dn_j$$

From the empirical fact that the energy change for a reversible process in a closed system can be specified by specifying dS , dV , and the $d\theta_k$, it follows that

$$\sum_{j=1}^{\omega} \mu_j dn_j = 0$$

for any such process. Implicitly using this fact in [Section 10.1](#), we find that $(\partial E / \partial S)_V = T$ and $(\partial E / \partial V)_S = -P$ for reversible processes in which all of the work is pressure–volume work. We can extend the argument to a reversible process involving any form of work in a closed system. It follows that

$$\left(\frac{\partial E}{\partial S}\right)_{V, \theta_m, n_j} = T$$

$$\left(\frac{\partial E}{\partial V}\right)_{S, \theta_m, n_j} = -P$$

$$\left(\frac{\partial E}{\partial \theta_k}\right)_{S, V, \theta_{m \neq k}, n_j} = \Phi_k$$

and

$$\sum_{k=1}^{\lambda} \left(\frac{\partial E}{\partial \theta_k}\right)_{S, V, \theta_{m \neq k}, n_j} d\theta_k = dw_{NPV}$$

Substituting into

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V, \theta_m, n_j} dS + \left(\frac{\partial E}{\partial V}\right)_{S, \theta_m, n_j} dV$$

$$+ \sum_{k=1}^{\lambda} \left(\frac{\partial E}{\partial \theta_k}\right)_{S, V, \theta_{m \neq k}, n_j} d\theta_k$$

$$+ \sum_{j=1}^{\omega} \left(\frac{\partial E}{\partial n_j}\right)_{S, V, \theta_m, n_{p \neq j}} dn_j$$

we have

$$dE = TdS - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

with

$$\sum_{j=1}^{\omega} \mu_j dn_j = 0$$

for any reversible process in a closed system.

Reversible processes in open systems

Let us suppose that an open system is undergoing a reversible change and that we instantaneously stop any further exchange of matter between the system and its surroundings. Before this action, the system is open; thereafter, it is closed. The act of closure does not change the system's state functions. If, after closure, the system continues to change reversibly, $dE = TdS - PdV + dw_{NPV}$ must be valid. Closure of the system introduces a constraint that reduces the number of independent variables. However, S , V , and the θ_k remain independent after closure, and the act of closure cannot alter the laws that describe the interaction of the system with its surroundings during a reversible process. The relationships $(\partial E / \partial S)_V = T$, $(\partial E / \partial V)_S = -P$, and $\sum_{k=1}^{\lambda} (\partial E / \partial \theta_k)_{S, V, \theta_{m \neq k}, n_j} d\theta_k = dw_{NPV}$ are valid for the closed system. We infer that they are also valid for the open system, so that the total differential for a system undergoing reversible change is

$$dE = TdS - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

whether the system is open or closed. This comparison implies that

$$\sum_{j=1}^{\omega} \mu_j dn_j = 0$$

for any reversible process, whether the system is open or closed. (As noted below, however, our model implicitly assumes that $\mu_j = \hat{\mu}_j$; that is, μ_j has the same value whether the change dn_j is the result of internal transformation, movement of the j -th

substance across the system boundary, or a combination of the two.)

Spontaneous processes

We hypothesize that the same mathematical model describes energy changes for both spontaneous and reversible processes in both open and closed systems, so long as the process occurs in such a way that all of the system's state functions behave as continuous variables. For reversible systems, we conclude that this model is

$$dE = TdS - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

By hypothesis, the model also describes spontaneous processes, so long as the state functions behave as continuous variables. We base the development of our thermodynamic theory for spontaneous reactions on this hypothesis. It is, of course, the utility of the resulting theory, not the logical force of the reasoning by which we reach it, that justifies our acceptance of the hypothesis.

In [Section 9.19](#), we find that $(dE)_{SV} < dw_{NPV}$ for a spontaneous process, and we reach this conclusion by an argument that is independent of the composition of the system. For a spontaneous process at constant entropy and volume, our model becomes

$$(dE)_{SV} = dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

and since $(dE)_{SV} < dw_{NPV}$, it follows that

$$\sum_{j=1}^{\omega} \mu_j dn_j < 0$$

for any spontaneous process.

All of the variables that appear in our model for dE are properties of the system. The surroundings can affect the behavior of the system by imposing particular values on one or more of the system's thermodynamic functions. (For example, immersing a reacting system in a constant-temperature bath ensures that the system reaches equilibrium only when $T = \hat{T}$.) When the surroundings impose particular values on the system's thermodynamic functions, the system's state functions must approach the imposed values as the system approaches equilibrium.

Internal entropy and chemical potential

Substituting the internal and external entropies that we introduce in [Section 9.16](#), our model for the incremental energy change during a spontaneous composition change becomes

$$dE = Td_iS + dq + dw_{PV} + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

Our first-law equation is $dE = dq + dw_{PV} + dw_{NPV}$. It follows that

$$Td_iS + \sum_{j=1}^{\omega} \mu_j dn_j = 0$$

and we find

$$d_iS = -\frac{1}{T} \sum_{j=1}^{\omega} \mu_j dn_j$$

The change criteria

$$d_iS \geq 0$$

and

$$\sum_{j=1}^{\omega} \mu_j dn_j \leq 0$$

are equivalent.

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