Chapter 14: Focusing on Chemical Reactivity

Hydrogen peroxide, which is used as a topical disinfectant, decomposes to give O_2 gas in a highly exothermic reaction. This reaction is often used as a rather spectacular chemical demonstration:

$$2\ H_2O_2\ (aq) \rightleftarrows 2\ H_2O\ (l) + O_2\ (g)$$

Hydrogen peroxide is also important in redox reactions in the environment and in biological processes. During this reaction many things can change: V, P, S, T, U, H, and the mole amounts of the reactants and products. Keeping track of all these variables can be daunting. How can we simplify the definition of our system to focus on chemical changes?

The main goal of physical chemistry is to understand chemical reactivity. Up to this point we have discussed entropy changes in closed systems and systems that don't involve chemical reactions. Now that we have introduced entropy, we can add the effects of chemical reactions. We first need to discuss open systems and then systems where mole amounts change through chemical processes. We then need to discuss how to use constraints to focus specifically on chemical reactivity.

14.1 Chemical Potentials Express the Change in Energy for Open Systems

The combined First and Second Laws of thermodynamics, Eq. 12.1.5, can be extended for open systems. For a system with two components:

$$dU = TdS - PdV + \mu_1\, dn_1 + \mu_2\, dn_2 \qquad 14.1.1$$

where dn_1 is the change in the moles of component 1, dn_2 is the change in the number of moles of component 2, μ_1 is the **chemical potential** of component 1, and μ_2 is the chemical potential of component 2. For example, to make a sugar solution component 1 is water and component 2 is sugar. The independent variables implied by this last equation are now $U(S,V,n_1,n_2)$. For comparison we can also write the total differential of U as:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2} dV + \left(\frac{\partial U}{\partial n_1}\right)_{V,S,n_2} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{V,S,n_1} dn_2 \qquad 14.1.2$$

Comparing Eq. 14.1.1 with Eq. 14.1.2 gives the chemical potentials as:

$$\mu_1 \equiv \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2} \qquad \mu_2 \equiv \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1} \qquad 14.1.3$$

Notice that these equations are in the general form of thermodynamic forces. In general, work is in the form $w = F\, dx$. Then $\mu_1\, dn_1$ is the chemical work for changes in the amount of component 1. The chemical potential is the thermodynamic force for the change in the amount of the component. For pure substances, the chemical potential for a component is simply the internal energy per mole, $\mu_1 = \Delta_f U_{m,1}$ and $\mu_2 = \Delta_f U_{m,2}$. The chemical potential for a substance is the driving force for chemical change. The chemical potential is central to our understanding of spontaneity and equilibrium, and will be our primary tool in the next several chapters.

We should also consider the general case for multiple components. Taking U as a function of S, V, and all the n_i gives the general form of the total differential as:

$$dU = T\,dS - P\,dV + \sum_{i=1}^{c} \mu_i\,dn_i \qquad \text{(open)} \qquad 14.1.4$$

The sum is over all c components for the system. For the derivatives of the entropy and volume, all of the n_i mole amounts are held constant. Comparison of terms with Eq. 14.1.2 shows that:

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} \qquad 14.1.5$$

is the chemical potential with respect to component i. For systems with chemical work, all the potential energy functions in thermodynamics are derived from Eq. 14.1.4.[1] The restriction of the sum in Eq. 14.1.4 to the components insures all the specified independent variables are independent of each other.

14.2 The Thermodynamic Components are the Independent Set of Chemical Constituents

For Eq. 14.1.4 to accurately determine the internal energy change for a system, the variables used to give the changes for the process must be independent of each other. By **independent**, we mean that we can change a given variable without corresponding changes in the other variables. For example, for an ideal gas in a closed system we can only change two variables independently. If we choose P and T for example, the volume is automatically specified as $V = nRT/P$. For a closed system with no chemical reactions, we can again only choose two of S, T, P, and V as independent variables. For internal energy, as we have seen, the combined First and Second Laws lead to the choice of S and V as the independent variables. How do we specify the state of an open system or a system with chemical reactions? In thermodynamics, the components for a system and the constituents are distinct concepts. A **chemical constituent** is any chemical species found in the system. For example, for a solution of ethanol in water, ethanol and water are the two constituents. For a solution of sodium chloride, the constituents are H_2O, Na^+, and Cl^-. The thermodynamic **components** of a system are a set of independent constituents. For the example of a solution of ethanol in water, the components are the same as the constituents. For a sodium chloride solution, there are two components, because the concentration of the Na^+ ions must equal the concentration of Cl^- ion as required by charge neutrality. The chemical components can then be chosen as the moles of H_2O and the moles of NaCl used to make up the solution. In other words, $[Na^+]$ and $[Cl^-]$ are dependent on each other and cannot both be chosen as components. The number of components is also the minimum number of substances that must be available in the laboratory to make up the system.

The number of components for a system is given by the number of chemical constituents, n_s, minus the number of distinct chemical reactions and minus any chemical constraints:

$$c = n_s - \text{no. of reactions} - \text{no. of chemical constraints} \qquad 14.2.1$$

Chemical constraints include charge balance and any conditions placed on the preparation of the system. For example, consider the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$. There are three constituents, PCl_5, PCl_3, and Cl_2, giving $n_s = 3$. If a system is prepared by mixing arbitrary amounts of these three constituents there are two components. Any two of the constituents may be chosen as components and then the third can be calculated from the equilibrium expression:

$$K_p = \frac{P_{PCl_3}\,P_{Cl_2}}{P_{PCl_5}} \qquad 14.2.2$$

Conversely, if the system is prepared from only PCl_5, there is one chemical constraint. Then c = 3 species – 1 reaction – 1 chemical constraint, resulting in only one component. In other words, if the system is prepared from only PCl_5 then from the stoichiometry of the reaction, $P_{PCl_3} = P_{Cl_2}$.

Example 14.2.1

Consider a solution of solid NaH_2PO_4 in water. The two dissociation equilibria are:

$$H_2PO_4^- \overset{K_{a2}}{\rightleftarrows} HPO_4^{2-} + H^+$$

$$HPO_4^{2-} \overset{K_{a3}}{\rightleftarrows} PO_4^{3-} + H^+$$

Determine the constituents, the chemical components, and a possible set of chemical contraints.

Answer: The constituents are: Na^+, H^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and H_2O. There are two components, NaH_2PO_4 and water. With two components, there must be two chemical constraints: c = 6 – 2 – 2 = 2. The charge balance is one chemical constraint:

$$[Na^+] + [H^+] = [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}]$$

The remaining chemical constraint can be expressed in several forms. The Na^+ ion concentration is unchanged by the chemical reactions. The mass balances are, then:

$$[Na^+] = [Na^+]_o \qquad [H_2PO_4^-]_o = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

Since NaH_2PO_4 is the only source of both Na^+ and phosphate, $[Na^+]_o = [H_2PO_4^-]_o$, and the second chemical constraint can be expressed as:

$$[Na^+] = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

The reaction has six constituents, but only 2 components.

Example 14.2.2

Determine the number of constituents and chemical components in a solution made from NaH_2PO_4 and Na_2HPO_4 in water.

Answer: The constituents are the same as the previous example: Na^+, H^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and H_2O. But there are now 3 components, NaH_2PO_4, Na_2HPO_4, and H_2O. The extra component results because there are now two independent sources of phosphate, which introduces an additional variable into the mass balances:

$$[H_2PO_4^-]_o + [HPO_4^{2-}]_o = [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$
$$[Na^+] = [H_2PO_4^-]_o + 2\,[HPO_4^{2-}]_o$$

14.3 Constraints Provide Focus on Chemical Reactivity

The world is complex. Figuring out how to analyze a complex system is often difficult. One of the most powerful contributions of thermodynamics is to provide a way to simplify a system so that the underlying chemical relationships can be studied. The specification of the system and its constraints is a critical part of a thermodynamic analysis. As in any other area of science, you want to keep as many variables constant as possible while still allowing the chemically important variables to change. Constraints are used to keep the values of variables fixed. Constraints are useful for simplifying systems so that we can focus our attention on chemically significant processes without undue complexity. There are two general types of constraints placed on systems. Physical constraints act as constraints for extensive variables and reservoirs act as constraints for intensive variables. Chemical constraints are one type of physical constraint; physical barriers also act as constraints.

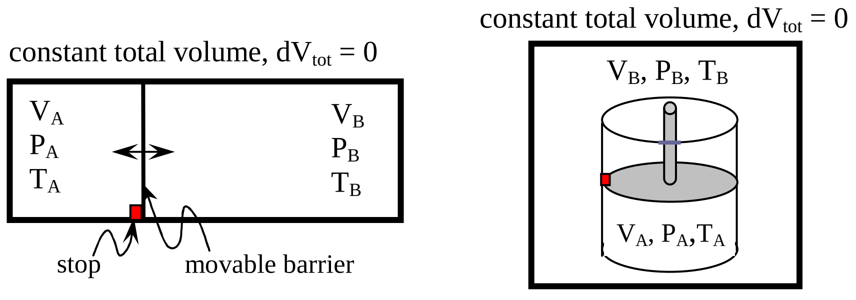
Physical Barriers Act as Constraints for Extensive Variables: The most commonly constrained extensive variables are the volume, the amounts of components, and the internal energy. Constant volume conditions are maintained by rigid walls of a container, which is one example of a physical barrier. For closed systems, mass or mole amounts of components are also constrained by physical barriers. For a simple example of a closed system, we often use a perfectly sealing piston. Internal energy is constrained in an isolated system, where the physical barriers are thermal insulation and rigid walls. Physical constraints have an important effect on the variables for the system. We start by discussing volume, since volume is easiest to visualize.

Constant volume: Consider a closed system with PV work as a simple example. Assume that the system has one thermodynamic component, for example one mole of a gas, and one phase. The combined First and Second Laws give the internal energy as:

$$dU = TdS - PdV \qquad \text{(closed)} \qquad 14.3.1$$

Constraining the volume sets $dV = 0$ and the system now has one fewer degree of freedom. This constrained system is now ideal for helping us understand entropy-temperature relationships. In other words, constraints simplify the system and help us focus on the issue at hand.

Now consider a system with two compartments separated by a movable barrier, Figure 14.3.1a. Such a system is called a **composite**.



(a) (b)

Figure 14.3.1 (a). A two-compartment system at constant total volume: $dV_A = -dV_B$. (b). A two-compartment system can also be drawn with system A confined in a piston. The barrier must be fixed by a stop, otherwise the system will attain equilibrium with $P_A = P_B$.

For this two-compartment system, the total volume is $V_{tot} = V_A + V_B$ with $dV_{tot} = dV_A + dV_B$. If the two-compartment system is constrained to be at constant volume, then $dV_{tot} = 0$ as before. However, a PV process can still occur. If the pressures of the two compartments are not equal, $P_A \neq P_B$, the barrier can move and work can be done. However, because the total volume is constrained:

$$dV_{tot} = 0 = dV_A + dV_B \qquad (\text{cst.}V_{tot}) \qquad 14.3.2$$

The volumes of the subsystems are now <u>dependent</u> variables with

$$dV_A = -\, dV_B \qquad (\text{cst.}V_{tot}) \qquad 14.3.3$$

No generality is lost if we construct the composite with system A confined in a piston and system B as occupying the remainder of the closed vessel, Figure 14.3.1b. The position of the movable barrier must be fixed with a stop to keep P_A and P_B different. When the stop is removed, the barrier moves until the system attains equilibrium with $P_A = P_B$. The barrier with the stop is called a temporary **internal constraint**. The result of removal of the temporary internal constraint is an irreversible, spontaneous process if the forces are imbalanced.

Irreversible Processes Can Be Studied Using Thermodynamics: We want to use thermodynamics to determine the spontaneous direction for the process in Figure 14.3.1. However, thermodynamics only applies to equilibrium systems. How can equilibrium thermodynamics be used to predict the outcome of an irreversible process? Let the internal energy of the system before the temporary internal constraint is removed be U_1 and the internal energy after the system reaches equilibrium be U_2. The change in the internal energy for the process is $\Delta U = U_2 - U_1$. Before the removal of the constraint, the system is at equilibrium with P_A and P_B constrained and $P_A \neq P_B$. After the process, the system is at equilibrium with $P_A = P_B$, so both endpoints for the calculation of ΔU are equilibrium systems. Not until the removal of the constraint is the irreversible process possible, but then ΔU is a state function and is independent of the path. The same arguments apply to the change in any state function for the process. Temporary internal constraints allow the enthalpy, entropy, and as we shall soon see the Gibbs energy to be calculated before and after an irreversible process, as long as the initial and final states are at equilibrium.

Constraints on composite systems have the same effect as on simple systems; the constraints simplify the system by decreasing the number of independent thermodynamic variables. This effect of constraints is particularly important for closed systems with chemical reactions, which we explore next.

Closed Systems Have Constant Mole Amounts of Components: Consider a one-component open system. For an open, one-thermodynamic-component system with PV and chemical work:

$$dU = TdS - PdV + \mu_1\, dn_1 \qquad 14.3.4$$

For a closed system, $dn_1 = 0$, and $dU = TdS - PdV$. A barrier of some type must be used that will not allow substances to pass, for example, an impermeable membrane or just a sealed flask. The physical barrier decreases the number of independent extensive variables. Closed systems are particularly important for understanding chemical equilibria.

Chemical Reactions in Closed Systems are Expressed in Terms of the Extent: Now assume that a chemical reaction occurs in the system. To keep things simple for now, assume that the reaction has the stoichiometry:

$$A \rightarrow B \qquad 14.3.5$$

Such reactions include all isomerizations. In the strict thermodynamic sense, such a system still has only one component, but it now has two constituents that can interconvert through the chemical reaction. The total amount of the component is given by the mole balance equation, $n_1 = n_A + n_B$, and since this is a closed system:

$$dn_1 = 0 = dn_A + dn_B \qquad \text{(closed)} \qquad 14.3.6$$

The composition variables are now <u>dependent</u> with $dn_B = - dn_A$. In other words, at first you might suppose that closed systems are uninteresting from a chemical perspective. Instead, closed systems help us to simplify a system to allow us to focus on the chemical reactions. In fact, when we want to study a chemical reaction in the laboratory, we normally mix fixed amounts of reactants and then watch the reaction proceed. After the reactants are mixed we effectively close the system by not adding any more of the reactants or products. In other words, the system is closed after we prepare the system. So working with closed systems is quite natural from a laboratory perspective.

Consider the general equation for the change in internal energy for a process with PV work and chemical work as given by Eq. 14.1.4. For a closed system, the amounts of the various components are fixed and are no longer independent variables. Instead, the constituents are interrelated by the mole balance equations. The changes are given by dn_i as before, but now the i indexes all the constituents. These changes are related to the extent of the reaction, ξ, using the stoichiometric coefficients, ν_i. For the general reaction:

$$a\,A + b\,B \rightarrow c\,C + d\,D \qquad 14.3.7$$

following Eq. 3.1.4, the changes are related by:

$$dn_i = \nu_i\, d\xi \qquad 14.3.8$$

Remember that ν_i is negative for a reactant and positive for a product. For a closed system then:[1]

$$dU = TdS - PdV + \sum_{i=1}^{n_s} \nu_i\, \mu_i\, d\xi \qquad \text{(closed, PV \& chemical work)} \qquad 14.3.9$$

where the sum is over all constituents, n_s. The stoichiometric coefficients are unitless, the units of ξ are moles, and ξ is an extensive quantity. Alternatively, Eq. 14.3.9 can be written as

$$dU = TdS - PdV + \sum_{i=1}^{n_s} \mu_i\, dn_i \qquad \text{(closed, PV \& chemical work)} \qquad 14.3.10$$

<u>if</u> it is remembered that the sum is over all constiuents, and the constitutents are all dependent variables according to Eq 14.3.8. If you are reading along in another text, which is a good idea, you will notice that the difference between Eq. 14.1.4 and Eq. 14.3.10 is often a point of confusion.

Example 14.3.1

Determine the change in internal energy for the following reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

$$PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g) \qquad 14.3.11$$

Answer: $dU = TdS - PdV + \mu_{PCl_3}\, d\xi + \mu_{Cl_2}\, d\xi - \mu_{PCl_5}\, d\xi$ 14.3.12

Example 14.3.2

The disproportionation of hydrogen peroxide is:

$$2\ H_2O_2\ (aq) \rightleftarrows 2\ H_2O\ (g) + O_2\ (g) \qquad 14.3.13$$

Determine the change in internal energy for the reaction in terms of the change in extent of the reaction, $d\xi$, for a closed system.

Answer:

$$dU = TdS - PdV + 2\ \mu_{H_2O}\, d\xi + \mu_{O_2}\, d\xi - 2\ \mu_{H_2O_2}\, d\xi \qquad 14.3.14$$

Internal Constraints for Chemical Reactions: Consider a typical chemical reaction:

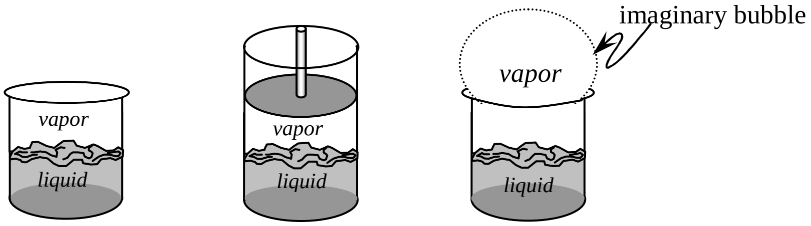
$$A + B \rightarrow C + D \qquad 14.3.15$$

The temporary internal constraint for this reaction depends on the process that you want to study. The simplest case is just a barrier between two compartments, one containing pure A and the other containing pure B. Often, however, we wish to study the reaction beginning right after the reagents have mixed. The commonly applied rule is that equilibrium thermodynamics applies as long as the measurements are made at times longer than five times the characteristic relaxation times for the system. This rule suggests that after mixing the reactants, the system can be considered as at equilibrium with respect to temperature, pressure, and concentration gradients, but not at equilibrium with respect to the overall course of the chemical reaction. The time interval between attainment of the initial equilibrium after mixing but before any appreciable reaction has taken place may be quite short for some reactions. But during this interval it is allowable to treat the initial mixture of reactants as a metastable, non-reacting mixture for the purposes of calculating the reaction internal energy, entropy, and Gibbs energy changes.[2] For the prediction of spontaneity, it is not necessary to be able to physically realize this initial state, as long as it is theoretically possible from a thermodynamic perspective. In other words, at $\xi = 0$ the initial state is just the mixture of reactants. Before the removal of the constraint, the system is at equilibrium with ξ constrained at zero. The internal energy, entropy, and Gibbs energy of this initial state are easy to calculate from standard tabulations. After the process, the system attains the equilibrium value of ξ. So both endpoints are equilibrium systems.

Phase Transitions are Equivalent to Chemical Reactions: Eq. 14.3.5-10 can also be used to describe phase transitions. For example, for the vaporization of water in a closed system:

$$H_2O\ (l) \rightarrow H_2O\ (g) \qquad 14.3.16$$

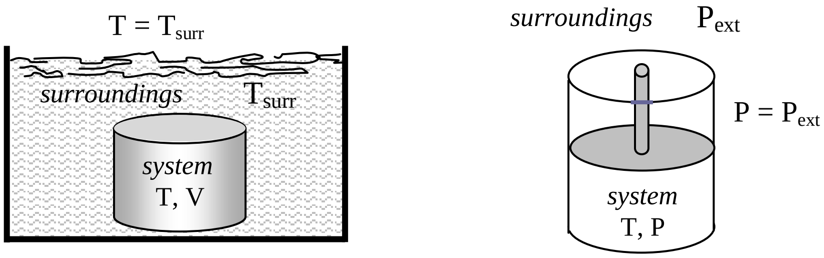
where A applies to the liquid and B applies to the vapor: $dn_A = -\,dn_B$ becomes $dn_{vap} = -\,dn_{liq}$. To establish the closed system, we can think of the liquid and vapor as enclosed in a piston or even by an imaginary soap bubble, Figure 14.3.2. The physical barrier can be replaced by a physical boundary like an imaginary soap bubble, as long as the boundary encompasses the total moles of all constituents. Chemical reactions can also be thought of as closed by an imaginary soap bubble.



$H_2O\ (l) \rightarrow H_2O\ (g)$

Figure 14.3.2: Phase transitions and chemical reactions can be considered as closed systems and visualized as enclosed in a piston or even an imaginary bubble. These particular systems are at constant pressure with $P = P_{ext} = P_{atm}$.

*Intensive Variables are Constrained by Reservoirs***:** Intensive variables are constrained by placing the system in contact with a corresponding reservoir. For example, a constant temperature bath is commonly used as a constant temperature reservoir in the laboratory, Figure 14.3.3a. Exchanges of energy between the system and the bath maintain the temperature of the system as a constant, $T = T_{surr}$. The system may also be held at constant pressure by contact with a constant pressure reservoir, Figure 14.3.3b. Placing the system in a piston is a convenient way to allow contact with the constant pressure reservoir. Any process open to the atmosphere is at constant pressure with the atmosphere acting as the constant pressure reservoir with $P = P_{ext}$.



(a) Constant temperature reservoir (b) Constant pressure reservoir

Figure 14.3.3: (a) Constant temperature is maintained by placing the system in contact with a constant temperature reservoir. A constant temperature bath is a constant temperature reservoir, which can be considered part of the surroundings. (b) Constant pressure is maintained by contact with a constant pressure reservoir.

The System and the Surroundings Form a Composite: Consider the composite in Figure 14.3.4a. Assume that the part of the system that we wish to study is in system A. For example, a chemical reaction might occur in system A. If system B is much larger in size than system A, then system B can act as a constant temperature and constant pressure reservoir for system A. Under these circumstances, it is convenient to call system A just the "system" and to call system B the "surroundings," Figure14.3.4b, as we did in Figure 12.5.1. If the composite is isolated, then we can apply the Second Law of thermodynamics. It doesn't matter whether we use the "system A—system B" designation or the "system—surroundings" designation, the interactions are the same. We can also consider the universe as divided into two parts: the system and the surroundings.

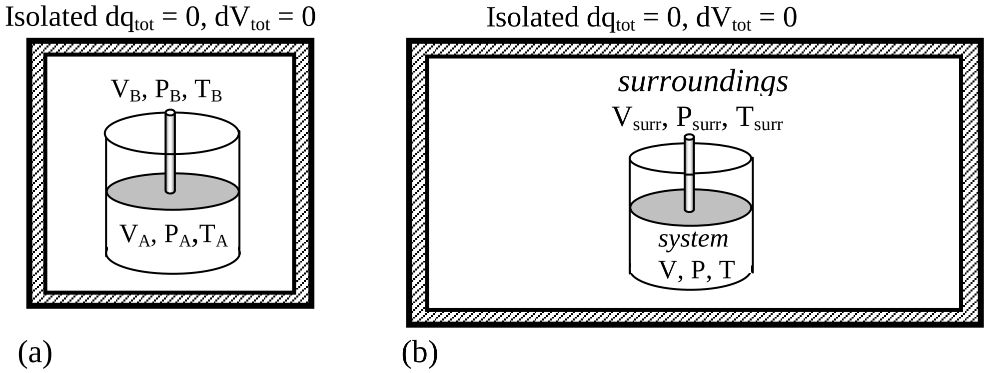


Figure 14.3.4: (a.) Isolated composites constrain the total volume, moles, and internal energy. (b.) The surroundings are assumed to be large in extent.

What makes up the surroundings? The surroundings are composed of everything not included in the system. If the system is held in a constant temperature bath, from the perspective of the system, the constant temperature bath is part of the surroundings. If an explicit constant temperature bath is not present, the surroundings act as a constant temperature bath, assuming sufficient time is allowed to establish thermal equilibrium. The key point is that transfers of energy to or from the surroundings do not change the temperature of the surroundings, assuming thermal equilibrium. The temperatures of the system and the surroundings are equalized by small transfers of heat, with:

$$\text{đ}q = -\,\text{đ}q_{surr} \qquad 14.3.17$$

The contact of the system with the surroundings keeps the system at constant temperature, which decreases the number of independent intensive variables by one.

When the surroundings act as a constant pressure reservoir, Figure 14.3.3b, the pressures of the system and the surroundings are equalized by small changes in the volume of the system, with:

$$dV = -\,dV_{surr} \qquad 14.3.18$$

This contact is a constraint that decreases the number of intensive variables by one. If the surroundings simultaneously act as a constant temperature and a constant pressure reservoir, the constraints are: $T = T_{surr}$, $P = P_{surr}$, $\text{đ}q = -\,\text{đ}q_{surr}$, $\text{đ}w = -\,\text{đ}w_{surr}$, and $dV = -\,dV_{surr}$.

Isolated Systems Constrain the Internal Energy: The Second Law of thermodynamics applies only to isolated systems. An isolated system is constrained so that no energy in the form of heat or work can be transferred into or from the closed system. We can make the composite in Figure 14.3.1 isolated by insulating the walls of the constant volume container; the result is shown in Figure 14.3.4. The interactions are the same if we label the systems A and B, or the system and the surroundings. Let dU_{tot} be the internal energy of the composite, $dU_{tot} = dU_A + dU_B$, or equivalently $dU_{tot} = dU + dU_{surr}$. For a process in an isolated composite, $dU_{tot} = 0$ from the First Law and:[2]

$$đq_A = -\,đq_B,\ đw_A = -đw_B,\ dV_A = -dV_B, \text{ and } dU_A = -\,dU_B \qquad \text{(isolated)} \quad 14.3.19$$

or written in terms of the system and the surroundings:

$$đq = -\,đq_{surr},\ đw = -\,đw_{surr},\ dV = -\,dV_{surr}, \text{ and } dU = -\,dU_{surr} \qquad \text{(isolated)} \quad 14.3.20$$

and at equilibrium: $T_A = T_B$, $P_A = P_B$, or equivalently: $T = T_{surr}$, $P = P_{surr}$.

14.4 Other Forms of Work

In the analysis above, we used chemical work as an example of non-PV work. Any other form of work follows the same pattern. Remember that non-PV work can be cast in the form of a force multiplied by a displacement, dw = F dx. To study processes involving this kind of non-PV work, we need to set a constraint for the extensive variable with constant total x. Consider the work of extension, such as the work in stretching a spring, a rubber band, or a muscle. To help visualize this process, think of two springs or rubber bands attached to a movable barrier in analogy to the volume constraint we used in Figure 14.3.1. Such a system is diagrammed in Figure 14.4.1. We can apply the Second Law of thermodynamics to this system if we specify an isolated composite.

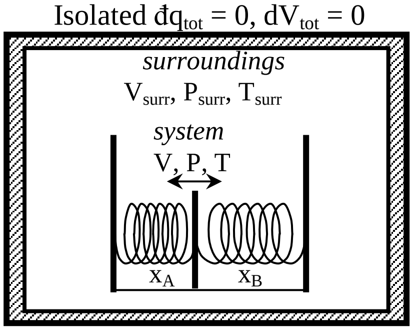


Figure 14.4.1: The total displacement is constrained for generalized work, dx = 0, with $dx = dx_A + dx_B$.

The net result is that $x = x_A + x_B$, and the constant displacement constraint gives dx = 0, with $dx = dx_A + dx_B = 0$. The x_A and x_B extensive variables are dependent with

$$dx_B = -\,dx_A \qquad 14.4.1$$

In addition, conservation of energy gives:

$$dU_{tot} = dU_A + dU_B + dU_{surr} \qquad 14.4.2$$

Assuming that the volume of the combined springs is constant, no work is done on the surroundings, $\text{đ}w_{surr} = 0$. The total work is then given as the sum for the two compartments:

$$\text{đ}w = \text{đ}w_A + \text{đ}w_B \qquad \text{(constant V)} \qquad 14.4.3$$

Then $\text{đ}w_B = -\,\text{đ}w_A$. This lack of interaction with the surroundings is analogous to a closed system when considering chemical work.

This type of two-part system is convenient for studying membrane potentials; Figure 7.9.4 is reproduced below with an explicit realization as an isolated composite.[3] We will use this isolated composite in the next several chapters to study membrane potentials.

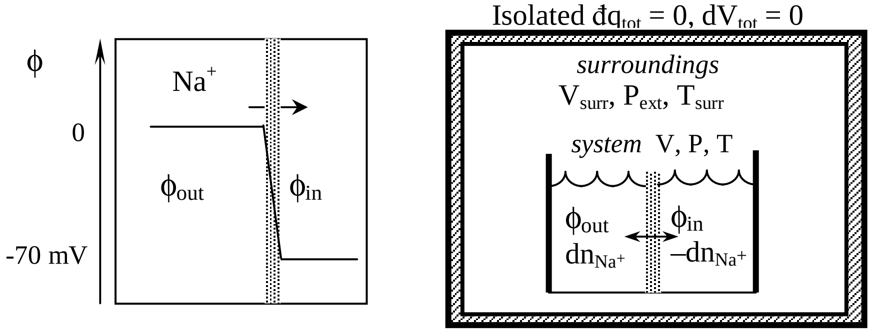


Figure 14.4.2: The two-part system for transfer across a semi-permeable membrane. The membrane potential is $\Delta\phi = \phi_{in} - \phi_{out}$. The composite is isolated.

In the case of a neuron, the inside compartment on the right is a cell and the outside compartment on the left is the extracellular matrix. The extensive variable for electrical work is the charge. However, the charge transferred is given by the change in mole amounts, $dq_i = z_i F\, dn_i$, so we can use dq_i or dn_i interchangeably as the extensive variable. The constraint is that the total ion concentrations are constant. For the Na^+ ion, $dn_{tot}(Na^+) = dn_{in}(Na^+) + dn_{out}(Na^+)$ and the constriant gives $dn_{in}(Na^+) = -\,dn_{out}(Na^+)$. This constraint is identical to a closed system for chemical reactions, except that the process is the change in concentration from one point to another instead of a chemical reaction:

$$Na^+ \text{ (outside)} \rightarrow Na^+ \text{ (inside)} \qquad 14.4.4$$

The total energy is conserved with $dU_{tot} = dU_{in} + dU_{out} + dU_{surr}$, $dq = dq_{in} + dq_{out} = -\,dq_{surr}$, and $dV = dV_{in} + dV_{out} = -\,dV_{surr}$. At equilibrium, $T = T_{surr}$ and $P = P_{ext}$. The transfer of charge or moles is driven by a difference in concentration and electric potential across the membrane.

14.5 Summary – Looking Ahead:

Specifying a constant volume or a closed system simplifies the system by decreasing the number of independent extensive variables. Placing the system in contact with a constant temperature or pressure reservoir constrains the corresponding variable and decreases the number of independent intensive variables. An isolated system constrains the total volume, mole amounts, and total internal energy. Isolated systems provide the simplest systems that we can use to study physical or chemical transformations. The universe can be considered an isolated system under many practical circumstances.

Temporary internal constraints are used to allow the calculation of the state of the system before the process begins. The system is at equilibrium before the internal constraint is released and after the process is complete.

A glass of water on the desktop and a chemical reaction open to the atmosphere are examples of constant temperature and pressure systems, if we allow sufficient time to establish equilibrium with the surroundings. Isothermal, constant pressure processes are the most common type of chemical processes, because we often work with beakers that are open to the atmosphere. Most importantly, living systems are at constant temperature, either at ambient temperature or at a carefully regulated internal temperature, and at constant pressure, if they are open to the atmosphere.

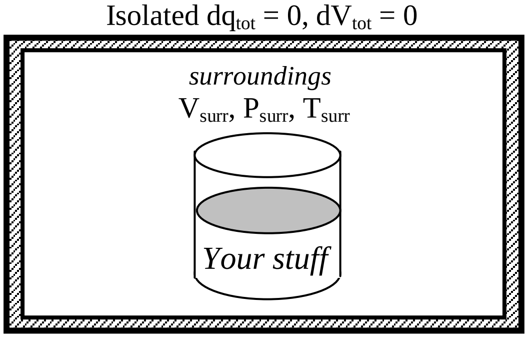


Figure 14.5.1: Thermodynamics applies to all physical processes at equilibrium. An isolated composite focuses attention on the processes that occur in the system.

One of the strengths of thermodynamics is its generality. One way to phrase this is to note that nature is very “economical and efficient.” Nature doesn’t have different sets of rules for rocks, trees, people, and chemical reactions. All physical systems are governed by a very few laws. One of the difficulties of thermodynamics is that this generality can sometimes make it difficult to see how these laws apply to your specific system. We often draw the system as just a box, a circle, or a piston. The circle may represent a mass of iron, or a beaker containing a chemical reaction, or a cell, or a mouse. What you need to do is to fill the box or piston with your stuff, what ever interests you, Figure 14.5.1. Thermodynamics will then help you keep track of the flow of heat and work and the response of the system to changes in constraints.

Chapter Summary

1. The combined First and Second Laws of thermodynamics for open systems is given as:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i$$

2. The chemical potential of a component is defined as: $\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}$

3. The number of components for a system is given by:

   $c = n_s$ – no. of reactions – no. of chemical constraints

4. Extensive variables are constrained by physical barriers, boundaries, and any conditions placed on the preparation of the system.
5. Isolated systems constrain total volume, energy, and mole amounts for each thermodynamic component.
6. A constrained extensive variable may be applied to a composite. For volume in a constrained composite $dV_A = – dV_B$. The constrained extensive variable is converted into a dependent set of variables.
7. A closed system constrains the thermodynamic components. In a closed system the constituents are related by the extent of any chemical reaction or the progress of a phase transition.: $dn_i = \nu_i \, d\xi$

   For a phase transition such as vaporization: $dn_{vap} = – dn_{liq}$

8. A temporary internal constraint is used to allow the calculation of the state of the system before the process begins.
9. The physical barrier that establishes a closed system can be an imaginary bubble that encloses all of the thermodynamic components of the system.
10. Intensive variables are constrained by reservoirs.
11. A composite may be divided into a system and the surroundings. This division is useful if the portion that corresponds to the surroundings is large in extent.
12. The surroundings can act as a constant temperature and pressure reservoir: then $T = T_{surr}$ and $P = P_{surr} = P_{ext}$.
13. An isolated composite-system consisting of the system and surroundings gives: $dV = –dV_{surr}$, $dU = –dU_{surr}$, $đq = –đq_{surr}$, $đw = –đw_{surr}$, $dn_i = \nu_i \, d\xi$. With the system in contact with the surroundings at thermal and mechanical equilibrium, $T = T_{surr}$, $P = P_{surr}$.
14. Each constraint decreases the number of independent variables by one.
15. The system can be anything you are interested in. The thermodynamic name for your system is “your stuff.”

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1. S. E. Wood, R. Battino, *Thermodynamics of Chemical Systems*, Cambridge University Press, Cambridge, England, 1990. Sections 5.2.-5.13.
2. F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Chapt. 8.
3. S. R. Caplan, A. Essig, *Bioenergetics and Linear Nonequilibrium Thermodynamics*, Harvard University Press, Cambridge, MA, 1999. Section 2.4.

Further Reading

Constraints and Irreversible Processes:

H. B. Callen, *Thermodynamics: an introduction to the physical theories of equilibrium thermostatics and irreversible thermodynamics*, Wiley, New York, NY, 1960, Sections 1.5, 1.8, 2.4.

F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Chapt. 11, 21, 22.

Membrane Systems and Constraints

S. R. Caplan, A. Essig, *Bioenergetics and Linear Nonequilibrium Thermodynamics*, Harvard University Press, Cambridge, Massachusetts, 1999. Section 2.4.

Problems: Focusing on Chemical Reactivity

1. Find the number of thermodynamic constituents and components for a solution of hexane and chloroform. Find the expression for dG for changes in the number of components in an open system at constant temperature and pressure.

2. Lime is made commercially through the thermal decomposition of limestone, which is composed primarily of calcium carbonate:

$$CaCO_3\ (s) \rightleftarrows CaO\ (s) + CO_2\ (g)$$

Find the number of thermodynamic components starting with only $CaCO_3$. In other words, assume that there are no other sources of CaO or CO_2 other than the decomposition of $CaCO_3$.

3. Solid ammonium chloride decomposes at high temperatures to give ammonia and hydrogen chloride gas:

$$NH_4Cl\ (s) \rightleftarrows NH_3\ (g) + HCl\ (g)$$

Find the number of components for a system prepared from only NH_4Cl (s).

4. Gas phase ammonia and hydrogen chloride gas react to form solid ammonium chloride:

$$NH_3\ (g) + HCl\ (g) \rightleftarrows NH_4Cl\ (s)$$

(a). Find the number of components for a system prepared from arbitrary amounts of NH_3 and HCl. (b). Find the number of components for a system prepared from equal-molar amounts of NH_3 and HCl.

5. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$

Find the number of constituents and thermodynamic components starting with only acetic acid and water. In other words, assume that there are no other sources of CH_3COO^- other than the dissociation of CH_3COOH. Also, include the dissociation of water as a source of H^+. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

6. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$

Find the number of constituents and thermodynamic components starting with a solution prepared from acetic acid, sodium acetate, and water. Also, include the dissociation of water as a source of H^+. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

7. Find the number of constituents and thermodynamic components starting with a solution prepared from phosphoric acid, sodium hydroxide, and water. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

8. Hydrogen peroxide, which is used as a topical disinfectant, decomposes to give O_2 gas in a highly exothermic reaction. This reaction is often used as a rather spectacular chemical demonstration:

$$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

Hydrogen peroxide is also important in redox reactions in the environment and in biological processes. During this reaction many things can change: V, P, S, T, U, H, and the mole amounts of the reactants and products. Keeping track of all these variables can be daunting. How can we simplify the definition of our system so that we can focus on the chemical changes?

9. For the reaction in the last problem, evaluate the change in entropy of the system, the surroundings, and the total change in entropy. Don't use any specific numbers; just consider the appropriate equations and inequalities. Compare the results for the entropy with the results from the last problem for the change in internal energy.

10. The decomposition of hydrogen peroxide is a spontaneous process:

$$2\ H_2O_2\ (aq) \rightleftarrows 2\ H_2O\ (l) + O_2\ (g)$$

How can we use thermodynamics, which only applies to systems at equilibrium, to study this process?

11. Consider the following chemical reaction at room temperature and in the absence of a catalyst:

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l)$$

This reaction is spontaneous and therefore the process is irreversible. This reaction is in fact the primary source of propulsion for the space shuttle. Describe how we can apply thermodynamics to calculating the change in internal energy and entropy for this process when the reaction goes to equilibrium by an irreversible reaction.

12. Devise an internal constraint for an electrochemical reaction that you wish to maintain at the initial conditions. For example consider the reaction:

$$AgCl\ (s) + \tfrac{1}{2}\ H_2\ (g,\ 1\ bar) \rightarrow Ag\ (s) + Cl^-\ (1\ m) + H^+\ (1\ m)$$

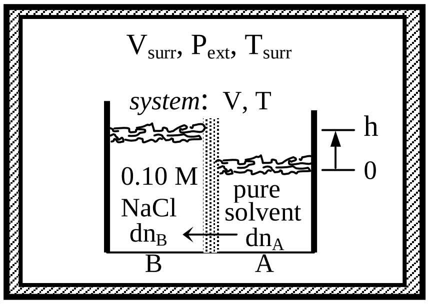
13. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

$$\tfrac{1}{2}\ N_2\ (g) + {}^{3}/_{2}\ H_2\ (g) \rightarrow NH_3\ (g)$$

14. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

$$C_6H_{12}O_6\ (s) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (l)$$

15. A 0.10 M NaCl aqueous solution is separated from pure water by a semi-permiable membrane. The height difference between the solution and the pure solvent is h and the corresponding equilibrium osmotic pressure is π. The system and the surroundings are in equilibrium. Assume the molar volume of the solvent in the solution is essentially the pure molar volume. Construct a isolated composite with this membrane system and the surroundings. Consider the transfer of dn_A moles of solvent from the pure solvent through the membrane into the solution. Consider $h = 0$ as the reference height. Relate P_{ext} and T_{surr} with P_A, P_B, and T, where P_A is the pressure at $h = 0$ for the pure solvent and P_B is the pressure at $h = 0$ for the NaCl solution. Relate dU, $\text{đ}q$, $\text{đ}w$, and dV for the total composite, the surroundings, the system (A and B), and for the pure solvent (A) and the NaCl solution (B).



16. (*Challenge Problem*) For the previous problem, find the PV-work, $\text{đ}w$, for the the transfer of dn_A moles of solvent from the pure solvent through the membrane into the NaCl solution.