

## 10.7: Reversibility and Thermodynamic Variables in General

We have found total differentials for the principal thermodynamic functions with  $V$  and  $T$  and with  $P$  and  $T$  as the independent variables. In §6, we see how to find such differentials,  $dM = M_X dX + M_Y dY$ , for any pair of independent variables,  $X$  and  $Y$ . These equations express our physical theory as a mathematical structure. Because  $E, T, S, P, V, H, A$ , and  $G$  are state functions, the mathematical properties of state functions enable us to obtain the relationships  $M_X = (\partial M / \partial X)_Y$ ,  $M_Y = (\partial M / \partial Y)_X$ , and  $(\partial M_Y / \partial X) = (\partial M_X / \partial Y)$  that we find in §1. These equations apply to reversible processes in closed systems when only pressure–volume work is possible. Using these equations to describe reversible processes involves a number of important ideas. Let us consider four cases: [GrindEQ\_1\_] None of  $M, X$ , and  $Y$  are constant; [GrindEQ\_2\_]  $M$  is constant, but  $X$  and  $Y$  are not; [GrindEQ\_3\_]  $X$  is constant, but  $M$  and  $Y$  are not; [GrindEQ\_4\_]  $X$  and  $Y$  are constant, but  $M$  is not.

**None of  $M, X$ , and  $Y$  is constant.**– The properties of state functions and the existence of the exact differential,  $dM = M_X dX + M_Y dY$  imply that  $M$  is a function of  $X$  and  $Y$ ,  $M = M(X, Y)$ . If  $M_X$  and  $M_Y$  are single-valued and continuous along some path in the  $XY$ -plane, we can evaluate the line integral of  $dM$  along this path. Given  $M$  at a first point,  $M(X_1, Y_1)$ , we can find  $M$  at a second point,  $M(X_2, Y_2)$ , by evaluating this line integral along some path in the  $XY$ -plane between the points  $(X_1, Y_1)$  and  $(X_2, Y_2)$ . Given the values of  $X$  and  $Y$ , the value of  $M$  is uniquely determined;  $M(X, Y)$  is a two-dimensional surface in the three-dimensional space whose dimensions are  $M, X$ , and  $Y$ .

The  $M(X, Y)$  surface is just the set of points that are accessible to the system in reversible processes in which  $X$  and  $Y$  change. Conversely, the only values of  $M$  that are accessible to the system in reversible processes in which  $X$  and  $Y$  change correspond to those points that lie on the surface. In §5, we find the total differentials for  $dE, dS, dH, dA$ , and  $dG$  using  $P$  and  $T$  as the independent variables. Evidently, for a reversible process in a closed system, there is a surface representing each of  $E, S, H, A$ , and  $G$  over the  $P - T$ -plane. Since the system is also characterized by an equation of state that relates the values of  $P, V$ , and  $T$ , there is also a surface representing  $V$  over the  $P - T$ -plane.

In general, a given system can also undergo spontaneous changes. Suppose that a system is originally at equilibrium at temperature  $T_1$  and pressure  $P_1$ . If we contact this system with surroundings at some arbitrary  $\hat{T}$  and we arrange for the pressure applied to the system to have some arbitrary value,  $P_{\text{applied}}$ , the system will respond, eventually reaching equilibrium with the system temperature equal to  $\hat{T}$  and the system pressure equal to  $P_{\text{applied}}$ . (The change-enabled state in which  $P_{\text{system}} = P_1$  and  $T_{\text{system}} = T_1$ , while the applied pressure is  $P_{\text{applied}}$  and the surroundings temperature is  $\hat{T}$ , is a hypothetical state. It is not an equilibrium state, because  $P_{\text{system}} \neq P_{\text{applied}}$  and  $T_{\text{system}} \neq \hat{T}$ . The change-enabled state can undergo spontaneous change; however, its thermodynamic functions have the same values as they have in the original equilibrium state, in which  $P_{\text{system}} = P_1$  and  $T_{\text{system}} = T_1$ .) Since this change is spontaneous, it may not be possible to trace the path of the system in the  $P - T$ -plane as the change occurs. If we can trace the path in the  $P - T$ -plane, the energy of the system can be described as a line in  $E - P - T$ -space, but this line will not lie on the reversible-process surface specified by the function  $E = E(P, T)$ . Nevertheless, we can select paths in the  $P - T$ -plane that connect the initial point  $(P_1, T_1)$  to the final point  $(P_{\text{applied}}, \hat{T})$ . There are reversible processes that correspond to these paths. By evaluating the line integral for any state function along any of these paths, we can find the change that occurs in the state function during the spontaneous process.

Cases arise in which  $M$  is not single-valued or continuous along some or all of the paths that connect points  $(X_1, Y_1)$  and  $(X_2, Y_2)$ . Then  $M_X$  or  $M_Y$  may not exist for some points  $(X, Y)$ . In this case, it may not be possible to evaluate the line integral to find the change  $M(X_2, Y_2) - M(X_1, Y_1)$ . This can occur when there is a phase change. If  $(P_{vp}, T_{bp})$  specifies a state of liquid–vapor equilibrium, the enthalpy of the system is not single-valued. Below, we consider the thermodynamic surfaces of water when a phase change occurs. In §8, we see that  $M$  may not be single-valued when  $V$  and  $P$  or when  $T$  and  $S$  are the independent variables.

**$M$  is constant,  $X$  and  $Y$  are not.**– If  $M$  is constant, we have  $dM = 0$ . If  $X$  and  $Y$  are not constant, if  $M_X$  and  $M_Y$  are defined, and if  $M_Y \neq 0$ , we can apply the divide-through rule to obtain

$$\left( \frac{\partial Y}{\partial X} \right)_M = -\frac{M_X}{M_Y}$$

Such relationships are useful. In Chapter 12, we discuss the Clapeyron and Clausius-Clapeyron equations, which we obtain from  $dG = -SdT + VdP$  using this argument.

**X is constant, M and Y are not.**— If  $X$  is constant, we have  $dX=0$ . Instead of ,  $dM = M_X dX + M_Y dY$  , we have ,  $dM = M_Y dY$  , and we must ask whether  $M$  is indeed expressible as a function of  $Y$  only. If  $M$  can be expressed as a function of  $Y$  only, so that  $M_Y$  is single-valued and continuous, we can integrate to find

$$M_2 + M_1 = \int_{Y_1}^{Y_2} M_Y dY$$

**X and Y are constant, M is not constant.**— An interesting and important case arises when  $X$  and  $Y$  are constant, but  $M$  is not constant. When  $X$  and  $Y$  are constant,  $dX = dY = 0$  , and from  $dM = M_X dX + M_Y dY$  , it follows that  $dM = 0$  . Nevertheless, we can readily identify processes in which some state function,  $M$ , changes while two (or more) others,  $X$  and  $Y$ , remain constant. In this case, it is clear that  $X$  and  $Y$  are not sufficient to model the change in  $M$ . Recall from our discussion of Duhem's Theorem that, while two independent variables are sufficient to describe a reversible process in which pressure-volume work is the only work, which pair of variables is adequate depends on the system.

Below we discuss the reversible vaporization of water at constant  $P$  and  $T$ . For this process we have  $dG = 0$  . However, we know that  $dS > 0$  . For independent variables  $P$  and  $T$ , our differential expressions for  $dG$  and  $dS$  are

$$dG = VdP - SdT$$

and

$$dS = \frac{1}{T} \left( \frac{\partial H}{\partial T} \right)_P dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

Setting  $dP = dT = 0$  in these equations correctly gives  $dG = 0$  ; however,  $dS = 0$  is false. Evidently, variables  $P$  and  $T$  are not sufficient to model the entropy change in this process.

However, at constant  $P$  and  $T$ , variables  $V$  and  $T$  are adequate. We have

$$dS = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial T} \right)_V dV$$

In [Section 12.10](#) we develop the Clausius-Clapeyron equation for this vaporization process; we find

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{P \Delta_{vap} \bar{H}}{RT^2}$$

( $\Delta_{vap} \bar{H}$  is the enthalpy of vaporization per mole.) Since the volume of the system is essentially the volume of the gas phase, we have, assuming the vapor behaves as an ideal gas,  $V = n_g RT / P$ , and

$$dV = \frac{RT}{P} dn_g$$

The entropy equation then becomes

$$\begin{aligned} dS &= \left( \frac{\partial P}{\partial T} \right)_V dV \\ &= \frac{P \Delta_{vap} \bar{H}}{RT^2} \cdot \frac{RT}{P} dn_g \\ &= \frac{\Delta_{vap} \bar{H}}{T} dn_g \end{aligned}$$

so that the entropy change for this reversible process is directly proportional to the number of moles of vapor produced.

We see that we must introduce an extensive variable to model the entropy change in the vaporization process. The system volume serves this purpose, although we wind up expressing this volume in terms of the number of moles of vapor in the system.

From another perspective, we can write the entropy as a function of  $P$ ,  $T$ , and  $n_g$ :  $S = S(P, T, n_g)$ . Then

$$dS = \frac{1}{T} \left( \frac{\partial H}{\partial T} \right)_P dT - \left( \frac{\partial V}{\partial T} \right)_T dP + \left( \frac{\partial S}{\partial n_g} \right)_{PT} dn_g$$

which becomes

$$(dS)_{PT} = \left( \frac{\partial S}{\partial n_g} \right)_{PT} dn_g$$

with

$$\left( \frac{\partial S}{\partial n_g} \right)_{PT} = \frac{\Delta_{vap} \bar{H}}{T}$$

In [Chapter 14](#), we extend all of our thermodynamic models to include variables that specify the system composition—the number of moles of the substances present in the system.

### Thermodynamic surfaces in the reversible vaporization of water

To illustrate the fact that  $dT = dP = 0$  has different implications for  $dS$  than it does for  $dG$ , let us consider the reversible vaporization of one mole of water at constant  $P$  and  $T$ .  $\Delta G$  for this process is zero, but  $\Delta S$  and  $\Delta H$  are not. We can describe a system comprised of one mole of liquid water using pressure and temperature as the independent variables. There is a wide range of pressure and temperature values that is consistent with the system remaining entirely liquid. Every combination of pressure and temperature at which the system remains entirely liquid can be reached by a reversible process from any other such combination of pressure and temperature. For every combination of pressure and temperature within this range, there is one and only one value for every other thermodynamic function. Choosing the enthalpy function to be specific, we can say that the set of enthalpy–pressure–temperature-points for which the system remains entirely liquid is a thermodynamic surface on which reversible change is possible.

We can say all of these same things about a system that consists of one mole of gaseous water. Of course, the enthalpy surface for gaseous water is a different surface from the enthalpy surface for liquid water. At any given temperature, there is a pressure at which liquid and gaseous water are at equilibrium. Above this pressure, the system is entirely liquid; below it, the system is entirely gas. The enthalpy surface of the liquid lies over a different part of the pressure–temperature-plane than does that of the gas. (If the liquid can be superheated or the gas can be supercooled, a given pressure and temperature may be represented by a point on the enthalpy surfaces for both the pure liquid and the pure gas.) The enthalpy surface for the gaseous system lies at higher energies than that for the liquid system; the two enthalpy surfaces do not intersect.

To reversibly transform pure liquid water to pure gaseous water, we must move on the enthalpy surface of the liquid to a pressure and temperature at which the liquid and the gas are at equilibrium. At this pressure and temperature, we can reversibly increase the volume of the system, causing the reversible vaporization of liquid water, and we can continue this process until all of the liquid has been vaporized. When all of the liquid has been vaporized, the system is on the enthalpy surface of the gas. Thereafter, we can change the pressure and temperature of the system to reversibly change the state of the pure gas. While we can describe this process in terms of the successive changes that we impose on the state functions of a system that consists of one mole of water, we are considering three different systems when we describe the overall process from the perspective afforded by Gibbs' phase rule.

1. The first system is one mole of pure liquid. This system has one phase. There are two degrees of freedom, which we take to be pressure and temperature.
2. The second system is one mole of water, of which  $x_\ell$  mole is liquid and  $1 - x_\ell$  mole is gas, at equilibrium, at a fixed pressure and temperature. In the vaporization process, the pressure and temperature are constant while the volume of the system increases ( $x_\ell$  decreases) reversibly. The one mole of water is described by this system from the time the first bubble of gas appears to the time the last drop of liquid vaporizes. There are two phases and one degree of freedom. When we reversibly vaporize water at a fixed pressure and temperature, one variable must describe the composition: We can take it to be the volume of the system or the liquid mole fraction,  $x_\ell$ . (Of course, we can reversibly vaporize water in a process in which the pressure, temperature, and composition all change; however, because there is only one degree of freedom, specifying a temperature change uniquely determines the pressure change, and conversely. In  $H - P - T$ -space, a reversibly vaporizing system traces a path on a vertical plane between the enthalpy surfaces of the liquid and the gas. If pressure and temperature are constant, this path is a vertical line. If reversibility is achieved through synchronous variation of pressure and temperature, the path is not vertical, but it remains in a vertical plane.)
3. The third system describes the mole of water after all of the water has been converted to the gas. This system has one phase and two degrees of freedom, which we again take to be pressure and temperature.

We can say that this description of the reversible conversion of liquid water to gaseous water involves three Gibbsian  $H - P - T$  - manifolds. Two of these are the enthalpy surfaces for the gas and the liquid. The third is a line of enthalpies at constant pressure and temperature; successive points on this line represent different mole fractions of liquid water.

We can track the reversible conversion of one mole of pure liquid water to pure gas on other thermodynamic surfaces. For example, if we consider enthalpy as a function of volume and temperature, the entire process can be traced on a single  $H(V, T)$  surface; that is, every volume–temperature point,  $(V, T)$ , specifies a unique state of the system, and conversely.

When we use pressure and temperature as the independent variables, the Gibbs free energy provides the criterion for reversibility. Unlike the corresponding enthalpy surfaces, which never meet, the Gibbs free energy surfaces for the pure liquid and the pure gas intersect along a line of pressure and temperature values. At an equilibrium pressure and temperature, the Gibbs free energy change for the reversible vaporization of water is zero, which means that the Gibbs free energy for a mole of liquid water is the same as the Gibbs free energy for a mole of gaseous water at that pressure and temperature.

When we trace the reversible conversion of a mole of liquid water to a mole of gaseous water on the Gibbs free energy surfaces, the point representing the state of the mole of water moves on the Gibbs free energy surface of the liquid from the initial pressure and temperature to the pressure–temperature equilibrium line. The pressure–temperature equilibrium line is formed by the intersection of the Gibbs free energy surface of the liquid with the Gibbs free energy surface of the gas. (The projection of this line of intersection onto the  $P - T$ -plane is a line of points in the  $P - T$ -plane that satisfies the differential relationship  $0 = -\Delta_{vap}SdT + \Delta_{vap}VdP$ . The point  $P = 1 \text{ atm}$ ,  $T = 373.15 \text{ K}$ , lies on this line.)

The conversion of liquid to gas can occur while the mole of water remains at the same point in pressure–temperature–Gibbs free energy space, and the mole fractions,  $x_\ell$  and  $1 - x_\ell$ , vary continuously over the range  $0 < x_\ell < 1$ . During this reversible vaporization process,  $dG = dT = dP = 0$ , while  $\Delta_{vap}V > 0$ ,  $\Delta_{vap}H > 0$ , and  $\Delta_{vap}S > 0$ . (We find  $\Delta_{vap}H$  and  $\Delta_{vap}S$  by measuring the heat required to vaporize a mole of water at  $P$  and  $T$ . Then  $q_P = \Delta_{vap}H$ , and  $q_P/T = \Delta_{vap}S$ . Since the process is reversible, we have  $\Delta_{vap}S = -\Delta_{vap}\hat{S}$ , and  $\Delta_{vap}S + \Delta_{vap}\hat{S} = 0$ .) When the conversion of liquid to gas is complete, reversible changes to the one mole of gaseous water correspond to motion of a point on the Gibbs free energy surface of the gas.

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