

## 17.4: Chemical Potential

It is a truth universally acknowledged that, if we add some heat reversibly to a closed thermodynamic system at constant volume, its internal energy will increase by  $\left(\frac{\partial U}{\partial S}\right)_V dS$ ; or, if we allow it to expand without adding heat, its internal energy will increase by  $\left(\frac{\partial U}{\partial V}\right)_S dV$ . (In most cases the derivative  $\left(\frac{\partial U}{\partial V}\right)_S$  is negative, so that an increase in volume results in a decrease of internal energy.) If we do both, the increase in internal energy will be

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \quad (17.4.1)$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dU = TdS - PdV. \quad (17.4.2)$$

Likewise, it is a truism that, if we add some heat reversibly to a closed thermodynamic system at constant pressure, its enthalpy will increase by  $\left(\frac{\partial H}{\partial S}\right)_P dS$ ; or if we increase the pressure on it without adding heat, its enthalpy will increase by  $\left(\frac{\partial H}{\partial P}\right)_S dP$ . If we do both, the increase in internal energy will be

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP. \quad (17.4.3)$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dH = TdS + VdP. \quad (17.4.4)$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant volume, its Helmholtz function will increase by  $\left(\frac{\partial A}{\partial T}\right)_V dT$ ; or, if we allow it to expand at constant temperature, its Helmholtz function will increase by  $\left(\frac{\partial A}{\partial V}\right)_T dV$ . (In most cases both of the derivatives are negative, so that an increase in temperature at constant volume, or of volume at constant temperature, results in a decrease in the Helmholtz function.) If we do both, the increase in the Helmholtz function will be

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV. \quad (17.4.5)$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dA = -SdT - PdV. \quad (17.4.6)$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant pressure, its Gibbs function will increase by  $\left(\frac{\partial G}{\partial T}\right)_P dT$ . (In most cases the derivative  $\left(\frac{\partial G}{\partial T}\right)_P$  is negative, so that an increase in temperature at constant pressure results in a decrease in the Gibbs function.) If we increase the pressure on it at constant temperature, its Gibbs function will increase by  $\left(\frac{\partial G}{\partial P}\right)_T dP$ . If we do both, the increase in Gibbs function will be

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP. \quad (17.4.7)$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dG = -SdT + VdP. \quad (17.4.8)$$

So much, we are already familiar with. However, we can increase any of these thermodynamical functions of a system without adding any heat to it or doing any work on it – merely by adding more matter. You will notice that, in the above statements, I referred to a “closed” thermodynamical system. By a “closed” system, I mean one in which no matter is lost or gained by the system. But, if the system is not closed, adding additional matter to the system obviously increases the (total) thermodynamical functions. For example, consider a system consisting of several components. Suppose that we add  $dN_i$  moles of component  $i$  to the system at constant temperature and pressure, by how much would the Gibbs function of the system increase?

We might at first make the obvious reply: “ $dN_i$  times the molar Gibbs function of component  $i$ ”. This might be true if the component were entirely inert and did not interact in any way with the other components in the system. But it is possible that the added component might well interact with other components. It might, for example, shift the equilibrium position of a reversible reaction  $A + B \leftrightarrow C + D$ . The best we can do, then, is to say merely that the increase in the (total) Gibbs function of the system would be  $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i$ . Here,  $N_j$  refers to the number of moles of any component other than  $i$ .

In a similar manner, if  $dN_i$  moles of component were added at constant volume without adding any heat, the increase in the internal energy of the system would be  $\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i$ . Or if  $dN_i$  moles of component were added at constant pressure without adding any heat, the increase in the enthalpy of the system would be  $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j} dN_i$ . Or if  $dN_i$  moles of component were added at constant temperature and volume, the increase in the Helmholtz function of the system would be  $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$ . If we added a little bit more of all components at constant temperature and volume, the increase in the Helmholtz function would be  $\sum \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i$ , where the sum is over all components.

Thus, if the system is not closed, and we have the possibility of adding or subtracting portions of one or more of the components, the formulas for the increases in the thermodynamic functions become

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_i} dV + \sum \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} dN_i, \quad (17.4.9)$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N_i} dP + \sum \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j} dN_i, \quad (17.4.10)$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N_i} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N_i} dV + \sum \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} dN_i, \quad (17.4.11)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N_i} dP + \sum \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} dN_i. \quad (17.4.12)$$

The quantity  $\left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j}$  is the same as  $\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_j}$  or as  $\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j}$  or as  $\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$ , and it is called the *chemical potential* of species  $i$ , and is usually given the symbol  $\mu_i$ . Its SI units are J kmole<sup>-1</sup>. (We shall later refer to it as the “partial molar Gibbs function” of species  $i$  – but that is jumping slightly ahead.) If we make use of the symbol  $\mu_i$ , and the other things we know from application of the first and second laws, we can write equations 17.4.9 to 17.4.12 as

$$dU = TdS - PdV + \sum \mu_i dN_i \quad (17.4.13)$$

$$dH = TdS + VdP + \sum \mu_i dN_i, \quad (17.4.14)$$

$$dA = -SdT - PdV + \sum \mu_i dN_i \quad (17.4.15)$$

and

$$dG = -SdT + VdP + \sum \mu_i dN_i \quad (17.4.16)$$

It will be clear that

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V,N_i} &= T; & \left(\frac{\partial U}{\partial V}\right)_{S,N_i} &= -P; & \left(\frac{\partial U}{\partial N_i}\right)_{V,S,N_j} &= \mu_i; \\ \left(\frac{\partial H}{\partial S}\right)_{P,N_i} &= T; & \left(\frac{\partial H}{\partial P}\right)_{S,N_i} &= V; & \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j} &= \mu_i; \\ \left(\frac{\partial A}{\partial T}\right)_{V,N_i} &= -S; & \left(\frac{\partial A}{\partial V}\right)_{T,N_i} &= -P; & \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} &= \mu_i; \\ \left(\frac{\partial G}{\partial T}\right)_{P,N_i} &= -S; & \left(\frac{\partial G}{\partial P}\right)_{T,N_i} &= V; & \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} &= \mu_i. \end{aligned} \quad (17.4.17)$$

Since the four thermodynamical functions are functions of state, their differentials are exact and their mixed second partial derivatives are equal. Consequently we have the following twelve Maxwell relations:

$$\begin{aligned}
 \left(\frac{\partial T}{\partial V}\right)_{S,N_i} &= -\left(\frac{\partial P}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,V,N_j} &= +\left(\frac{\partial \mu_i}{\partial S}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{S,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i}; \\
 \left(\frac{\partial T}{\partial P}\right)_{S,N_i} &= +\left(\frac{\partial V}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial T}{\partial N_i}\right)_{S,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial S}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{S,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial P}\right)_{S,N_i}; \\
 \left(\frac{\partial S}{\partial V}\right)_{T,N_i} &= +\left(\frac{\partial P}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial T}\right)_{V,N_i}; & \left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} &= -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}; \\
 \left(\frac{\partial S}{\partial P}\right)_{T,N_i} &= -\left(\frac{\partial V}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} &= -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i}; & \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} &= +\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i}.
 \end{aligned} \tag{17.4.18}$$

Refer to equations 17.4.13 to 17.4.16, and we understand that:

If we add  $dN_1$  moles of species 1,  $dN_2$  moles of species 2,  $dN_3$  moles of species 3, etc., in a insulated constant-volume vessel ( $dS$  and  $dV$  both zero), the increase in the internal energy is

$$dU = \sum \mu_i dN_i. \tag{17.4.19}$$

If we do the same in an insulated vessel at constant pressure (for example, open to the atmosphere, but in a time sufficiently short so that no significant heat escapes from the system, and  $dS$  and  $dP$  are both zero), the increase in the enthalpy is

$$dH = \sum \mu_i dN_i. \tag{17.4.20}$$

If we do the same in a closed vessel (e.g. an autoclave or a pressure cooker, so that  $dV = 0$ ) in a constant temperature water-bath ( $dT = 0$ ), the increase in the Helmholtz function is

$$dA = \sum \mu_i dN_i. \tag{17.4.21}$$

If we do the same at constant pressure (e.g. in an open vessel on a laboratory bench, so that  $dP = 0$ ) and kept at constant temperature (e.g. if the vessel is thin-walled and in a constant-temperature water bath, so that  $dT = 0$ ), the increase in the Gibbs free energy is

$$dG = \sum \mu_i dN_i. \tag{17.4.22}$$

We have called the symbol  $\mu_i$  the *chemical potential* of component  $i$  – but in what sense is it a “potential”? Consider two phases,  $\alpha$  and  $\beta$ , in contact. The Gibbs functions of the two phases are  $G^\alpha$  and  $G^\beta$  respectively, and the chemical potential of species  $i$  is  $\mu_i^\alpha$  in  $\alpha$  and  $\mu_i^\beta$  in  $\beta$ . Now transfer  $dN_i$  moles of  $i$  from  $\alpha$  to  $\beta$ . The increase in the Gibbs function of the system is  $\mu_i^\beta dN_i - \mu_i^\alpha dN_i$ . But for a system of two phases to be in chemical equilibrium, the increase in the Gibbs function must be zero. In other words, the condition for chemical equilibrium between the two phases is that  $\mu_i^\beta = \mu_i^\alpha$  for all species, just as the condition for thermal equilibrium is that  $T^\alpha = T^\beta$ , and the condition for mechanical equilibrium is that  $P^\alpha = P^\beta$ .

Students of classical mechanics may see an analogy between equation 17.4.44 and the principle of Virtual Work. One way of finding the condition of static equilibrium in a mechanical system is to imagine the system to undergo an infinitesimal change in its geometry, and then to calculate the total work done by all the forces as they are displaced by the infinitesimal geometrical alteration. If the system were initially in equilibrium, then the work done by the forces, which is an expression of the form  $\sum F_i dx_i$ , is zero, and this gives us the condition for mechanical equilibrium. Likewise, if a system is in chemical equilibrium, and we make infinitesimal changes  $dN_i$ , at constant temperature and pressure, in the chemical composition, the corresponding change in the Gibbs function of the system,  $\sum \mu_i dN_i$ , is zero. At chemical equilibrium, the Gibbs function is a minimum with respect to changes in the chemical composition.

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