

## Chapter 6

# Describing Phase Transitions and Equilibrium

### 6.1 The 2<sup>nd</sup> Law of Thermodynamics

The 1<sup>st</sup> Law of Thermodynamics states that energy is conserved. We use Equation 1.1 and Equation 1.4 to express this conservation in terms of heat and work. The 2<sup>nd</sup> Law of Thermodynamics consists of two expressions. The first is Equation 5.12, which, as we have discussed, relates  $dQ$  to  $dS$  by the temperature  $T$ . The other expression of the 2<sup>nd</sup> Law of Thermodynamics states that any spontaneously occurring process within a system will result in the entropy of that system remaining the same or increasing. We can express this condition as

$$\Delta S \geq 0 \quad (6.1)$$

Equation 6.1 implies that the entropy of a system will evolve toward a maximum value and then remain constant at that value. We refer to this final state as the *equilibrium* state of the system. Similarly, processes associated with the equality in Equation 6.1 are referred to as *equilibrium* processes.

### 6.2 Equilibrium Conditions

Entropy will be maximum at equilibrium since this corresponds to the most probable state of the system (and follows from entropy's relationship to multiplicity described in Equation 3.7). Let's suppose that we have two systems, A and B, in contact with one another and that can exchange energy with one another. The total energy of our system is the sum of the energy of System A and the energy of System B.

$$E_{total} = E_A + E_B$$

The total multiplicity of the combined system - System A and System B - is the product of the multiplicity of these two systems and therefore from Equation 3.7 the total entropy of the system is

$$\Omega_{total} = \Omega_A \Omega_B \quad \rightarrow \quad \mathcal{S}_{total} = \mathcal{S}_A + \mathcal{S}_B$$

### Thermal Equilibrium

Since the entropy of the combined system must be a maximum at equilibrium, any changes in the entropy associated with the exchange of energy (*e.g.*, in the form of heat) between the systems must be positive or zero.

$$d\mathcal{S}_{total} \geq 0 \quad \rightarrow \quad \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V dE_A + \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V dE_B \geq 0$$

As shown in this equation, we are limiting ourselves for the moment to exchanges of energy occurring at constant volume so that we don't have to worry about work being done. If the combined system is isolated,  $E_{total}$  is constant. Then  $dE_{total} = 0$  and  $dE_A + dE_B = 0$  or, equivalently, that  $dE_A = -dE_B$ .

$$\left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V dE_A - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V dE_A \geq 0 \quad \rightarrow \quad \left[ \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V \right] dE_A \geq 0$$

Let's first consider the case where the systems are not in equilibrium, but are exchanging energy (*i.e.*, exchanging heat since volume is constant) as part of the process of approaching equilibrium.

$$\left[ \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V \right] dE_A > 0$$

If  $dE_A > 0$ , energy is absorbed by System A. A positive value for  $dE_A > 0$  also means that

$$\left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V > 0 \quad \rightarrow \quad \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V > \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V$$

It follows from Equation 3.26 that if  $dE_A > 0$

$$\beta_A > \beta_B \quad \rightarrow \quad T_A < T_B$$

Thus, if System A is absorbing energy from System B, the temperature of System A must be less than the temperature of System B. A similar calculation shows that if System B is absorbing energy from System A, the temperature of System B must be less than the temperature of System A. We therefore conclude that while in the process of moving toward equilibrium, heat will flow from the warmer system to the cooler system. In other words, heat spontaneously flows from hot to cold.

Let's now turn to the situation when we are at equilibrium. In that case, any exchange of heat must result in no change in the entropy of the system.

$$\left[ \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V \right] dE_A = 0$$

Since this equation must be true for any values of  $dE_A$  (*i.e.*, for any amount of energy exchanged between the two systems), the bracketed term in this equation must be zero.

$$\left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V - \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V = 0 \quad \rightarrow \quad \left( \frac{\partial \mathcal{S}_B}{\partial E_B} \right)_V = \left( \frac{\partial \mathcal{S}_A}{\partial E_A} \right)_V$$

Thus, it follows from Equation 3.26 that the temperatures of the two systems will be identical when the systems are in equilibrium.

$$\beta_B = \beta_A \quad \rightarrow \quad T_B = T_A$$

For example, if heat flows from system A to system B, the entropy of system A will decrease and the entropy of system B will increase. In order for the combined system to remain at its maximum entropy (*i.e.*, for the combined systems to be in equilibrium), the magnitude of decrease in the entropy of system A must equal the magnitude of the increase of the entropy of system B. Since the parameter  $\beta$  is a measure of how entropy changes with energy, the values of  $\beta$  for the two systems must be equal when the two systems are in equilibrium.

Well, sure, because if it weren't we likely wouldn't be here. Indeed, we just learned that heat will spontaneously flow from higher temperature systems to lower temperature systems in order to maximize the combined entropy of those systems. Since heat capacity is always positive, this exchange of heat will raise the temperature of the lower temperature system and lower the temperature of the higher temperature system. Thus, this exchange of heat will move the two systems toward thermal equilibrium. But, if heat capacity were negative, this exchange of heat would result in the colder system getting colder and the hotter system getting hotter, which would move the two systems further away from thermal equilibrium rather than closer to it. This would result in the systems never being able to achieve equilibrium, which would create an overall unstable universe.

### Mechanical Equilibrium

We can play a similar game with exchanges of volume between the two systems. In that case,

$$d\mathcal{S}_{total} = 0 \quad \rightarrow \quad \left( \frac{\partial \mathcal{S}_A}{\partial V_A} \right)_E dV_A + \left( \frac{\partial \mathcal{S}_B}{\partial V_B} \right)_E dV_B \geq 0$$

As shown in this equation, we are limiting ourselves to exchanges of volume occurring at constant energy. If the combined system is isolated,  $V_{total}$  is constant. Then  $dV_{total} = 0$  and  $dV_A + dV_B = 0$  or, equivalently, that  $dV_A = -dV_B$ .

$$\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E dV_A - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E dV_A \geq 0 \quad \rightarrow \quad \left[\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E\right] dV_A \geq 0$$

Let's first consider the case where the systems are not in equilibrium, but are exchanging volume as part of the process of approaching equilibrium.

$$\left[\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E\right] dV_A > 0$$

If  $dV_A > 0$ , the volume of System A is increasing. A positive value for  $dV_A > 0$  also means that

$$\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E > 0 \quad \rightarrow \quad \left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E > \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E$$

It follows from Equation 3.26 that if  $dV_A > 0$

$$\beta_A P_A > \beta_B P_B$$

If the two systems are already an equilibrium with respect to energy exchange (*i.e.*, if  $\beta_A = \beta_B$ ) then,

$$\beta_A = \beta_B \quad \rightarrow \quad P_A > P_B$$

Thus, if the volume of System A is increasing, the pressure of System A must be larger than the pressure of System B. A similar calculation shows that if the volume of System B is expanding, the pressure of System B must be larger than the pressure of System A. We therefore conclude that while in the process of moving toward equilibrium, high pressure systems will expand and low pressure systems will contract. Let's now turn to the situation when we are at equilibrium. In that case, any change of volume must result in no change in the entropy of the system.

$$\left[\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E\right] dV_A = 0$$

Since this equation must be true for any values of  $dV_A$  (*i.e.*, for any amount of volume exchanged between the two systems), the bracketed term in this equation must be zero.

$$\left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E - \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E = 0 \quad \rightarrow \quad \left(\frac{\partial \mathcal{S}_B}{\partial V_B}\right)_E = \left(\frac{\partial \mathcal{S}_A}{\partial V_A}\right)_E$$

We can use Equation 3.26 to express this equation as

$$\beta_B P_B = \beta_A P_A \quad \rightarrow \quad P_B = P_A$$

The simplification in this expression follows from the fact that since the system is in equilibrium we already know that  $\beta_A = \beta_B$ . Thus, if the two systems are able to exchange volume with one another, the pressures of the two systems will be identical when the two systems are in equilibrium.

### Diffusive Equilibrium

We can now perform a similar derivation to determine the equilibrium condition when particles can be exchanged between systems. We begin by recognizing that the combined entropy of the two systems will be a maximum when the systems are in equilibrium. Thus, when approaching equilibrium, any exchange of particles between the two systems must be associated with either an increase or no change in the combined entropy of the two systems.

$$\left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} dN_A + \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V} dN_B \geq 0$$

As shown in this equation, we are limiting ourselves for the moment to exchanges of particles occurring at constant energy and volume; this is equivalent to assuming that the two systems are already in thermal and mechanical equilibrium. If the combined system is isolated,  $N_{total}$  is constant. Then  $dN_{total} = 0$  and  $dN_A + dN_B = 0$  or, equivalently, that  $dN_A = -dN_B$ . Thus,

$$\begin{aligned} \left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} dN_A - \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V} dN_A &\geq 0 \\ \left[ \left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} - \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V} \right] dN_A &\geq 0 \end{aligned}$$

Let's first consider the case where the systems are not in equilibrium, but are exchanging particles as part of the process of approaching equilibrium.

$$\left[ \left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} - \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V} \right] dN_A > 0$$

If  $dN_A > 0$ , the number of particles in System A is increasing. A value for  $dN_A > 0$  also means that

$$\left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} - \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V} > 0 \rightarrow \left(\frac{\partial \mathcal{S}_A}{\partial N_A}\right)_{E,V} > \left(\frac{\partial \mathcal{S}_B}{\partial N_B}\right)_{E,V}$$

It follows from Equation 3.26 that if  $dN_A > 0$

$$\beta_A \mu_A > -\beta_B \mu_B \rightarrow \beta_A \mu_A < \beta_B \mu_B$$

If the two systems are already an equilibrium with respect to energy exchange (*i.e.*, thermal equilibrium with  $\beta_A = \beta_B$  or  $T_A = T_B$ ) then,

$$\beta_A = \beta_B \rightarrow \mu_A < \mu_B$$

Thus, if the number of particles in System A is increasing, the chemical potential of System A must be smaller than the chemical potential of System B. A similar calculation shows that if the number of particles in System B is increasing, the

chemical potential of System B must be smaller than the chemical potential of System A. We therefore conclude that *while in the process of moving toward equilibrium, particles will always move toward lower chemical potential.*

Let's now turn to the situation when we are at equilibrium. In that case, any change in the number of particles must result in no change in the entropy of the system.

$$\left[ \left( \frac{\partial \mathcal{S}_A}{\partial N_A} \right)_{E,V} - \left( \frac{\partial \mathcal{S}_B}{\partial N_B} \right)_{E,V} \right] dN_A = 0$$

Since this equation must be true for any values of  $dN_A$  (*i.e.*, for any number of particles exchanged between the two systems), the bracketed term in this equation must be zero.

$$\left( \frac{\partial \mathcal{S}_A}{\partial N_A} \right)_{E,V} - \left( \frac{\partial \mathcal{S}_B}{\partial N_B} \right)_{E,V} = 0 \quad \rightarrow \quad \left( \frac{\partial \mathcal{S}_B}{\partial N_B} \right)_{E,V} = \left( \frac{\partial \mathcal{S}_A}{\partial N_A} \right)_{E,V}$$

We can use Equation 3.26 to express this equation as

$$-\beta_B \mu_B = -\beta_A \mu_A \quad \rightarrow \quad \mu_B = \mu_A$$

The simplification in this expression follows from the fact that since the system is in equilibrium we already know that  $T_A = T_B$ . Thus, if the two systems are able to exchange particles with one another, the chemical potentials of the two systems will be identical when the two systems are in equilibrium.

### 6.3 Equilibrium Temperature Of Interacting Systems

Let's consider the situation where we have two systems, A and B, that are allowed to exchange energy (*i.e.*, heat) with one another; the two systems are at initial temperatures  $T_A$  and  $T_B$ , respectively. As we learned earlier, these systems will exchange energy until they achieve the same temperature (*i.e.*, until they are in thermal equilibrium). Since this process of approaching equilibrium is associated with an increase in the overall entropy of the combined system, we have

$$\Delta S_A + \Delta S_B > 0 \quad \rightarrow \quad \int_{T_A}^{T_F} \left( \frac{\partial S_A}{\partial T} \right) dT + \int_{T_B}^{T_F} \left( \frac{\partial S_B}{\partial T} \right) dT > 0$$

In this expression, the variable  $T_F$  denotes the final equilibrium temperature of the two systems. We can express the partial derivatives in this expression in terms of the heat capacities of the systems.

$$\int_{T_A}^{T_F} \frac{C_A}{T} dT + \int_{T_B}^{T_F} \frac{C_B}{T} dT > 0$$

If these heat capacities are constant, we can take them outside of the integrals.

$$C_A \int_{T_A}^{T_F} \frac{dT}{T} + C_B \int_{T_B}^{T_F} \frac{dT}{T} > 0 \quad \rightarrow \quad C_A \ln \left( \frac{T_F}{T_A} \right) + C_B \ln \left( \frac{T_F}{T_B} \right) > 0$$

$$C_A \ln T_F - C_A \ln T_A + C_B \ln T_F - C_B \ln T_B > 0$$

$$(C_A + C_B) \ln T_F - (C_A \ln T_A + C_B \ln T_B) > 0$$

$$\ln T_F > \frac{C_A \ln T_A + C_B \ln T_B}{C_A + C_B}$$

There is therefore a lower limit of what the final equilibrium temperature can be. If we assume that the two systems are isolated from the rest of the universe, we can calculate the final equilibrium temperature by recognizing that the heat released by one system must be equal to the heat absorbed by the other system.

$$\dot{d}Q_A + \dot{d}Q_B = 0 \quad \rightarrow \quad \int_{T_A}^{T_F} C_A dT + \int_{T_B}^{T_F} C_B dT = 0$$

As before, if these heat capacities are constant, we can take them outside of the integrals.

$$C_A \int_{T_A}^{T_F} dT + C_B \int_{T_B}^{T_F} dT = 0 \quad \rightarrow \quad C_A (T_A - T_F) + C_B (T_B - T_F) = 0$$

$$C_A T_A + C_B T_B = T_F (C_A + C_B) \quad \rightarrow \quad T_F = \frac{C_A T_A + C_B T_B}{C_A + C_B}$$

The final equilibrium temperature is the weighted average of the initial temperatures of the systems, weighted by their respective heat capacities.

## 6.4 Steam Engines

A lot of the initial work on thermodynamics was focused on improving the efficiency of steam engines. A model for a steam engine, more generally referred to as a heat engine, is shown in Figure 6.1. The engine absorbs energy from a high

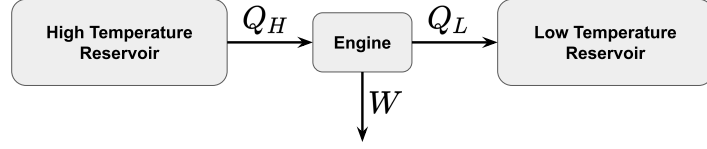


Figure 6.1: A canonical heat engine. The engine absorbs heat  $Q_H$  from a high temperature reservoir, performs work  $W$ , and releases heat  $Q_L$  to a low temperature reservoir.

temperature reservoir, performs work, and releases energy to a low temperature reservoir.

The efficiency of a steam engine is frequently denoted by the variable  $\eta$  and is defined as the ratio of the net work done by the engine to the heat absorbed by the engine.

$$\eta = \frac{W_{net}}{Q_{abs}}$$

The highest efficiency occurs when the internal energy of the engine does not change during its operation. In that case, we recognize from the conservation of energy that the net work performed by the engine is equal to the difference between the heat absorbed and the heat released.

$$\eta = \frac{W_{net}}{Q_H} \rightarrow \eta = \frac{Q_H - Q_L}{Q_H} \rightarrow \eta = 1 - \frac{Q_L}{Q_H}$$

The exchange of energy (*i.e.*, heat) between the engine and the reservoirs will result in the entropy of the entire system changing. According to the 2<sup>nd</sup> Law of Thermodynamics (Equation 6.1) this change in entropy must be greater than or equal to zero.

$$\Delta S_{system} \geq 0$$

Applying Equation 5.12 and assuming that the temperatures of the reservoirs remain constant then yields

$$\Delta S_{system} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \rightarrow -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0$$

$$\frac{Q_L}{T_L} \geq \frac{Q_H}{T_H} \rightarrow \frac{Q_L}{Q_H} \geq \frac{T_L}{T_H}$$

The 2<sup>nd</sup> Law of Thermodynamics thus places a limit on the efficiency of the engine.

$$\eta = 1 - \frac{Q_L}{Q_H} \rightarrow \frac{Q_L}{Q_H} = 1 - \eta \rightarrow 1 - \eta \geq \frac{T_L}{T_H}$$



$$\eta \leq 1 - \frac{T_L}{T_H}$$

The equality in this equation occurs for a system consisting of reversible processes.

## 6.5 Thermodynamic Potentials and Free Energy

The thermodynamic potentials are scalar “potential energies” that are sometimes useful for describing systems. They consist of the internal energy,  $E$ , plus one or more sets of conjugate variables.

- Internal Energy:  $E = TS - PV + \mu N$
- Helmholtz Free Energy:  $F = E - TS$
- Enthalpy:  $H = E + PV$
- Gibbs Free Energy:  $G = E - TS + PV$

### 6.5.1 Internal Energy

If we differentiate the equation for the internal energy we obtain

$$dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

If we substitute the equation for  $dE$  that we derived previously from Equation 5.14 into this expression we obtain

$$TdS - PdV + \mu dN = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

$$0 = SdT - VdP + Nd\mu \quad (6.2)$$

Equation 6.2 is the Gibbs-Duhem equation, which expresses the fact that none of the intensive variables describing a system (temperature, pressure, and chemical potential) can vary independently of each other.

### 6.5.2 Helmholtz Free Energy

If we differentiate the equation for the Helmholtz free energy we obtain

$$dF = dE - TdS - SdT$$

If we substitute the equation for  $dE$  that we derived previously from Equation 5.14 into this expression we obtain

$$dF = (TdS - PdV + \mu dN) - TdS - SdT$$

$$dF = -PdV - SdT + \mu dN$$

It follows from this expression that

$$-P = \left( \frac{\partial F}{\partial V} \right)_{T,N} \quad -S = \left( \frac{\partial F}{\partial T} \right)_{V,N} \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,P} \quad (6.3)$$

The Helmholtz free energy is therefore a function of the independent variables temperature, volume, and particle number (*i.e.*,  $F = F(T, V, N)$ ). The Helmholtz free energy is therefore useful in describing systems in which temperature, volume and particle number can be externally controlled (or regulated).

Consider two systems interacting mechanically and diffusively, but held at constant temperature ( $dT = 0$ ). For each system the change in the Helmholtz free energy is given by

$$dT = 0 \rightarrow dF = -PdV + \mu dN$$

Thus the total change in the Helmholtz free energy for these two systems is

$$dF_{total} = dF_1 + dF_2 \rightarrow dF_{total} = -P_1 dV_1 + \mu_1 dN_1 - P_2 dV_2 + \mu_2 dN_2$$

If these two combined systems are isolated from the rest of the universe, their total volume and particle number must be constant. Thus,

$$dV_2 = -dV_1 \quad dN_2 = -dN_1$$

Thus,

$$dF_{total} = -(P_1 - P_2) dV_1 + (\mu_1 - \mu_2) dN_1$$

Since we know that the change in volume is larger for the system with higher pressure and that the change in particle number is larger for the system with lower chemical potential we have

$$-(P_1 - P_2) dV_1 \leq 0 \quad \text{and} \quad (\mu_1 - \mu_2) dN_1 \leq 0$$

Thus,

$$dF_{total} \leq 0$$

Therefore, the Helmholtz free energy of isothermal systems will be at a minimum at equilibrium.

The Helmholtz free energy can also be expressed in terms of the partition function using Equation 3.27 and Equation 5.11.

$$F = E - TS \rightarrow F = E - T[k_B(\ln Z + \beta E)]$$

$$F = E - k_B T \ln Z - T k_B \beta E \quad \rightarrow \quad F = E - \frac{1}{\beta} \ln Z - E$$

$$F = -\frac{1}{\beta} \ln(Z) \quad (6.4)$$

It follows from Equation 6.3 and Equation 6.4 that the pressure of a system can be expressed in terms of the partition function for that system.

$$P = - \left( \frac{\partial}{\partial V} \right)_{T,N} \left( -\frac{1}{\beta} \ln Z \right)$$

$$P = \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} \quad (6.5)$$

Similarly, we can express the entropy of a system in terms of the partition function for that system using Equation 6.3 and Equation 6.5.

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} \quad \rightarrow \quad S = - \left( \frac{\partial}{\partial T} \right)_{V,N} \left( -\frac{1}{\beta} \ln Z \right)$$

$$S = \left( \frac{\partial}{\partial T} \right)_{V,N} (k_B T \ln Z)$$

$$S = k_B \ln Z + k_B T \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N} \quad (6.6)$$

or, equivalently

$$S = \ln Z - \beta \left( \frac{\partial \ln Z}{\partial \beta} \right)_{V,N} \quad (6.7)$$

Equation 6.7 is identical to Equation 4.4, and reinforces that we can determine an expression for the entropy of a system if we have an expression for the partition function of a system.

### Ideal Gas Tangent

Substituting Equation 5.3 into Equation 6.4 gives us

$$F = -\frac{1}{\beta} \ln \left( \left( \frac{V e}{N} \right)^N \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3N}{2}} \right)$$

$$F = -\frac{N}{\beta} \ln \left[ \left( \frac{V e}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] \quad (6.8)$$

Thus, from Equation 6.3 we have

$$P = - \left( \frac{\partial}{\partial V} \right)_{T,N} \left[ -\frac{N}{\beta} \ln \left[ \left( \frac{V e}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] \right]$$

$$P = \frac{N}{\beta} \left( \frac{\partial}{\partial V} \right)_{T,N} \left[ \ln V + \ln \left( \frac{e}{N} \right) + \ln \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right]$$

$$P = \frac{N}{\beta} \left( \frac{1}{V} \right) \rightarrow PV = \frac{N}{\beta}$$

This agrees with Equation 5.2. Next we can calculate the entropy using Equation 6.3 and 6.8.

$$S = - \left( \frac{\partial}{\partial T} \right)_{V,N} \left[ - \frac{N}{\beta} \ln \left[ \left( \frac{Ve}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] \right]$$

$$S = Nk_B \left( \frac{\partial}{\partial T} \right)_{V,N} \left[ T \ln \left[ \left( \frac{Ve}{N} \right) \left( \frac{2m\pi k_B T}{h^2} \right)^{\frac{3}{2}} \right] \right]$$

$$S = Nk_B \left[ \ln \left[ \left( \frac{Ve}{N} \right) \left( \frac{2m\pi k_B T}{h^2} \right)^{\frac{3}{2}} \right] + T \left( \frac{3}{2} \frac{1}{T} \right) \right]$$

$$S = Nk_B \left[ \ln \left( \frac{V}{N} \right) + \ln(e) + \ln \left( \frac{2m\pi k_B T}{h^2} \right)^{\frac{3}{2}} + \frac{3}{2} \right]$$

$$S = Nk_B \left[ \ln \left( \frac{V}{N} \right) + \ln \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} + \frac{5}{2} \right]$$

This agrees with our previously derived expression. Finally, we can use and Equation 6.3 and Equation 6.8 to determine an expression for the chemical potential of an ideal gas

$$\mu = \left( \frac{\partial}{\partial N} \right)_{T,P} \left( - \frac{N}{\beta} \ln \left[ \left( \frac{Ve}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] \right)$$

Holding  $T$  constant is the same as holding  $\beta$  constant.

$$\mu = - \frac{1}{\beta} \ln \left[ \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] - \frac{N}{\beta} \left( - \frac{1}{N} \right)$$

$$\mu = - \frac{1}{\beta} \left[ \ln \left[ \left( \frac{eV}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] - 1 \right]$$

$$\ln(e) = 1 \rightarrow \mu = - \frac{1}{\beta} \left[ 1 + \ln \left[ \left( \frac{V}{N} \right) \left( \frac{2m\pi}{\beta h^2} \right)^{\frac{3}{2}} \right] - 1 \right]$$

As stated earlier, it is customary to express chemical potential in terms of particle density.

$$\mu = \frac{1}{\beta} \left[ \ln \left( \frac{N}{V} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$$

This result is identical to Equation 5.19, which makes us happy.

**Alternate Definition**

Let's now define a different form of the Helmholtz free energy  $\mathcal{F}$  that is related to  $F$  by  $\beta$ .

$$\mathcal{F} = \beta F$$

Then,

$$F = E - TS \quad \rightarrow \quad \frac{\mathcal{F}}{\beta} = E - T(k_B S)$$

$$\mathcal{F} + S = \beta E$$

This looks like our general equation for the Legendre transform. We can therefore write

$$\mathcal{F}(\beta) + S(E) = \beta E$$

indicating that  $\beta$  and  $E$  are conjugate variables.

**6.5.3 Enthalpy**

If we differentiate the equation for the enthalpy we obtain

$$dH = dE + PdV + VdP$$

If we substitute the equation for  $dE$  that we derived previously from Equation 5.14 into this expression we obtain

$$dH = (TdS - PdV + \mu dN) + PdV + VdP$$

$$dH = TdS + VdP + \mu dN$$

It follows from this expression that

$$T = \left( \frac{\partial H}{\partial S} \right)_{P,N} \quad V = \left( \frac{\partial H}{\partial P} \right)_{S,N} \quad \mu = \left( \frac{\partial H}{\partial N} \right)_{S,P}$$

The enthalpy is therefore a function of the independent variables entropy, pressure, and particle number (*i.e.*,  $H = H(S, P, N)$ ). The enthalpy is therefore useful in describing systems in which entropy, volume and particle number can be externally controlled (or regulated).

Consider two systems interacting thermally and diffusively, but held at constant pressure<sup>1</sup> ( $dP = 0$ ). For each system the change in the enthalpy is given by

$$dH = dE + PdV$$

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<sup>1</sup>The fancy word for this is *isobaric*

Therefore the change in enthalpy for these two systems combined is

$$dH_{total} = dH_1 + dH_2 \rightarrow dH_{total} = dE_1 + P_1 dV_1 + dE_2 + P_2 dV_2$$

If these two combined systems are isolated from the rest of the universe, their total energy and volume must be constant. Thus,

$$dE_2 = -dE_1 \quad dV_2 = -dV_1$$

Thus,

$$dH_{total} = 0 + (P_1 - P_2) dV_1$$

Since we know that the change in volume is larger for the system with higher pressure we have

$$(P_1 - P_2) dV_1 \geq 0 \rightarrow dH_{total} \geq 0$$

Therefore, the enthalpy of isobaric systems will be at a maximum at equilibrium. It's also worth noting that for processes which are non-diffusive ( $dN = 0$ ) and isobaric ( $dP = 0$ ) the enthalpy measures the heat transferred.

$$dH = TdS = \delta Q$$

This is why some people love enthalpy. Finally, we also recognize that since  $dH = TdS + VdP + \mu dN$ , we can express  $C_P$  as

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P,N}$$

Thus, the heat capacity at constant volume reflects how the energy of the system changes with temperature whereas the heat capacity at constant pressure reflects how the enthalpy of the system changes with temperature.

#### 6.5.4 Gibbs Free Energy

If we differentiate the equation for the Gibbs free energy we obtain

$$dG = dE - SdT - TdS + PdV + VdP$$

If we substitute the equation for  $dE$  that we derived previously from Equation 5.14 into this expression we obtain

$$dG = (TdS - PdV + \mu dN) - SdT - TdS + PdV + VdP$$

$$dG = -SdT + VdP + \mu dN$$

It follows from this expression that

$$-S = \left( \frac{\partial G}{\partial T} \right)_{P,N} \quad V = \left( \frac{\partial G}{\partial P} \right)_{T,N} \quad \mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

The Gibbs free energy is therefore a function of the independent variables temperature, pressure, and particle number (*i.e.*,  $G = G(T, P, N)$ ). The Gibbs free energy is therefore useful in describing systems in which temperature, volume and particle number can be externally controlled (or regulated).

Consider two systems interacting diffusively, but held at constant pressure ( $dP = 0$ ) and temperature ( $dT = 0$ ). For each system the change in the Gibbs free energy is given by

$$dG = \mu dN$$

Therefore the change in Gibbs free energy for these two systems combined is

$$dG_{total} = dG_1 + dG_2 \rightarrow dG_{total} = \mu_1 dN_1 + \mu_2 dN_2$$

If these two combined systems are isolated from the rest of the universe, their total particle number must be constant. Thus,

$$dN_2 = -dN_1 \rightarrow dG_{total} = (\mu_1 - \mu_2) dN_1$$

Since we know that the particles will diffuse toward lower chemical potential we have

$$(\mu_1 - \mu_2) dN_1 \leq 0 \rightarrow dG_{total} \leq 0$$

Therefore, the Gibbs free energy of isothermal and isobaric systems will be at a minimum when the system is at diffusive equilibrium.

We now have yet another way to calculate the chemical potential of an ideal gas.

$$G = E - TS + PV$$

$$G = \frac{3}{2} N k_B T - T \left[ N k_B \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) + \frac{5}{2} \right] \right] + N k_B T$$

$$G = N k_B T \left[ \frac{3}{2} - \ln \left( \frac{V}{N} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) - \frac{5}{2} + 1 \right]$$

$$G = N k_B T \left[ -\ln \left( \frac{V}{N} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$$

Now let's express this equation in terms of the pressure and temperature using Equation 5.2 and  $\beta = \frac{1}{k_B T}$ .

$$G = N k_B T \left[ -\ln \left( \frac{k_B T}{P} \right) - \frac{3}{2} \ln \left( \frac{2m\pi k_B T}{h^2} \right) \right]$$

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P} \rightarrow \mu = k_B T \left[ -\ln \left( \frac{k_B T}{P} \right) - \frac{3}{2} \ln \left( \frac{2m\pi k_B T}{h^2} \right) \right]$$

I prefer to think about chemical potential in terms of  $N$ ,  $V$ , and  $\beta$  so let's go back to those.

$$\mu = \frac{1}{\beta} \left[ \ln \left( \frac{N}{V} \right) - \frac{3}{2} \ln \left( \frac{2m\pi}{\beta h^2} \right) \right]$$

This is what we derived previously, which is encouraging.

Finally, we note that the Gibbs free energy can be calculated from the partition function

$$G = E - TS + PV \rightarrow G = F + PV$$

and since

$$P = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_T \rightarrow PV = k_B T \left( \frac{\partial \ln Z}{\partial \ln V} \right)_T$$

Thus,

$$H = k_B T \left[ \left( \frac{\partial \ln Z}{\partial \ln T} \right)_V + \left( \frac{\partial \ln Z}{\partial \ln V} \right)_T \right]$$

$$G = -k_B T \left[ \ln Z - \left( \frac{\partial \ln Z}{\partial \ln V} \right)_T \right]$$

### 6.5.5 Maxwell Relations

Since each of the thermodynamic potentials is an exact differential, their second mixed partial derivatives must be equal. For example,

$$dE = TdS - PdV + \mu dN$$

$$\left( \frac{\partial E}{\partial S} \right)_{V,N} = T \quad \text{and} \quad \left( \frac{\partial E}{\partial V} \right)_{S,N} = -P$$

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \rightarrow \left( \frac{\partial}{\partial V} \right) \left( \frac{\partial E}{\partial S} \right)_{V,N} = \left( \frac{\partial}{\partial S} \right) \left( \frac{\partial E}{\partial V} \right)_{S,N}$$

Thus,

$$\left( \frac{\partial}{\partial V} \right) (T) = \left( \frac{\partial}{\partial S} \right) (-P) \rightarrow \left( \frac{\partial T}{\partial V} \right)_S = \left( \frac{\partial P}{\partial S} \right)_V$$

**Derived from**  $E = E(S, V, N)$



$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

**Derived from**  $F = F(T, V, N)$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

**Derived from**  $H = H(S, P, N)$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

**Derived from**  $G = G(T, P, N)$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

These expressions are referred to as the Maxwell relations. They are often a convenient way of changing the variables we are using to describe our system. We'll end up using them at some point later on.

## 6.6 Variable Transformations

Since we've already traveled pretty far down the math road, we might as well keep going.

### 6.6.1 Legendre Transforms

Let's consider a function of two independent variables  $f(x, y)$ . Its differential is

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Let's now define  $u = \left(\frac{\partial f}{\partial x}\right)_y$  and  $w = \left(\frac{\partial f}{\partial y}\right)_x$ . Then,

$$df = u dx + w dy$$

As we learned earlier, we refer to  $x$  and  $u$  as *conjugate* variables; similarly,  $y$  and  $w$  are conjugate variables. Let's now define a new function  $g(x, w) = wy - f(x, y)$ . The differential of this function is

$$dg = w dy + y dw - df \rightarrow dg = w dy + y dw - (u dx + w dy)$$

$$dg = y dw - u dx$$

We refer to  $g(x, w)$  as the *Legendre transform* of  $f(x, y)$  and that this transform results in switching the conjugate variables  $y$  and  $w$ .

### Lagrangian and Hamiltonian

The Lagrangian of a system is the difference between the kinetic and potential energies of that system.

$$L(q, \dot{q}) = K - U$$

In this equation, the variable  $q$  is the generalized position coordinate and  $\dot{q}$  is the derivative of  $q$  with respect to time. We can use the procedure described above to transform  $L(q, \dot{q})$  into a new function  $H(q, p)$  where  $p$  is the generalized momentum; we recognize  $H$  as the Hamiltonian of the system. To mimic the previous process as much as possible, let's define  $f = L$ ,  $x = q$ ,  $y = \dot{q}$ , and  $w = \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial L}{\partial \dot{q}}\right)_q = p$ . Then,

$$g = wy - f \rightarrow g = p\dot{q} - L$$

We recognize  $g$  as the Hamiltonian.

$$g = p\dot{q} - L = (mv)(v) - \left(\frac{1}{2}mv^2 - U\right) = \frac{1}{2}mv^2 + U = H$$

In this case, the Hamiltonian is the total energy of the system.

### Thermodynamic Potentials

Let's start the first law of thermodynamics

$$dE = TdS - PdV$$

The variables  $T$  and  $S$  are conjugate variables as are  $P$  and  $V$ . We recognize from this equation that the internal energy is a function of the entropy and volume of the system -  $E = E(S, V)$ . Let's transform this function into a function of  $S$  and  $P$  by defining  $f = E$ ,  $x = S$ ,  $y = V$ , and  $w = \left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial E}{\partial V}\right)_S = P$ . Then,

$$g = wy - f \rightarrow g = (P)V - E \rightarrow g = -(E - PV)$$

We recognize  $g$  as the negative of the enthalpy. This negative sign doesn't bother use because we could have simply defined the Legendre transform to be  $g = f - wy$  to remove it.

## 6.7 Phase Transitions

Now let's consider a system that consists of two phases, such as a solid and a liquid, labeled by the subscripts 1 and 2, kept at constant temperature  $T$  and pressure  $P$  through contact with an external reservoir. The chemical potentials of the two phases are equal when the phases are in diffusive equilibrium with

each other. For these two phases to remain in equilibrium as  $T$  and  $P$  change, the chemical potentials of the two phases must change by the same amount.

$$d\mu_1 = d\mu_2$$

Since the temperature and pressure of this system are regulated through contact with an external reservoir, the Gibbs free energy is the appropriate thermodynamic potential for describing the system.

$$d\mu_1 = d\mu_2 \quad \rightarrow \quad \frac{-S_1 dT + V_1 dP}{N_1} = \frac{-S_2 dT + V_2 dP}{N_2}$$

It is customary to denote the entropy per molecule  $s = \frac{S}{N}$  and volume per molecule  $v = \frac{V}{N}$  in the further derivation of this expression<sup>2</sup>.

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP \quad \rightarrow \quad (s_2 - s_1) dT = (v_2 - v_1) dP$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \quad (6.9)$$

Equation 6.9 is the Clausius-Clapeyron equation.

### Latent Heat

the entropy changes when the phase changes. From the 2nd law we know that this means there must be heat exchanged. We call this the latent heat.

$$\Delta S = \frac{L}{T}$$

It is also common to define the latent heat in terms of the change in the entropy per molecule<sup>3</sup>. In that case, we can include the latent heat in Equation 6.9.

$$\Delta s = \frac{L}{T} \quad \rightarrow \quad \frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

For most substances, the volume per molecule increases when heat is absorbed and  $\frac{L}{T(v_2 - v_1)} > 0$ . Thus, for these substances, increasing the pressure increasing the equilibrium temperature of the phases. This is why the boiling point of water decreases as altitude increases and thus atmospheric pressure decreases.

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<sup>2</sup>Our chemistry friends prefer entropy per mole and volume per mole, which is also okay.

<sup>3</sup>Or change in entropy per mole if you are a chemist.

### Order Parameter

Let's continue our discussion of systems consisting of two phases that are in contact with an external reservoir maintaining a constant temperature and pressure. As long as the two phases remain in equilibrium, any changes in the Gibbs free energy per particle ( $dg$ ) must be the same for the two phases. Since the both the entropy per particle and volume per particle are positive, we see from the equation for  $dg$

$$dg = -s dT + v dP$$

that the Gibbs free energy per particle ( $g$ ) decreases with increasing temperature and increases with increasing pressure. Of course, since both  $s$  and  $v$  can be functions of temperature and pressure, the dependence of  $g$  on changes in temperature and pressure will not be constant. Furthermore, from the partial derivatives of  $g$

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \quad \left(\frac{\partial g}{\partial P}\right)_T = v$$

we see that there may be a discontinuity in the first derivatives of  $g$  between the two phases. For example, the entropy per particle and volume per particle are different for liquid water and water vapor. Thus, there is a discontinuity in the first derivatives of  $g$  during the transition between these two phases. Because this discontinuity occurs in the first derivative of  $g$ , we refer to this phase transition as a *first-order* phase transition.

For a *second-order* phase transition, the first derivatives of  $g$  are continuous, but the second derivatives of  $g$  are not continuous<sup>4</sup>. A discontinuity in the heat capacity of the system is an indication of a second-order phase transition as heat capacity is proportional to the second derivative of  $g$ .

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P \rightarrow \left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\frac{C_P}{T}$$

Finally, we note that while a latent heat is associated with a first-order phase transition as there is a change in entropy per particle, there is no latent heat associated with a second-order phase transition.

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<sup>4</sup>Second-order or higher-order phase transitions are often called *continuous* phase transitions.