

Lecture 14

Thermodynamic potentials

The internal energy U is a state function, meaning, a system undergoes the same change when it moves from one state of equilibrium to another, irrespective of the route taken.

This makes U an important thermodynamic quantity. However, this is not the only one. We can add various combinations of P, V, T and S with U (preserving the dimension of energy) and find useful number of functions of states. These new functions of state are called the thermodynamic potentials.

Internal energy, U

We have found that we can write $U=U(S,V)$, by the fundamental equation,

$$dU = TdS - \cancel{dV}$$

So, if S and V are held constant, $dU=0$, meaning U is a constant.

$$\text{Now, recall that, } dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\text{which implies that, } T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } P = -\left(\frac{\partial U}{\partial V}\right)_S.$$

For an isochoric process, $dU = dTS$ where volume is a constant, $dU = TdS$ and for a reversible isochoric process,

$$dU = dQ_{rev} = C_v dT$$

$$\therefore \Delta U = \int_{T_1}^{T_2} C_v dT$$

Since,
 $dQ_{rev} = TdS$

This is true only if the volume is a constant. We want to extend this idea to constant pressure, and this can be done using a thermodynamic potential called enthalpy.

Enthalpy, H

$$\text{We define enthalpy as, } H = U + PV$$

$$\therefore dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$\therefore dH = TdS + VdP$$

So, the natural variables for H is S and P and we have $H \equiv H(S, P)$.

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

$$\therefore T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

For an isobaric process, there is no change in pressure, so $dP = 0$.

$$\therefore dH = TdS$$

For a ~~deven~~ reversible isobaric process then,

$$dH = \frac{dQ_{rev}}{T} = C_p dT \quad (\text{since } dQ_{rev} = TdS)$$

$$\therefore \Delta H = \int_{T_1}^{T_2} C_p dT$$

So, for the reversible isobaric process, the change in enthalpy gives the heat absorbed by the system. If you add heat to the system, H goes up and if heat leaves your system H goes down.

Isobaric conditions are generally easy to achieve. For example, an experiment open to the air in a laboratory is at constant pressure, since the pressure is given by the atmosphere. We also conclude, if S and P are constant, $dH = 0$.

However, both internal energy and enthalpy has the drawback that, ~~they~~ one of their natural variables is entropy, which is not really an easily measurable quantity. If we could replace this with temperature, it would be much more convenient, since T is an easily measurable quantity.

Helmholtz free energy, F

We define, $F = U - TS$

$$\therefore dF = dU - TdS - SdT = TdS - PdV - TdS - SdT$$

$$\therefore dF = -SdT - PdV$$

So, natural variables for F is T and V, and so,

$$F = F(T, V)$$

$$\therefore dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

with $S = \left(\frac{\partial F}{\partial T}\right)_V$ and $P = -\left(\frac{\partial F}{\partial V}\right)_T$.

For an isothermal process, $dT = 0$, and so,

$$dF = -PdV \quad \text{and so, } \Delta F = - \int_{V_1}^{V_2} PdV$$

So, if ΔF is positive, it represents reversible work done on the system by the surroundings and vice versa. We will soon see that, F represents the maximum amount of work you can get out of a system at constant temperature.

Gibb's free energy, G

We define Gibb's free energy by,

$$G = H - TS$$

$$\therefore dG = dH - TdS - SdT = TdS + Vdp - TdS - SdT$$

$$\therefore dG = Vdp - \cancel{T} SdT$$

and so the natural variables are p and T .

$$\therefore dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

giving $V = \left(\frac{\partial G}{\partial p}\right)_T$ and $S = -\left(\frac{\partial G}{\partial T}\right)_p$

Having p and T as natural variables is nice since these are the variables easiest to manipulate in experimental systems. If T and p are constant, $dG=0$. So, in an isobaric isothermal process, G is a constant.

Constraints

We have seen that thermodynamic potentials are valid states of function. However, one might think that they are artificial quantities, where U is the only natural one. We will show that this

is not the case. However, which of these functions of ~~the~~ state is most useful depends on the context of the ~~the~~ problem, and in particular, the type of constraint that is applied to the system.

Consider a large mass at some height. The system has a potential to provide useful work since one can connect it to a pulley and lift another object to that height. However, once it is in the ground, no more useful work can be attained. It is very useful to have a quantity that depends on the amount of ^{available} useful work a system can provide. We call such a quantity, the free energy. In working out what the free energy is, in any particular situation, we have to remember that a system exchange energy with its surrounding, and how it does depends on the sort of constraint that the surrounding imposes on the system. We will first demonstrate this for a particular case and then generalize this.

Consider a system with fixed volume, held at temperature T by its surroundings. If heat $d\vartheta$ enters the system, the entropy S_0 of the surrounding changes by $dS_0 = -\frac{d\vartheta}{T}$, and the change in entropy of the system must be such that total entropy of the system, must be such that total change in entropy of the universe, $dS + dS_0 > 0$.

$$\therefore dS - \frac{d\vartheta}{T} \geq 0$$

$$\therefore TdS > d\vartheta$$

Now, by the first law, ~~$d\vartheta = dU - dW$~~ and so the work added to the system must satisfy,

$$dW > dU - TdS$$

Now, since T is fixed, $dF = d(U - TS) = dU - TdS$,

$$\text{and hence, } dW > dF$$

What we have shown here is, work added to the system increases system's Helmholtz free energy. In reversible process, $dW = dF$ and work added to the system goes directly to increase in F . If we extract a certain amount of heat from the system, $\xrightarrow{(dW_{CO})}$ this will at least be associated with a drop in system's Helmholtz free energy. Now, as with our analogy, adding work to the system +

lets the mass to go at the height at first, and it gives the potential to do work in future (adding free energy to the system), extracting work from the system occurs by letting the mass drop down, that reduces the potential to provide work (drop of free energy of the system). Note that, if the system is mechanically isolated, so no work can be done, $dF \leq 0$, so any process will cause the change in F to be negative. Once the system settles down to equilibrium, F will be constant but in a minimum level. Hence, equilibrium can only be achieved by minimizing F .

Availability

Availability

We want to work out how to find the equilibrium properties of a system when it is placed in contact with its surroundings. In general, a system can exchange heat with the surroundings, do work on the surroundings if the volume of the system changes (mechanical work). Yet, the surroundings is at temperature T_0 and pressure P_0 . If we transfer energy dU and volume dV from the surroundings to the system. The internal energy of the surroundings changes by dU_0 , where,

$$dU_0 = -dU = T_0 dS_0 - P_0 (-dV)$$

where the minus sign implies the surroundings is

Surroundings
System
 T_0, P_0

losing energy and volume.

$$\therefore dS_o = - \left[\frac{dU + P_0 dV}{T_0} \right]$$

which is the change in entropy of the surroundings.

If the change in entropy of the system is dS , then

$$dS_{\text{tot}} = dS_o + dS$$

Since, $dS_{\text{tot}} \geq 0$, we get,

$$\therefore dS_{\text{tot}} = - \frac{dU + P_0 dV}{T_0} + dS \geq 0$$

$$\therefore T_0 dS_{\text{tot}} = - [dU + P_0 dV - T_0 dS] \geq 0$$

$$\therefore dU + P_0 dV - T_0 dS \leq 0$$

If we define availability as, $A = U + P_0 V - T_0 S$,

and since P_0 and T_0 are constants, then,

$$dA = dU + P_0 dV - T_0 dS$$

$$\therefore dA \leq 0$$

So, the changes in A is always negative. As system settles down to equilibrium, any changes will force A downward. Once the equilibrium is reached, A will be a constant in the minimum level and equilibrium can only be achieved by minimizing A .

However, the type of equilibrium achieved depends on the nature of constraint.

1. System with fixed entropy and volume: In this case, $dA = dU \leq 0$ and we must minimize U to find the equilibrium state.

2. System with fixed entropy and pressure:
Now, $dA = dU + T_0 dV = dH \leq 0$. So, we must minimize H to find the equilibrium state.

3. System ~~with~~ that is thermally isolated and has fixed volume: In this case, no heat can enter and no mechanical work can be done.
So, $dU = 0$. So, $dA = -T_0 dS$ and hence $dS \geq 0$. So, we must maximize S to find the equilibrium state.

4. System with fixed volume and constant temperature: $dA = dU - T_0 dS \leq 0$. But since $dT = 0$, so, ~~$dA = dF \leq 0$~~ . So, we must minimize F to find the equilibrium state.

5. System at constant temperature and pressure;

In this case, $dT=0$ and $dP=0$. Now,

$$G = H - TS \Rightarrow dG = dH - TdS - SdT$$
$$\Rightarrow dG = dU + PdV + VdP - TdS - SdT$$
$$\Rightarrow dG = dU + PdV - TdS$$

\therefore Here, $dA = dG \leq 0$. So, we must minimize Gibbs free energy G to find the equilibrium state.

Chemistry laboratories are usually at constant pressure. Since, $dA = TdS + VdP$, it means $dH = TdS = dQ_{rev}$. So, ΔH is the reversible heat added to the system, that is heat absorbed by any reaction (dQ_{rev} is the heat entering the system). Now,

(i) If $\Delta H < 0$, then heat will be emitted and the reaction is called exothermic.

(ii) If $\Delta H > 0$, heat will be absorbed and the reaction is called endothermic.

However, this doesn't tell you anything about the spontaneity of an equation, that is

whether a reaction will actually proceed or not. Usually reactions are at constant ϕ and T (well, the temperature may rise during the process, but waiting enough will give the same temperature as room; one only has to think about the end points, since thermodynamic potentials are state functions). So, G must be minimized for equilibrium. Our discussion above tells us that, second law of thermodynamics implies, if $\Delta G < 0$, then the reaction will spontaneously occur.

Maxwell's relations

We are going to show four equations that are known as Maxwell's relations. These equations are very important in thermodynamics, each of them relates the partial derivative of one quantity that is hard to measure to partial derivative of a quantity that is easily measured.

We know, $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$ if df is exact. We can also write, $df = F_x dx + F_y dy$ and so,

$$F_x = \left(\frac{\partial f}{\partial x}\right)_y, \quad \text{and} \quad F_y = \left(\frac{\partial f}{\partial y}\right)_x$$

Now, the necessary condition for the ~~function~~ differential of f to be exact is,

$$\frac{\partial F_x}{\partial y} = \frac{\partial F_y}{\partial x}$$

We will use this idea to each of the state variables U, H, F and G .

$$(i) dU = TdS - PdV \quad \text{and} \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\therefore U_s = \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad U_v = \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Now, the ~~exact~~ differential U is exact if,

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

For others,

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

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

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

Maxwell's
relations

All the Maxwell's relations can be summarized as,

$$\left(\frac{\partial a}{\partial b}\right)_e = \pm \left(\frac{\partial d}{\partial e}\right)_b$$

where a and e , d and b are conjugate variables. So, if $a = S$, then $e = T$, and $d = P$, $b = V$.

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

Moreover, if V and T are on the same side, we have to incorporate a minus sign.

Finding important quantities

(i) We know, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{T dS}{dT}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$

$$\text{and } C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

So, it relates the partial derivatives of Maxwell relations to heat capacities.

(ii) Generalized susceptibility: A generalized susceptibility κ quantifies how much a particular variable changes when a generalized force is applied. A generalized force such as T or p is a differential of internal energy with respect to some other parameter.

$$dU = TdS - pdV \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial V}{\partial N}\right)_T$$

One

The generalized susceptibility can be written as $\left(\frac{\partial V}{\partial T}\right)_N$, which implies, keeping N constant, how much V changes when you change temperature T .

The isobaric expansivity ($p=\text{constant}$) is defined as,

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

and the adiabatic expansivity ($S=\text{constant}$) is defined as

$$\beta_S = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S$$

due to $\frac{1}{V}$ term

where expansivities measure the fractional change in volume with a change in temperature.

Isothermal compressibility is defined as, $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$

Adiabatic

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$$

where the compressibility κ measures how large

a fractional volume changes when you apply pressure. Although it might seem that compressibility is negative its not. Since $\frac{\partial V}{\partial P}$ is negative, ~~is~~ Because if you apply pressure, volume decreases. So, the compressibility is positive.

Entropy of 1 mole ideal gas

For one mole ideal gas, $PV = RT$. Consider, the entropy S as a function of volume and temperature, $S = S(T, V)$.

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ &= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \end{aligned}$$

But, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$ from $PV = RT$.

$$dS = \frac{C_V}{T} dT + \cancel{\frac{R}{V} dV}$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

$$\Delta S = C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

or, $S = C_V \ln T + R \ln V + \text{constant}$

if C_V is not a function of T (which is true
 $\rightarrow C_V = \left(\frac{\partial V}{\partial T}\right)_P$ and $V = \frac{3}{2}RT$, so, $C_V = \frac{3}{2}R$ for ideal gas)

2)

for all ideal gas. So, the entropy of an ideal gas increases with ~~constant~~ \rightarrow increasing volume and temperature.

Problems

1. Show that, $Q_p - C_v = \frac{VT\beta_p^2}{k_B T}$ considering $S = S(T, V)$.

2. Show that, $\frac{k_T}{k_S} = \gamma$. and ~~$k_T = \frac{1}{P}$~~ and

For ideal gas, also show that, $k_T = \frac{1}{P}$ and $k_g = \frac{1}{\delta P}$.