Physics 467/667: Thermal Physics **Spring 2019**

Lecture 15: Free Energy

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15.1 Outline

In the previous chapter, we applied the laws of thermodynamics to study cyclic processes. Now let's turn to chemical reactions and other phase transformations of matter. One complication is that the system usually involves interactions with its surroundings, in thermal, mechanical, chemical ways. Therefore, energy is not conserved in these cases. Instead, T, P, μ become crucial parameters.

15.2 Free Energy

The first task is to develop the conceptual tools needed to understand constant T, P processes. Recall we have defined the concept of enthalpy (H),

$$H \equiv U + PV \tag{15.1}$$

Let's understand it in this way. If you could completely annihilate the system, H is the energy cost you need to pay. In addition to its internal energy (U), you also need to plus PV work.

Similarly, we have two more useful quantities that are related to energy and analogous to H,

$$F \equiv U - TS \qquad \text{(Helmholtz free energy, constant temperature)} \tag{15.2}$$

$$G \equiv U - TS + PV \qquad \text{(Gibbs free energy, constant temperature, constant pressure)} \tag{15.3}$$

The four functions U, H, F, G are collectively called thermodynamic potentials. Their relations are shown as follows,

$$\begin{array}{cc} & -TS \\ +PV & \begin{array}{|c|c|} \hline U & F \\ \hline H & G \\ \hline \end{array} \end{array}$$

15.3 How to measure ΔG

The easiest way is,

1. measure the heat absorbed when the reaction takes place, ΔH;
2. calculate ΔS according to the heat capacities C_P and the initial/final temperature;
3. $\Delta G = \Delta H - T\Delta S$

Consider the production of ammonia from nitrogen and hydrogen at 298 K and 1 bar,
$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

From the values of ΔH and S, compute ΔG for this reaction and check that it is consistent with the value given in the table.

15.4 Electrochemical Reactions

Consider the chemical reaction of the electrolysis of water to hydrogen and oxygen gas,

$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}\,O_2(g)$

Type	$H_2O(l)$	$H_2(g)$	$O_2(g)$	Total
ΔH(kJ)	-285.8	0	0	285.8
S (J/K)	69.9	130.7	205.1	-163.4
$P\Delta V$(kJ)				3.7
ΔU(kJ)				282.1
$T\Delta S$(kJ)				-48.3
ΔG(kJ)				237.1

The reverse reaction is the combustion of hydrogen gas, a reaction that might replace the internal combustion engine in future automobiles (fuel cell). In the process of producing the electric work, the fuel cell will also dump 49 kJ of waste heat. But the waste heat is only 17% of heat generated from this reaction. So an ideal hydrogen fuel cell has an 'efficiency' of 83%, much better than any practical engine.

15.5 Thermodynamic Identities

In the previous chapter, we already learned

$$dU = TdS - PdV + \mu dN \tag{15.4}$$

What will happen on H, F, G?

$$\begin{aligned} dH =& dU + PdV + VdP \\ =& TdS + VdP + \mu dN \end{aligned} \tag{15.5}$$

Similarly, we could derive that

$$\begin{aligned} dF =& dU - (TdS + SdT) \\ =& -SdT - PdV + \mu dN \end{aligned} \tag{15.6}$$

$$\begin{aligned} dG =& dF + PdV + VdP \\ =& -SdT + VdP + \mu dN \end{aligned} \tag{15.7}$$

Accordingly, we can derive the partial derivatives from G,

$$S = -(\frac{\partial G}{\partial T})_{P,N} \tag{15.8}$$

$$V = (\frac{\partial G}{\partial P})_{T,N} \tag{15.9}$$

$$\mu = (\frac{\partial G}{\partial N})_{T,P} \tag{15.10}$$

15.6 Maxwell Relation

Functions encountered in physics are generally well enough behaved that their mixed partial derivatives do not depend on which derivatives are taken first. For instance,

$$\frac{\partial}{\partial V}(\frac{\partial U}{\partial S}) = \frac{\partial}{\partial S}(\frac{\partial U}{\partial V}) \tag{15.11}$$

From the thermodynamic identities (for U), we can evaluate the partial derivatives,

$$(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V \tag{15.12}$$

Similarly, we apply it on H,F,G,

$$\frac{\partial}{\partial P}(\frac{\partial H}{\partial S}) = \frac{\partial}{\partial S}(\frac{\partial H}{\partial P}) \quad \rightarrow \quad (\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P \tag{15.13}$$

$$\frac{\partial}{\partial V}(\frac{\partial F}{\partial T}) = \frac{\partial}{\partial T}(\frac{\partial F}{\partial V}) \quad \rightarrow \quad (\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \tag{15.14}$$

$$\frac{\partial}{\partial P}(\frac{\partial G}{\partial T}) = \frac{\partial}{\partial T}(\frac{\partial G}{\partial P}) \quad \rightarrow \quad (\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P \tag{15.15}$$

These are **Maxwell relations**. It is useful because it could quantify the changes of entropy which are not directly measurable, in terms of measurable quantities like T, V, P. Here let me just give some of its applications. The thermal expansion coefficient is defined as follows,

$$\beta = \frac{\Delta V/V}{\Delta T} = -\frac{1}{V}(\frac{\partial V}{\partial T})_P \tag{15.16}$$

Plugging in the Maxwell relation,

$$\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{1}{V}(\frac{\partial S}{\partial P})_T \tag{15.17}$$

According to the 3rd law, entropy approaches to 0 or some constant regardless of P. Hence $\beta = 0$ when T goes to 0.

Now let's dig into the difference between C_V and C_P

$$dS = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV \tag{15.18}$$

$$dV = (\frac{\partial V}{\partial T})_p dT + (\frac{\partial V}{\partial P})_T dP \tag{15.19}$$

$$(dS)_P = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T (\frac{\partial V}{\partial T})_P dT \tag{15.20}$$

That is,

$$(\frac{\partial S}{\partial T})_P = (\frac{\partial S}{\partial T})_V + (\frac{\partial S}{\partial V})_T (\frac{\partial V}{\partial T})_P \tag{15.21}$$

$$C_P = C_V + T(\frac{\partial S}{\partial V})_T (\frac{\partial V}{\partial T})_P \tag{15.22}$$

$$C_P = C_V + T(\frac{\partial P}{\partial T})_V (\frac{\partial V}{\partial T})_P \tag{15.23}$$

from problem 1.46,

$$(\frac{\partial P}{\partial T})_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \tag{15.24}$$

Therefore,

$$C_P = C_V - T(\frac{\partial V}{\partial T})_P^2 / (\frac{\partial V}{\partial P})_T \tag{15.25}$$

Recall the definition of β and κ

$$\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P; \qquad \kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T \tag{15.26}$$

$$C_P - C_V = -T(\beta V)^2/(-\kappa_T V) = \frac{TV\beta^2}{\kappa_T} \tag{15.27}$$