Thermodynamics Lecture Notes: Chapter 10

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10.1 Basic relations of Thermodynamics

Remember the first law of TD: $dE_{int} = \delta Q - \delta W$ and $dE_{int} = TdS - PdV$ are always valid, but $\delta Q = TdS$ and $\delta W = PdV$ only for reversible processes. This is applicable to a special case, a *closed* system only.

Instead, for an "open system", matter exchange with the environment can occur. Remember from Chapter 6, the more general form of the first law is

$$dE_{int} = dQ - dW + dC$$

with C being the chemical potential.

Matter transport and chemical potential:

$$dC = \sum_{i=1}^{N} \mu_i dn_i$$

with dn_i being the number of moles of substance i and μ_i is the chemical potential for the substance i per mole. It describes the energy to add dn_i mole of substance i to the system at $dW = 0$ and $dQ = 0$.

$$\mu_i = \left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V const}$$

Every chemical reaction can be described by removing initial substances and adding final ones, e.g., $2H_2 + O_2 \rightarrow 2H_2O$ or $2\mu_1 + 1\mu_2 \rightarrow 2\mu_3$. Most generally, it can be expressed as

$$\sum_{i=1}^{k} \mu_i n_i \rightarrow \sum_{j=k+1}^{p} \mu_j n_j$$

A flow of matter is caused by a difference in the chemical potential (from higher to lower chemical potential). Instead, flow of work was caused by a difference in P/V, and a flow of heat was caused by a difference in T.

At given T, P, and V a system with more moles (higher particle concentration) has a higher chemical potential.

In most general form, we can write the first law of TD as the **"Gibbs' fundamental relation"**:

$$dE_{int} = TdS - PdV + \sum_i \mu_i dn_i;\ i.e.\ E_{int} = E_{int}(S, V, n)$$

The derivative of the internal energy can also be written as:

$$E_{int} = \frac{\partial E_{int}}{\partial S}\, dS + \frac{\partial E_{int}}{\partial V}\, dV + \sum_i \frac{\partial E_{int}}{\partial n_i}\, dn_i,$$

so that

$$T = \frac{\partial E_{int}}{\partial S};\ P = -\frac{\partial E_{int}}{\partial V};\ \mu_i = \frac{\partial E_{int}}{\partial n_i}.$$

The differential "Gibbs" equation also exists as a simple algebraic **"Euler"** relation (as the derivation in lecture slides shows):

$$E_{int} = TS - PV + \sum_i \mu_i n_i$$

Differentiating the Euler equation results in:

$$dE_{int} = TdS + SdT - PdV - VdP + \sum \mu_i dn_i + \sum n_i d\mu_i$$

With the Gibbs' relation, we obtain:

$$SdT - VdP + \sum n_i d\mu_i = 0$$

This is known as the **"Gibbs-Duhem" relation**.

10.2 Thermodynamic potentials and exact differentials

Physical meaning and motivation of TD potentials: TD potentials play the analogue role as potentials in classical mechanics: Forces are derived from the Gradient of the Potential: $\vec{F} = \vec{\nabla} U$. For the U being the gravitational potential $U = -\frac{GMm}{r}$, it follows for the gravitational force:

$$F_{grav} = \frac{\partial U}{\partial r} = \frac{GMm}{r^2}$$

Forces in classical mechanics lead to movements of particles/objects.

Analogy in TD: **Gradients/derivations of TD potentials result in state variables (V, P, T, S, ...), whose change introduce a TD process (expansion, compression etc.).** Such a TD process continues until the TD system is in equilibrium (no change with time without any influence from the outside) via reaching extrema (minima) of TD potentials.

E_{int} is a thermodynamic potential; the definition of a thermodynamic potential follows the mathematical concept of exact differentials:

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

Example: $f(x,y) = 3xy$ then $\left(\frac{\partial f}{\partial x}\right)_y = 3y$; $\left(\frac{\partial f}{\partial y}\right)_x = 3x$

Now let's define $P = \left(\frac{\partial f}{\partial x}\right)_y$ and $Q = \left(\frac{\partial f}{\partial y}\right)_x$, then we have $df = Pdx + Qdy$. From that follows that:

$$\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y$$

because of the Schwartz theorem, which needs to be fullfilled for an exact differential:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}.$$

In the above example, we would have $\left(\frac{\partial P}{\partial y}\right)_x = 3$ and $\left(\frac{\partial P}{\partial x}\right)_y = 3$. If a function fullfills these conditions, it is called an exact differential. Exact differentials are used to describe a quantity that can be integrated along any path between two points with the same result, such as a state function. The internal energy, which is a state function, is an example for an exact differential.

If we replace $f(x, y)$ with $dE_{int}(S, V, n)$, we obtain:

$$dE_{int} = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n} dS + \left(\frac{\partial E_{int}}{\partial V}\right)_{S,n} dV + \left(\sum \frac{\partial E_{int}}{\partial n_i}\right)_{S,V} dn_i$$

with

$$T = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n} \ ; \ P = -\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n} \text{ and } \mu_i = \left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}$$

Natural variables of a TD potential are that variables, which fully determine a TD potential, and which allow us to derive dependent variables directly from derivatives of the potential to the natural variables.

- *Example:* $E_{int} : S, V, n$ are natural variables $\rightarrow\ T, P, \mu$ can be derived.
- *Counter example:* T cannot be a natural variable of E_{int} because $\left(\frac{\partial E_{int}}{\partial T}\right)_V = C_V$!

Applying then the mathematical concept of exact differentials, we can further derive these so called **"Maxwell"** relations (based on the Schwartz theorem):

$$\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}$$

$$\left(\frac{\partial T}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial S}\right)_{V,n}$$

$$-\left(\frac{\partial P}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial V}\right)_{S,n}$$

In addition to the internal energy E_{int}, other TD potentials can be introduced in order to find other energy functions which have other sets of natural variables similarly simple as E_{int} with S, V, n. This can be of advantage as the natural variables of E_{int} are not very convenient to measure (e.g. entropy S) or to be held fixed. Thus, depending on the experiment, other TD potentials can be used, where natural variables are more easily measurable or be fixed (to make estimates on related equilibrium states).

Theoretically, we can transition from one TD potential and its natural variables to another via a **Legendre transformation**:
Imagine we have a state function f(x) and y(x) is the derivative of f(x) to x, i.e. $y(x) = \frac{df(x)}{dx}$. Then a Legendre transformation g(y) is defined as:

$$g(y) = f(x) - yx.$$

Meaning of the Legendre transform: It is a mathematical operation to transform one function into another such that the information contained in the original function is preserved, but is expresed via different (natural) variables.

10.3 Enthalpy H

The thermodynamic potential Enthalpy H is defined as the Legendre transform of internal energy E_{int} with respect to V (being the "x" in the equations above): $H = E_{int} + PV$. Differentiating H results in:

$$\begin{aligned} dH &= TdS - PdV + \sum \mu_i dn_i + PdV + VdP \\ &= TdS + VdP + \sum \mu_i dn_i \end{aligned}$$

Thus, the natural variables of H are S, P, and n so that we can rewrite dH also as:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{V,n_i} dP + \sum \left(\frac{\partial H}{\partial n_i}\right)_{S,P} dn_i$$

Thus:

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} \; ; \; V = \left(\frac{\partial H}{\partial P}\right)_{V,n_i} \; ; \; \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P}$$

And as for E_{int}, we can again derive the Maxwell equations; one example is:

$$\left(\frac{\partial T}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{P,n}$$

Application: assume we have an isobaric, reversible process (P = const) in a closed system (in equilibrium with work reservoir), then $dH = TdS = dQ$. In this example, the increase of Enthalpy corresponds to the heat added to the system.

10.4 Free Energy F

Free Energy F is defined as the Legendre transform of the internal energy E_{int} with respect to S: $F = E_{int} - TS$. Differentiating F leads to:

$$\begin{aligned} dF &= TdS - PdV + \sum \mu_i dn_i - TdS - SdT \\ &= -SdT - PdV + \sum \mu_i dn_i \end{aligned}$$

Thus, the natural variables of F are T, V, and n, and we can re-write the expression for dF as:

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,n} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n} dV + \sum \left(\frac{\partial F}{\partial n_i}\right)_{T,V} dn_i$$

Thus,

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,n_i} \; ; \; V = \left(\frac{\partial F}{\partial V}\right)_{T,n_i} \; ; \; \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V}$$

And as for E_{int} and H, we can again derive the Maxwell equations; one example is:

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

Application: Isothermal process (T = const) of a closed system: $dF = -PdV = -dW$; An increase of the free energy implies that work is done on this system (equal to the difference in free energy).

10.5 Gibbs Free Enthalpy G

The Free Enthalpy or the Gibbs Free Energy G is the Legendre transform of the internal energy with respect to S and V, or of the Enthalpy with respect to S: $G = E_{int} + PV - TS = H - TS$. Differentiating G leads to:

$$\begin{aligned} dG &= TdS + VdP + \sum_i \mu_i dn_i - TdS - SdT \\ &= -SdT + VdP + \sum_i \mu_i dn_i \end{aligned}$$

Thus, the natural variables of G are T, P, and n. We can re-write the expression for dG as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i$$

with

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,n} \; ; \; V = \left(\frac{\partial G}{\partial P}\right)_{T,n} \; ; \; \mu_i = \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

One example of the three Maxwell relations for G is:

$$-\left(\frac{\partial S}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

Relevance of the Gibbs' Potential G: Most chemical reactions happen at constant pressure P and temperature T. Thus, the Gibbs' Potential is the chemical potential, which can be shown by using the Euler relation for E_{int}:

$$G = H - TS = E_{int} + PV - TS = TS - PV + \sum_i \mu_i n_i + PV - TS$$

$$\rightarrow G = \sum_i \mu_i n_i$$

[Note that G is formerly noted as C.]

10.6 Equilibra of subsystems coupled to a reservoir

In this section, we characterise how an isolated system, composed of two simple subsystems coupled to a reservoir/thermal bath (in equilibrium with subsystems), approaches equilibria states under different conditions (i.e. minimisation of thermodynamic potentials). These systems have extensive state variables $S = S_1 + S_2$ and $V = V_1 + V_2$, where 1 and 2 refer to the quantities of the subsystems 1 and 2 (remember that P and T are intensive quantities, they are NOT additive). Equally, we can write to the thermodynamic potentials of the systems:

$$E_{int} = E_{int,1} + E_{int,2}$$

$$F = F_1 + F_2$$

$$H = H_1 + H_2$$

$$G = G_1 + G_2$$

1. Minimum of Free Energy

Assume we have an isolated, rigid system two subsystems which are kept in thermal equilibrium with a heat reservoir, i.e. $T_1 = T_2 = T_{res} = T$ and Volume V = constant. The Free Energy F of this system can be expressed as $dF = dE_{int} - TdS$. With $dE_{int} = \delta Q - \delta W$ and $\delta W = 0$ because of dV = 0, we obtain:

$$dF = \delta Q - TdS = \delta Q - TS_{prod} - \delta Q = -TdS_{prod} \leq 0$$

since $dS = dS_{prod} + \delta Q/T$. Equality to zero is achieved only for reversible processes as in that case no entropy is produced within the system ($dS_{prod} = 0$).

If a rigid system (V constant) is kept at constant temperature T (due to interactions with the heat reservoir), the equilibrium between subsystems minimises the free energy of the system: $dF \leq 0$. Inequality to zero describes the decrease of the Free Energy during irreversible processes.

2. Minimum of Enthalpy

Assume we have an isolated, closed system composed of two subsystems in mechanical equilibrium with a work reservoir (walls between subsystem and work reservoir are movable), i.e. $P_1 = P_2 = P_{res} = P$. Any work of resevoir done on (sub)systems is reversible so that $S = S_1 + S_2 = constant$. The Enthalpy of this system can be expressed as $dH = dE_{int} + PdV = \delta Q - \delta W + PdV = \delta Q$. We also know that $dS = 0$ so that:

$$\frac{\delta Q}{T} + dS_{prod} = 0 \;\rightarrow\; \frac{\delta Q}{T} = -dS_{prod} \leq 0$$

with equality only for reversible processes as there is no entropy production within the system. Thus, $dH = \delta Q \leq 0$.

If an isolated system composed of two subsystems is kept at constant pressure P with a work reservoir through reversible processes (S is constant), the equilibrium state minimises the enthalpy H of the system: $dH = \delta Q \leq 0$.

3. Minimum of Gibbs/Free Enthalpy

Lastly, assume we have an isolated, closed system composed of two subsystems that are kept at constant temperature T and constant pressure P due to their equilibrium with a heat and work reservoir (walls are both diathermal and movable). The Gibbs/Free Enthalpy of this system can be expressed as

$$dG = dE_{int} - TdS + PdV = \delta Q - \delta W - TdS + PdV = \delta Q - TdS = \delta Q - \delta Q - TdS_{prod}$$

$$\rightarrow\; dG = -TdS_{prod} \leq 0.$$

If constraint on wall separation (diathermal and movable) is relaxed, G will decrease (equality to zero for reversible processes only).

To summarise, if a system composed of two subsystems is kept at constant T and P (due to a heat and work reservoir), the equilibrium state between subsystems minimises the Gibbs/Free enthalpy of the system.