Review of Classical Thermodynamics and VLE

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All closed systems have a tendency to evolve toward states in which the properties are determined by intrinsic factors and not by external forces applied. These states are called equilibrium states. For example, a stirred cup of coffee returns to such a state eventually, the temperature in a room gradually becomes time invariant and homogenous etc. Classical thermodynamics is concerned with these equilibrium states. We follow the posutlatic formulation by Callen [1]. First, the concepts of simple and composite systems are given.

Definition 0.1. A **simple system** is a system which is macroscopically homogenous.

For example, a closed container with a mixture of gases is a simple system.

Definition 0.2. A **composite system** consists of *one or more* simple systems.

For example, two closed containers containing a mixture of gases considered together is a composiste system.

Definition 0.3. Constraints that prevent flow of matter, energy or volume among the simple systems constituting the composite system are called **internal constraints**.

For example, consider two simple systems separated by a piston. If the piston is made free to move, then the internal constraint of volume restriction is removed and volume is "free to flow".

Definition 0.4. If a composite system is surrounded by walls that restrict the flow of volume, energy and matter, then the system is said to be **closed**.

0.1 Fundamental Postulates

1. Postulate 1 : The concept of internal energy U gives rise to the first fundamental postulate of Thermodynamics : the equilibrium states of a *simple system* are only functions of the extensive parameters $U, V, N_1, N_2, \cdots, N_r$ where U, V, N_i are respectively, the internal energy, volume and the number of moles of species i.

   (a) Note that the internal energy of a system is not an absolute quantity. It is defined w.r.t. a fudicial (reference) state. The reference state is automatically given zero value for internal energy.

   (b) The above postulate is for simple systems, i.e. systems which are homogenous.

   (c) For composite systems, the above parameters for each sub-system must be specified to completely describe the equilibrium.

2. Postulate 2 : The second postulate states that there exists a function (called entropy S) of the extensive parameters of a composite system, i.e.,

$$S = S(U^{(1)}, V^{(1)}, N_1^{(1)}, N_2^{(1)}, \cdots, N_r^{(1)}, U^{(2)}, V^{(2)}, N_1^{(2)}, N_2^{(2)}, \cdots, N_r^{(2)}, \cdots, U^{(n)}, V^{(n)}, N_1^{(n)}, N_2^{(n)}, \cdots, N_r^{(n)})$$

defined for all equilibrium states of the constituent subsystems, such that for an *closed* composite system S reaches a maximum over the manifold of constrained equilibrium states when an internal constraint is removed.

Note that the first part of this postulate defines entropy. The second part is only applicable for composite systems containing atleast two simple subsystems since internal constraints only exist in this case.

3. Postulate 3: The third postulate states that

    (a) The entropy of a composite system is the sum of entropies of the individual systems and

    (b) The entropy of a simple system is continuous and differentiable and is a monotonically increasing function of U.

4. The fourth postulate states that for a simple system, in any state for which $(\frac{\partial U}{\partial S})_{V,N_1,\cdots,N_r} = 0$, the entropy of the system reaches zero.

All standard thermodynamic calculations are essentially applications of these four postulates alone. All the postulates still hold even if the reference state for internal energy is changed.

0.2 Entropy Maximum Condition

When an internal constraint in an closed system is removed, the system will reach a new equilibrium state. For a closed system, the total energy, total volume and total moles are conserved. Hence, in the new equilibrium after an internal constraint is removed the system can only choose between different equilibrium states which satisfy these constraints. The equilibrium states that satisfy these constrains form a manifold (a geometric object relating the extensive parameters of the system restricted by the constraints). The entropy of the composite system is maximized on this manifold.

As S is maximized when an internal constraint is removed, in the new equilibrium state we should have

$$\frac{\partial S}{\partial U^i} = \frac{\partial S}{\partial V^i} = \frac{\partial S}{\partial N_j^i} = 0 \ \forall i = 1, 2, \cdots, n, j = 1, 2, \cdots, r$$

It is very important to understand that these are partial derivatives over the mainfold of constrained equilibrium states. For example, if we remove a non-permeable partition between two simple sub-systems, then the "internal constraint", i.e., the partition is removed and hence the combined system reaches a new equilibrium state which can be found by using the above relations on $S = S_1 + S_2$ where S_1, S_2 are the entropies of the two sub-systems with the constraint that the total mole numbers are conserved etc.

0.3 Differentials

Let $f : \mathbb{R} \to \mathbb{R}$, then the differential of f is a function of two independent variables x and Δx given by

$$df(x, \Delta x) = f'(x)\Delta x$$

If $y = f(x)$ we write $dy = df(x, \Delta x)$. Since for $y = x$, $dy = dx = \Delta x$, we write $dy = f'(x)dx$ for notational simplicity.

For a function of several variables $f(x_1, x_2, \cdots, x_n)$, we have $df(x_1, x_2, \cdots, x_n, \Delta x_1, \Delta x_2, \cdots, \Delta x_n) = \frac{\partial f}{\partial x_1}\Delta x_1 + \frac{\partial f}{\partial x_2}\Delta x_2 + \cdots + \frac{\partial f}{\partial x_n}\Delta x_n$ Again, this is written for simplicity as $df = \frac{\partial f}{\partial x_1}dx_1 + \frac{\partial f}{\partial x_2}dx_2 + \cdots + \frac{\partial f}{\partial x_n}dx_3$

0.3.1 Maxima and Minima

If f attains a (local) maximum, then two conditions need to be satisfied 1) All partial derivatives should be zero and 2) Hessian is negative definite.

1. If all partial derivatives are zero then it is clear that $df(x_1, x_2, \cdots, x_n, \Delta x_1, \Delta x_2, \cdots, \Delta x_n) = 0$ for arbitrary values of $\Delta x_1, \Delta x_2, \cdots, \Delta x_n$. This statement is also true in the reverse.

2. Let $d^2f := \sum_{i=1}^n \frac{\partial^2 f}{\partial x_i^2}\Delta x_i^2 + 2\sum_{i<j}^n \frac{\partial^2 f}{\partial x_i x_j}\Delta x_i \Delta x_j$. Negative definiteness of the Hessian is equivalent to $d^2f < 0$ for arbitrary values of $\Delta x_1, \Delta x_2, \cdots, \Delta x_n$.

0.3.2 Differential of Internal Energy

As $S = S(U, V, N_1, \cdots, N_r)$ is monotonic in U, the relation can be reversed (by taking an inverse) so that $U = U(S, V, N_1, \cdots, N_r)$. Based on this fundamental dependence, the differential of U can be written as

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum_i \frac{\partial U}{\partial N_i} dN_i$$

Now, temperature is defined as $\frac{\partial U}{\partial S}$, pressure is defined as $-\frac{\partial U}{\partial V}$ and finally the chemical potential μ_i is defined as $\frac{\partial U}{\partial N_i}$. The newly defined variables, T, P, μ_i are called intensive parameters. In the new notation, the final equation looks like

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

As already stated, S is only defined for equilibrium states and dS is an infinitesimal change in entropy. Therefore, for the expression dS to be meaningful, the system has to be in equilibrium after the infinitesimal change has occured. Reversible processes, for example, proceed at such a slow pace that the system is always in equilibrium.

0.4 Thermodynamic Potentials

The previous equation is the only fundamental relation in thermodynamics. In a few occasions however, it is desirable to use other functions of the internal energy and entropy. These are called thermodynamic potentials and can be derived using the mathematical technique called Legendre transformation. The enthalpy H and the Gibbs free energy G are two such functions. For this course, these two are sufficient.

1. $H = H(S, P, N_1, N_2, \cdots, N_r), H = U + PV, dH = TdS + VdP + \sum_i \mu_i dN_i$

2. $G = G(T, P, N_1, N_2, \cdots, N_r), G = U - TS + PV, dG = -SdT + VdP + \sum_i \mu_i dN_i$

where $U, H, G, S, P, V, \mu_i, N_i$ are respectively the internal energy, enthalpy, entropy, pressure, volume, chemical potential of the $i$the species and number of moles of the $i$the species.

0.5 Equilibrium

We can derive similar criterion for the Enthalpy and Gibbs Free energy at equilibrium. They are given next.

1. Consider a system in contact with a pressure (P^r) reservoir. Then at equilibrium, $P = P^r$ and $dH = 0$ (H is minimum), i.e., $TdS + \sum_i \mu_i dN_i = 0$. This is applicable to systems which are separated from the reservoir by a diathermal (allows heat to pass), movable, impermeable (allows matter to pass) wall. What does this equation convey? It gives a relation between the infinitesimal changes in dS, dN_i at the new equilibrium. Therefore, for example, at the new equilibrium, an infinitesimal change in entropy should equal $-\frac{1}{T} \sum_i \mu_i dN_i$.

2. Consider a system in contact with a pressure (P^r), temperature (T^r) reservoir. Then at equilibrium, $T = T^r, P = P^r$ and $dG = 0$ (G is minimum), i.e., $\sum_i \mu_i dN_i = 0$. This is applicable to systems which are separated from the reservoirs by a diathermal, movable, impermeable (allows matter to pass) wall.

0.5.1 Vapor-Liquid Equilibrium

Assume a mixture of r components in Vapor-Liquid equilibrium in a container which is in contact with a constant temperature, pressure reservoir (e.g. ambient atmosphere). From the equilibrium condition above, it is clear that the Gibbs free energy of the system reaches a minimum at equilibrium i.e, $\sum_i \mu_i dN_i = 0$. Let dN_i^l, dN_i^v be some infinitesimal changes in the moles of the ith component in the liquid and the vapor phases respectively. Then, due to ith species balance, we have $dN_i^l = -dN_i^v$. This gives that $\sum_i (\mu_i^l - \mu_i^v) dN_i^l = 0$. Now, considering the fact that the dN_i^l for various i's can be varied independently of each other, we conclude that $\mu_i^l = \mu_i^v$.

0.6 Chemical Potential

For a multi-component system, $G = N \sum_i \mu_i x_i$, where N is the total moles of all the species put together. μ_i is called the partial molar Gibbs free energy. For a single component μ is called the molar Gibbs free energy.

0.6.1 Pure Ideal Gas

Consider one mole of the pure ideal gas in a closed (impermeable, diathermal and non-restrictive) container in contact with a temperature reservoir at temperature T^r. As $\mu = G$ we have $d\mu = dG = vdP - sdT$, where v, s are specific volume and entropy. At equilibrium, clearly, $T = T^r$ and therefore, $d\mu = vdP = \frac{RT}{P}dP$. Integrating both sides, we obtain $\mu^{\mathrm{Id},v}(T, P) = \mu^{\mathrm{Id},v}(T, P^0) + RT\ln(P/P^0)$. Typically, we can choose $P^0 = 1\mathrm{bar}$, so that $\mu^{\mathrm{Id},v}(T, P) = \mu^{\mathrm{Id},v}(T, 1\,\mathrm{bar}) + RT\ln(P)$. As the first term on the r.h.s. is independent of P, we write it as $\mu^0(T)$. Therefore, $\mu^{\mathrm{Id},v}(T, P) = \mu^0(T) + RT\ln(P)$.

0.6.2 Pure Non-Ideal Gas

Consider the same setup as above. We have, $d\mu = vdP$ but here the relation between v and T, P is given by some other equation of state. Nevertheless, to have a definition of chemical potential similar to the Ideal gas case, we define $\mu^v(T, P) = \mu^0(T) + RT\ln(f^v(T, P))$, where f^v is called the fugacity which depends on the temperature and pressure. The fugacity coefficient is defined as $\phi^v(T, P) = \frac{f^v(T,P)}{P}$. Note that the fugacity for gases can be calculated based on the Equation of State (Virial, Peng-Robinson, Soave Redlich Kwong etc.).

0.6.3 Pure Liquid

At the boiling point of the pure liquid, there exists an equilibrium with the vapor phase. Therefore, the chemical potential of the liquid and vapor should be the same. Hence, $\mu^l(T, P^{\mathrm{sat}}(T)) = \mu^v(T, P^{\mathrm{sat}}(T)) = \mu^0(T) + RT\ln(f^v(T, P^{\mathrm{sat}}(T)))$ where $P^{\mathrm{sat}}(T)$ is the saturation pressure at the temperature T. Using an equation of state for the liquid provides, V_l as a function of T, P. Then, from $d\mu = vdP$ we obtain $\mu^l(T, P) = \mu^l(T, P^{\mathrm{sat}}(T)) + \int_{P^{\mathrm{sat}}(T)}^{P} V_l dP$. Defining fugacity in a similar fashion as above, $\mu^l(T, P) = \mu^0(T) + RT\ln(f^l(T, P))$. Combining, these three equations, we obtain $f^l(T, P) = f^v(T, P^{\mathrm{sat}}(T)) \exp\left(\frac{\int_{P^{\mathrm{sat}}(T)}^{P} V_l dP}{RT}\right)$

0.6.4 Ideal Gas Mixture

It is easy to show that in this case, $\mu_i^{\mathrm{Id}}(T, P, y_i) = \mu^{\mathrm{Id}}(T, P) + RT\ln(y_i)$ where $\mu_i^{\mathrm{Id}}(T, P, y_i)$ represents the chemical potential of species i with mole fraction y_i in the mixture.

0.6.5 Ideal Mixture (both Vapor and Liquid)

Generalizing from the previouse case, we define an Ideal Mixture as the mixture for which $\mu_i^{\mathrm{Id\text{-}Mix}}(T, P, x_i) = \mu_i(T, P) + RT\ln(x_i)$ where $\mu_i^{\mathrm{Id\text{-}Mix}}(T, P, x_i)$ represents the chemical potential of species i with mole fraction x_i in the mixture and $\mu_i(T, P)$ represents the pure species chemical potential.

0.6.6 Non-Ideal Mixture

$\mu_i(T, P, x_i) = \mu^0(T) + RT\ln\left(\hat{f}_i(x_i)\right)$ where $\hat{f}_i(x_i)$ is the fugacity of the species in the mixture which depends on the mole fraction. We define the fugacity coefficient as $\hat{\phi}_i = \frac{\hat{f}_i(x_i)}{x_i P}$.

0.6.7 Activity Coefficient

From the two previous definitions, we have

$$\mu_i(T,P,x_i) - \mu_i^{\text{Id-Mix}}(T,P,x_i) = \mu^0(T) + RT\ln\left(\hat{f}_i(x_i)\right) - \mu_i(T,P) - RT\ln(x_i)$$

$$= \mu^0(T) + RT\ln\left(\hat{f}_i(x_i)\right) - \mu^0(T) - RT\ln(f_i) - RT\ln(x_i)$$

$$= RT\ln\left(\frac{\hat{f}_i(x_i)}{f_i x_i}\right)$$

The activity coefficient is defined as $\gamma_i = \frac{\hat{f}_i(x_i)}{f_i x_i}$. If $\gamma_i = 1$ then the mixture is ideal. The l.h.s. in the previous equation is called the Excess Gibbs free energy.

0.7 Calculating VLE constants

To compute the VLE constant, we can use definitions of fugaicty and activity coefficient. At equilibrium, by equating the chemical potentials in the Vapor and Liquid Phases, we get

$$\hat{f}_i^v = \hat{f}_i^l$$
$$\hat{\phi}_i^v y_i P = f_i^l x_i \gamma_i$$
$$K = \frac{y_i}{x_i} = \frac{f_i^l \gamma_i}{\hat{\phi}_i^v P} \tag{1}$$
$$K = \frac{\gamma_i P_i^{\text{sat}}(T)}{\Phi_i P}$$

where $\Phi_i = \frac{\hat{\phi}_i^v}{\phi_i^v}\exp\left(\frac{-\int_{P^{\text{sat}}(T)}^P V_l dP}{RT}\right)$. Now, we discuss how each of the quantities in the above equation are computed

1. $P_i^{\text{sat}}(T)$ is calculated using for e.g. the Antoine equation.

2. γ_i is computed by models such as Margules, NRTL, UNIQUAC etc.

3. $\hat{\phi}_i^v, \phi_i^v$ are computed using Predictive Soave-Redlich-Kwong (PSRK) method, Virial Equation of State etc. The PSRK method internally aslo uses a method for estimating activity coefficients.

4. The Poynting factor $\exp\left(\frac{\int_{P^{\text{sat}}(T)}^P V_l dP}{RT}\right)$ can again be calculated using the PSRK method . For low to moderate pressures, this factor is very close to unity and hence can be ignored.

0.8 Fugacities From Virial Equation of State

First conisder the case of one mole of a pure gas. Define the residual volume and residul Gibbs free energy as

1. $V^R(T,P) = V(T,P) - V^{Id}(T,P)$ where $V^{Id}(T,P)$ is the volume of ideal gas.

2. $G^R(T,P) = G(T,P) - G^{Id}(T,P)$

By definition of fugacity, we have $G^R(T,P) = RT\ln(f/P) = RT\ln(\phi)$. Therefore, by modelling the residual gibbs free energy, one can obtain f. The Virial equation of state is

$$\frac{PV}{RT} = 1 + BP + CP^2 + DP^3 + \cdots$$

where the constants $B, C, D, \cdots$ are functions of temperature only.

The compressibility factor is defined as $Z = \frac{PV}{RT}$. Using the Virial Equation, we have $Z = 1 + BP$. Since, $\frac{\partial(G^R/RT)}{\partial P} = \frac{V^R}{RT}$ and $V^R = \frac{RT}{P}(Z-1) = BRT$, we obtain, $\frac{\partial(G^R/RT)}{\partial P} = B$. Therefore, $\frac{G^R}{RT} = BP$. Combining this with, $G^R(T, P) = RT\ln(\phi)$ we obtain $\ln\phi = BP$. In summary, by modelling G^R one can obtain the fugacity of a pure gas.

Next, we will see how to obtain fugacities in mixtures. We know that

$$\hat{\mu}_i(T, P, N_1, N_2, \cdots, N_r) = \mu^{Id}(T, P, N_1, N_2, \cdots, N_r) + RT\ln\left(\hat{\phi}_i(T, P, N_1, N_2, \cdots, N_R)\right)$$

i.e.,

$$\frac{\partial G}{\partial N_i} = \frac{\partial G^{Id}}{\partial N_i} + RT\ln\left(\hat{\phi}_i(T, P, N_1, N_2, \cdots, N_R)\right)$$

Therefore,

$$\frac{\partial(G^R/RT)}{\partial N_i} = \ln\left(\hat{\phi}_i(T, P, N_1, N_2, \cdots, N_R)\right)$$

It was previously shown that $\frac{G^R}{RT} = BP$. In the case of mixtures, $B = \sum_{i \leq j} y_i y_j B_{ij}$ where y_i is the mole fraction of the i component and B_{ij} account for the bimolecular interactions. Hence, the $\hat{\phi}_i$'s can be computed.

0.9   Ideal Mixtures

As mentioned before an ideal mixture, is defined to be a mixture for which

$$\mu_i^{\text{Id-Mix}}(T, P, x_i) = \mu_i(T, P) + RT\ln(x_i)$$

Differentiating this expression w.r.t. P gives that the total volume of the mixture is the sum of the components. Similarly, differentiating w.r.t. T gives that the enthalpy of the mixture is equal to weighted sum of enthalpies of the the components where the weights are equal to the mole fractions.

References

[1] Herbert B. Callen. *Thermodynamics*. John Wiley & Sons, Inc., New York, N.Y., 1960.