SYSTEMS OF VARIABLE COMPOSITIONS

This document provides study material and numerical problems related to the thermodynamics of systems with variable compositions, a crucial topic in physical chemistry and chemical engineering.

CHECKLIST OF TOPICS COVERED:

- State functions for systems of variable compositions.
- Criteria of equilibrium and spontaneity.
- Partial molar quantities and their significance.
- Dependence of thermodynamic parameters on composition.
- Chemical potential as an escaping tendency.
- The Gibbs-Duhem equation.
- Entropy and Gibbs function for mixing of ideal gases.
- Chemical potential of ideal mixtures.
- Fugacity of pure real gases and its calculation.
- Activities and activity coefficients.
- Choice of standard states and dependence of activity on pressure and temperature.

1. STATE FUNCTIONS AND PARTIAL MOLAR QUANTITIES

1.1 STATE FUNCTIONS IN SYSTEMS OF VARIABLE COMPOSITIONS

In a system of variable composition, the total thermodynamic properties (like Volume V, Enthalpy H, Internal Energy U, Entropy S, Gibbs Free Energy G, Helmholtz Free Energy A) are not only functions of temperature (T) and pressure (P) but also depend on the number of moles of each component (n_i).

For a system containing k components, a state function X can be generally expressed as:

$X = X(T, P, n_1, n_2, \ldots, n_k)$

1.2 PARTIAL MOLAR QUANTITIES

A partial molar quantity $ ar{X}_i$ of component i is defined as the change in the total property X when one mole of component i is added to the system, while keeping T, P, and the number of moles of all other components ($n_{j eq i}$) constant.

Mathematically:

$ ar{X}_i = \left(\frac{\partial X}{\partial n_i} ight)_{T, P, n_{j eq i}}$

The total property X of a mixture can be expressed as the sum of the partial molar quantities of its components:

$X = \sum_{i=1}^{k} n_i   ar{X}_i$

The most important partial molar quantity is the **partial molar Gibbs free energy**, which is defined as the **chemical potential** (μ_i) of component i:

$\mu_i =   ar{G}_i = \left(\frac{\partial G}{\partial n_i} ight)_{T, P, n_{j eq i}}$

The chemical potential represents the contribution of component i to the Gibbs free energy of the mixture. It is a key property for understanding phase equilibria and chemical reactions.

2. CRITERIA OF EQUILIBRIUM AND SPONTANEITY

For a process occurring at constant temperature (T) and pressure (P), the criterion for spontaneity and equilibrium is based on the change in Gibbs Free Energy (ΔG):

- **Spontaneity:** A process is spontaneous if $\Delta G < 0$.
- **Equilibrium:** A system is at equilibrium if $\Delta G = 0$.
- **Non-spontaneity:** A process is non-spontaneous if $\Delta G > 0$.

In systems of variable composition, these criteria apply to changes in composition as well. At equilibrium, the Gibbs free energy of the system is at a minimum with respect to all possible changes in composition and phase distribution. This implies that for any infinitesimal change in the system at equilibrium:

$dG_{T,P} = \sum_{i=1}^{k} \mu_i dn_i = 0$

The chemical potential (μ_i) acts as the driving force for changes in composition. A component will move from a region of high chemical potential to a region of low chemical potential until equilibrium is reached.

3. THE GIBBS-DUHEM EQUATION

The Gibbs-Duhem equation relates the changes in the chemical potentials of the components in a mixture. It can be derived from the definition of total differential for Gibbs free energy ($G = \sum_i n_i \mu_i$) and the expression for dG from thermodynamics ($dG = -SdT + VdP + \sum_i \mu_i dn_i$).

The Gibbs-Duhem equation is:

$SdT - VdP + \sum_{i=1}^{k} n_i d\mu_i = 0$

For processes carried out at constant temperature and pressure ($dT = 0, dP = 0$), the equation simplifies to:

$\sum_{i=1}^{k} n_i d\mu_i = 0$

Or, in terms of mole fractions ($x_i = n_i / n_{total}$):

$\sum_{i=1}^{k} x_i d\mu_i = 0$

This equation signifies that the chemical potentials of the components in a mixture are not independent. If the chemical potential of one component changes, the chemical potentials of the other components must adjust accordingly to satisfy this relationship.

4. MIXING OF IDEAL GASES

When ideal gases mix at constant T and P, the process is spontaneous and leads to an increase in entropy. For the mixing of n_1 moles of gas 1 and n_2 moles of gas 2 to form an ideal mixture:

4.1 ENTROPY OF MIXING

The entropy change upon mixing is:

$\Delta S_{mix} = S_{mixture} - (S_{gas1} + S_{gas2})$

For ideal gases, $\Delta S_{mix} = -R \sum_{i} n_i \ln x_i$, where x_i is the mole fraction of component i in the mixture.

4.2 GIBBS FUNCTION OF MIXING

Using the relationship $\Delta G = \Delta H - T\Delta S$, and knowing that for ideal gases, $\Delta H_{mix} = 0$ (as interactions between different molecules are zero, and interactions between same molecules are not affected by mixing):

$\Delta G_{mix} = -T\Delta S_{mix} = RT \sum_{i} n_i \ln x_i$

Since $x_i < 1$, $\ln x_i < 0$, so ΔG_{mix} is always negative, confirming that mixing of ideal gases is spontaneous.

4.3 CHEMICAL POTENTIAL OF IDEAL MIXTURES

The chemical potential of component i in an ideal gas mixture is given by:

$\mu_i(ideal, mixture) = \mu_i^0(T, P) + RT \ln x_i$

Where:

- $\mu_i^0(T, P)$ is the chemical potential of pure gaseous component i at the same temperature T and pressure P as the mixture. This is often taken as the standard state chemical potential.
- x_i is the mole fraction of component i.

This equation shows that the chemical potential of a component in an ideal mixture is lower than that of the pure component, due to the presence of other gases and the entropy of mixing.

5. REAL GASES: FUGACITY

5.1 THE FUGACITY FUNCTION

Real gases do not behave ideally, especially at high pressures and low temperatures. The simple ideal gas law for chemical potential ($\mu_i = \mu_i^0 + RT \ln P$) is no longer accurate. To retain the convenient form of the ideal gas equation for chemical potentials, the concept of **fugacity (f_i)** is introduced. Fugacity is the 'effective pressure' of a real gas.

The chemical potential of a real gas component i is defined as:

$\mu_i(T, P, x_i) = \mu_i^0(T, P) + RT \ln \frac{f_i}{f^0}$

Where:

- $\mu_i^0(T, P)$ is the standard state chemical potential of pure component i.
- f^0 is the standard state fugacity (often taken as 1 bar or 1 atm).
- f_i is the fugacity of component i.

5.2 FUGACITY OF A PURE REAL GAS

For a pure real gas, its fugacity f is related to its pressure P by:

$RT \ln f = \int_{0}^{P} V_{m} dP'$

Where V_m is the molar volume of the real gas.

5.3 CALCULATION OF FUGACITY FOR A VAN DER WAALS GAS

The van der Waals equation of state for n moles is: $(P + \frac{n^2 a}{V^2})(V - nb) = nRT$. For one mole (molar volume $V_m = V/n$): $(P + \frac{a}{V_m^2})(V_m - b) = RT$. Solving for P: $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$.

The relationship between fugacity (f) and pressure (P) can be expressed using the compressibility factor $Z = PV_m / RT$, so $V_m = ZRT/P$.

The general expression for fugacity is often given by:

$\ln \frac{f}{P} = \int_{0}^{P} \left(\frac{Z-1}{P'} ight) dP'$

For a van der Waals gas, $Z = \frac{RT}{V_m - b} \frac{V_m}{RT} - \frac{a}{V_m^2} \frac{V_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m}$. Substituting $V_m = ZRT/P$, and simplifying, we get:

$\ln \frac{f}{P} = \frac{b P}{RT} - \frac{a}{RT V_m} + \dots$ (More complex derivation leads to)

A common result for the fugacity coefficient $(\phi = f/P)$ of a van der Waals gas is:

$\ln \phi = \ln \frac{f}{P} = \frac{bP}{RT} - \frac{a}{RT V_m} + \frac{a}{RT} \frac{1}{V_m} - \frac{a b}{RT V_m} \dots$ (Simplified form by integrating $Z-1$ over P')

The integrated form for van der Waals gas yields:

$\ln \frac{f}{P} = \frac{b}{V_m - b} - \frac{a}{RT V_m} - \ln\left(\frac{V_m-b}{V_m} ight)$

And it can also be expressed in terms of P if V_m is solved for P in the van der Waals equation, which is algebraically intensive. A commonly used result is:

$\ln \phi = \frac{b P}{RT} - \frac{a}{RT V_m}$ (Approximation valid at moderate pressures)

Or more accurately, after integration and substitution:

$\ln \phi = \frac{bP}{RT} + \left(\frac{a}{RT V_m} ight) - \ln\left(1 - \frac{b}{V_m} ight) - \frac{a}{RT V_m}$

A more practical formula obtained by integrating $(Z-1)/P'$ over P' leads to:

$\ln \phi = \frac{bP}{RT} - \frac{a}{RT V_m} - \ln(1 - \frac{b}{V_m})$ (This is a correct form).

To calculate f, one typically needs V_m at the given T and P, which might require solving the cubic van der Waals equation for V_m first.

6. ACTIVITIES AND ACTIVITY COEFFICIENTS

For real solutions (mixtures of liquids or solids), the deviation from ideal behavior is accounted for by introducing **activity (a_i)** and **activity coefficient ($ \gamma_i$)**.

The chemical potential of component i in a real solution is defined as:

$\mu_i = \mu_i^{std} + RT \ln a_i$

Where μ_i^{std} is the standard state chemical potential of component i.

The activity is related to the mole fraction (x_i) by the activity coefficient ($ \gamma_i$):

$a_i = \gamma_i x_i$

Thus, the chemical potential becomes:

$\mu_i = \mu_i^{std} + RT \ln (\gamma_i x_i)$

- **Ideal Solution:** If $\gamma_i = 1$ for all components, the solution is ideal, and $a_i = x_i$, leading to $\mu_i = \mu_i^{std} + RT \ln x_i$.
- **Non-ideal Solution:** If $\gamma_i eq 1$, the solution is non-ideal. $\gamma_i > 1$ indicates repulsive interactions and $a_i > x_i$. $\gamma_i < 1$ indicates attractive interactions and $a_i < x_i$.

6.1 CHOICE OF STANDARD STATES

The standard state for a component i is a reference state used to define $ \mu_i^{std}$. Its choice is arbitrary but must be consistent. Common standard states include:

- **Pure substance (liquid or solid) at a specified temperature and pressure (e.g., 1 bar):** Commonly used for solvents and pure components.
- **Ideal gas at 1 bar:** For gaseous components.
- **Gas at 1 bar:** For real gas components.
- **Solution at infinite dilution:** For solute components in dilute solutions. Here, the activity coefficient γ_i is defined such that $\gamma_i o 1$ as $x_i o 0$. The standard state chemical potential is then $\mu_i^{std} = \lim_{x_i o 0} (\mu_i - RT \ln x_i)$.

6.2 DEPENDENCE OF ACTIVITY ON PRESSURE AND TEMPERATURE

The standard state chemical potential μ_i^{std} depends on temperature and pressure. The relationship is derived from $dG = -SdT + VdP$. For a standard state at T and P:

$\left(\frac{\partial \mu_i^{std}}{\partial P} ight)_{T} = ar{V}_i^{std}$

Where $ ar{V}_i^{std}$ is the partial molar volume of component i in its standard state. For example, if the standard state is the pure liquid at 1 bar, $ ar{V}_i^{std}$ is the molar volume of the pure liquid.

$\left(\frac{\partial \mu_i^{std}}{\partial T} ight)_{P} = - ar{S}_i^{std}$

The standard state chemical potential can be related to the standard state enthalpy and entropy:

$\mu_i^{std}(T) = H_i^{std} - T S_i^{std}$

The activity a_i itself does not directly depend on P or T in its definition ($a_i = \gamma_i x_i$), but its value is implicitly determined by the choice of standard state and the composition (x_i), and the activity coefficient (γ_i) which itself is dependent on $T, P,$ and composition.

NUMERICAL PROBLEMS

PROBLEM 1: PARTIAL MOLAR VOLUME

The molar volume (V_m) of a binary mixture of components A and B at 25°C and 1 atm is given by $V_m = 100x_A + 80x_B + 20x_A x_B ext{ cm}^3/ ext{mol}$, where x_A and x_B are mole fractions. Calculate the partial molar volumes of A and B when the mixture is equimolar ($x_A = x_B = 0.5$).

Solution:

Total volume of the mixture $V = n V_m = (n_A + n_B) V_m$. Let $n = n_A + n_B$. $V = n (100 \frac{n_A}{n} + 80 \frac{n_B}{n} + 20 \frac{n_A}{n} \frac{n_B}{n})$.

$V = 100 n_A + 80 n_B + \frac{20}{n} n_A n_B$.

Partial molar volume $ ar{V}_A = (\frac{\partial V}{\partial n_A})_{n_B}$.

$ ar{V}_A = 100 + \frac{20}{n} n_B - \frac{20 n_A n_B}{n^2} = 100 + 20 \frac{n_B}{n} (1 - \frac{n_A}{n}) = 100 + 20 x_B (x_B)$.

$ ar{V}_A = 100 + 20 x_B^2$.

Similarly, $ ar{V}_B = (\frac{\partial V}{\partial n_B})_{n_A} = 80 + \frac{20}{n} n_A - \frac{20 n_A n_B}{n^2} = 80 + 20 x_A (x_A)$.

$ ar{V}_B = 80 + 20 x_A^2$.

For an equimolar mixture, $x_A = 0.5, x_B = 0.5$:

$ ar{V}_A = 100 + 20 (0.5)^2 = 100 + 20(0.25) = 100 + 5 = 105 ext{ cm}^3/ ext{mol}$.

$ ar{V}_B = 80 + 20 (0.5)^2 = 80 + 20(0.25) = 80 + 5 = 85 ext{ cm}^3/ ext{mol}$.

PROBLEM 2: MIXING OF IDEAL GASES

Consider mixing 2 moles of N$_2$ gas with 3 moles of O$_2$ gas at 298 K and 1 atm. Assume ideal gas behavior. Calculate the entropy change and Gibbs free energy change for mixing.

Solution:

Total moles $n = n_{N_2} + n_{O_2} = 2 + 3 = 5$ moles.

Mole fraction of N$_2$: $x_{N_2} = n_{N_2}/n = 2/5 = 0.4$.

Mole fraction of O$_2$: $x_{O_2} = n_{O_2}/n = 3/5 = 0.6$.

Entropy change of mixing:

$\Delta S_{mix} = -R (n_{N_2} \ln x_{N_2} + n_{O_2} \ln x_{O_2})$

$\Delta S_{mix} = -8.314 ext{ J/mol·K} imes (2 ext{ mol} imes \ln(0.4) + 3 ext{ mol} imes \ln(0.6))$

$\Delta S_{mix} = -8.314 imes (2 imes (-0.9163) + 3 imes (-0.5108))$

$\Delta S_{mix} = -8.314 imes (-1.8326 - 1.5324) = -8.314 imes (-3.365) \approx 27.98 ext{ J/K}$.

Gibbs free energy change of mixing:

$\Delta G_{mix} = RT (n_{N_2} \ln x_{N_2} + n_{O_2} \ln x_{O_2})$

$\Delta G_{mix} = 8.314 ext{ J/mol·K} imes 298 ext{ K} imes (0.4 \ln(0.4) + 0.6 \ln(0.6))$

$\Delta G_{mix} = 2477.57 imes (0.4 imes (-0.9163) + 0.6 imes (-0.5108))$

$\Delta G_{mix} = 2477.57 imes (-0.3665 - 0.3065) = 2477.57 imes (-0.673) \approx -1667.6 ext{ J} \approx -1.67 ext{ kJ}$.

PROBLEM 3: FUGACITY OF A REAL GAS (CONCEPTUAL)

A gas deviates significantly from ideal behavior at high pressure. Would you expect the fugacity (f) of the gas to be greater than, less than, or equal to its pressure (P) under these conditions? Explain briefly.

Solution:

Under high pressure, real gases typically have a larger molar volume than predicted by the ideal gas law because repulsive forces (due to finite molecular size) become more dominant than attractive forces. Alternatively, at very high pressures, attractive forces might be overcome by the proximity of molecules, leading to higher effective pressure than ideal. For most gases at high pressures, intermolecular repulsive forces dominate, causing the molar volume V_m to be greater than RT/P.

Since $f/P = \phi$ and $\ln \phi = \int_{0}^{P} \frac{Z-1}{P'} dP'$, if $Z > 1$ (which happens when $V_m > RT/P$ due to repulsive forces dominating), then $\frac{Z-1}

{P'} > 0$. The integral will be positive, meaning $\ln \phi > 0$, and thus $\phi > 1$. Therefore, the fugacity $f = \phi P$ would be **greater than** the pressure P.

Would you like to explore more numerical problems or delve deeper into any of these topics?