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ONLINE COURSE WARE

SUBJECT NAME: Thermodynamics and Kinetics

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Module 1

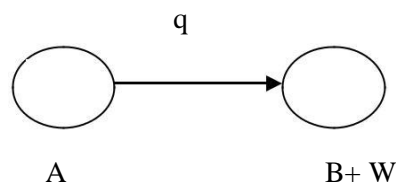
Lecture 1

Topics Covered: Review of 1st, 2nd and 3rd law of thermodynamics

The First Law of Thermodynamics states that energy can be converted from one form to another with the interaction of heat, work and internal energy, but it **cannot** be created nor destroyed, under any circumstances.

Helmholtz: Different forms of energy are interchangeable but when a quantity of one form of energy disappears an equivalent amount of other forms of energy appears.

Clausius: There might occur various changes and transformations of energy but the total energy of the universe must remain constant which is thus the Law of Conservation of Energy.



Consider a closed system in a state A having an internal energy U_A undergoing a change to state B. Let during the transformation q calories of heat are absorbed from the surroundings. Let also the system has done work w during the change. If U_B be the internal energy of the system at state B then

The net energy before transformation = $U_A + q$

And net energy after transformation = $U_B + W$

By the 1st law of Thermodynamics $U_A + q = U_B + W$

Or $q = U_B - U_A + W$

$q = \Delta U + W$

$q = \Delta U + PdV$ (for mechanical work)

For adiabatic process $U = -PdV$

For isothermal process $q = PdV$

All these observations concludes that 1st law is not enough in explaining all the natural phenomenon and reactions and there is need for 2nd Law of Thermodynamics

Second Law:

1. All spontaneous processes are thermodynamically irreversible.
2. The complete conversion of heat into work is impossible without leaving a permanent change elsewhere.
3. **Clausius Statement:** It is impossible for a self acting machine, unaided by an external agency, to transfer heat from a body to another at higher temperature.

Third Law:

A classical formulation by Nernst (actually a consequence of the Third Law) is:

It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

Lecture 2

Topics Covered: PVT behaviour of pure substances: graphical representation; triple point critical temperature and pressure; sub-critical and super-critical region, PV-diagram : graphical representation.

Pure Substance

A pure substance has a homogeneous and invariable chemical composition and may exist in more than one phase. Examples:

1. Water (solid, liquid, and vapor phases)
2. Mixture of liquid water and water vapor
3. Carbon dioxide, CO_2
4. Nitrogen, N_2
5. Mixtures of gases, such as air, as long as there is no change of phase

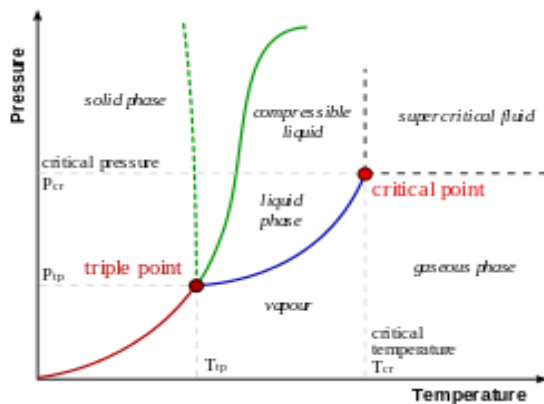
State Postulate

Again, the state postulate for a simple, pure substance states that the equilibrium state can be determined by specifying any two independent intensive properties.

P-V-T Behaviour of Pure Substances:

A typical P-T diagram showing the relationship between pressure and temperature of a pure substance is shown below:

The simplest phase diagrams are pressure–temperature diagrams of a single simple substance, such as water. The axes correspond to the pressure and temperature. The phase diagram shows, in pressure–temperature space, the lines of equilibrium or phase boundaries between the three phases of solid, liquid, and gas.

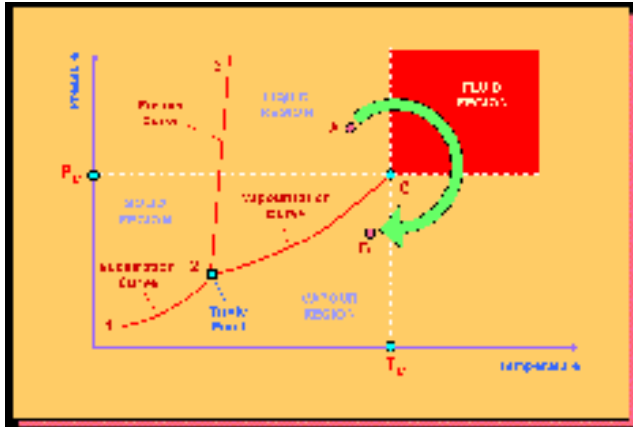


A typical phase diagram. The solid green line applies to most substances; the dotted green line gives the anomalous behavior of water. The green lines mark the freezing point and the blue line the boiling point, showing how they vary with pressure.

The curves on the phase diagram show the points where the free energy (and other derived properties) becomes non-analytic: their derivatives with respect to the coordinates (temperature and pressure in this example) change discontinuously (abruptly). For example, the heat capacity of a container filled with ice will change abruptly as the container is heated past the melting point. The open spaces, where the free energy is analytic, correspond to single phase regions. Single phase regions are separated by lines of non-analytical behavior, where phase transitions occur, which are called **phase boundaries**.

In the diagram on the left, the phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the critical point. This reflects the fact that, at extremely high temperatures and pressures, the liquid and gaseous phases become

indistinguishable, in what is known as a supercritical fluid. In water, the critical point occurs at around $T_c = 647.096 \text{ K}$ ($373.946 \text{ }^\circ\text{C}$), $p_c = 22.064 \text{ MPa}$ (217.75 atm) and $\rho_c = 356 \text{ kg/m}^3$.



The three lines 1-2, 2-3 and 2-C display conditions of P and T at which two phases may co-exist in equilibrium, and are boundaries for the single-phase regions of solid, liquid and vapour (gas).

Line 1-2 is known as the sublimation curve, and it separates the solid from the gas regions. Line 2-3 is known as the fusion curve, and it separates the solid and liquid regions. Line 2-C is known as the vapourization curve, and it separates the liquid and the gas regions. All three lines meet at Point 2, known as the Triple Point. This is a point where all 3 phases can co-exist in equilibrium.

The vapourization curve 2-C terminates at point C, known as the Critical Point. The pressure and temperature corresponding to this point are known as the critical pressure P_C and critical temperature T_C respectively. These are the highest pressure and temperature at which a pure substance can exist in vapour-liquid equilibrium.

At the critical point, the liquid and gas phases become indistinguishable, because their properties are the same. This observation is different from ordinary condition whereby the boundary between liquid and gas is very clear. For example, consider a path such as the one from A to B that lead from the liquid region to the gas region without crossing the vapourization curve 2-C. The transition from liquid to gas is gradual. On the other hand, paths that cross the vapourization curve will involve a vapourization or condensation step, where an abrupt change from liquid to gas occurs.

The shaded area shows the area existing at pressure and temperature greater than P_C and T_C . This region is called the fluid region.

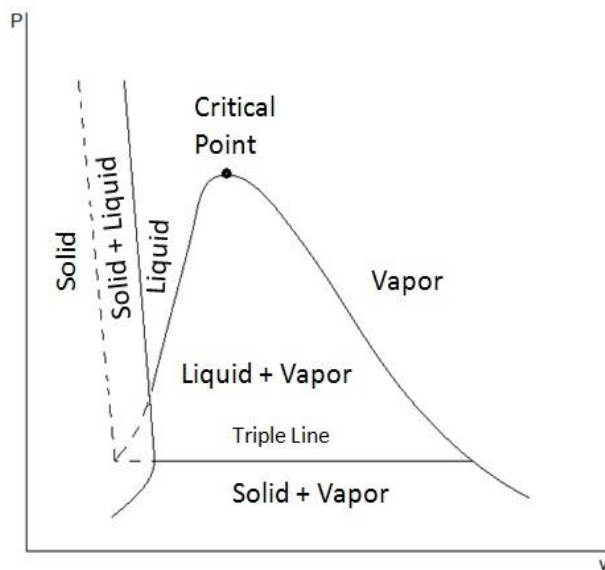
The gas region is sometimes divided into 2 parts, as indicated by the dotted vertical line through temperature T_C . A vapour region is the region to the left of this line and represent a gas that can be

condensed either by compression at constant temperature or by cooling at constant pressure. The region everywhere to the right of this line, including the fluid region, is termed supercritical.

P-V Diagram for Pure Substance

The P-T Diagram does not provide any information about volume. It merely displays the phase boundaries on as a function of pressure and temperature. The P-V Diagram - see Figure below - displays the regions (areas) where 2 phases of solid/liquid, solid/vapour, and liquid/vapour co-exist in equilibrium. For a given P and T, the relative amounts of the phases determine the molar (or specific) volume. On the P-V Diagram, the triple point appears as a horizontal line, where all 3 phases co-exist at a single temperature and pressure.

Isotherms are lines of constant temperature and these are superimposed on the P-V Diagram as shown in the Figure below:



Point C is the critical point. VC is the critical volume at this point. The isotherm labelled $T > T_C$ does not cross a phase boundary. The lines labelled T_1 and T_2 are isotherms for subcritical temperatures, and they consist of 3 segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapour in equilibrium, ranging from 100% liquid at the left end (curve B-C) to 100% vapour at the right end (curve D-C). Curve B-C represents saturated liquid at their boiling points, and curve D-C represent saturated vapours at their condensation points.

The 2-phase liquid-vapour region lies under the curve BCD, whereas subcooled liquid and superheated vapour regions lie to the left and right, respectively. Subcooled liquid exists at temperatures below the boiling point for the given pressure. Superheated vapour exists at temperatures above the boiling point for the given pressure.

Isotherms in the subcooled liquid region are very steep, because liquid volumes change little with large changes in pressure.

The horizontal segments of the isotherms in the 2-phase region become progressively shorter at higher temperatures, being ultimately reduced to a point at C, the critical point.

For instance, for a constant-composition fluid, the isobaric expansivity is defined by

$$\alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P, \text{ const } \{x_i\}, \quad (1.2)$$

the isothermal compressibility[†] is defined by

$$\beta_T \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T, \text{ const } \{x_i\}, \quad (1.3)$$

and the isentropic compressibility (often loosely called the adiabatic compressibility) is defined by

$$\beta_S \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_S, \text{ const } \{x_i\}, \quad (1.4)$$

where S denotes the molar entropy.

$$\kappa \equiv \frac{\beta_T}{\beta_S} = \frac{C_P}{C_V}, \text{ const } \{x_i\}. \quad (1.6)$$

Here, C_P denotes the molar heat capacity at constant pressure (molar isobaric heat capacity), and C_V is the molar heat capacity at constant volume (molar isochoric heat capacity).

Lecture 3

Topics Covered: Virial equation and state, Two forms of virial equation; Virial expansions and virial coefficient.

Equations of State

In the calculations of energy, enthalpy, and entropy of a substance we need an accurate representation of the relationship among pressure, volume, and temperature. Besides the tabular and graphical presentations of the $p-v-T$ relationship, analytical formulations, called *equation of state*, constitute another way of expressing the $p-v-T$ relationship. The equations of state are convenient for performing the mathematical operations required to calculate u , h , s , and other thermodynamic properties. We will discuss the virial, Van de Walls, and Soave-Redlick-Kwong (SRK) equation of states.

The Virial Expansion: The virial expansion, also called the virial equation of state, is the most interesting and versatile of the equations of state for gases. The virial expansion is a power series in powers of the variable, n/V , and has the form,

$$(1) \quad \frac{pV}{nRT} = Z = 1 + B(T) \frac{n}{V} + C(T) \frac{n^2}{V^2} + \dots \infty$$

The coefficient, $B(T)$, is a function of temperature and is called the "second virial coefficient. $C(T)$ is called the third virial coefficient, and so on. The expansion is, in principle, an infinite series, and as such should be valid for all isotropic substances. In practice, however, terms above the third virial coefficient are rarely used in chemical thermodynamics.

Notice that we have set the quantity pV/nRT equal to Z . This quantity (Z) is called the "compression factor." It is a useful measure of the deviation of a real gas from an ideal gas. For an ideal gas the compression factor is equal to 1.

The Boyle Temperature

The second virial coefficient, $B(T)$, is an increasing function of temperature throughout most of the useful temperature range. (It does decrease slightly at very high temperatures.) B is negative at low temperatures, passes through zero at the so-called "Boyle temperature," and then becomes positive. The temperature at which $B(T) = 0$ is called the Boyle temperature because the gas obeys Boyle's law to high accuracy at this temperature. We can see this by noting that at the Boyle temperature the virial expansion looks like,

$$(2) \quad \frac{pV}{nRT} = 1 + 0 + C \frac{n^2}{V^2} + \dots \infty$$

If the density is not too high the C term is very small so that the system obeys Boyle's law.

Alternate form of the virial expansion.

An equivalent form of the virial expansion is an infinite series in powers of the pressure.

$$(3) \quad \frac{pV}{nRT} = 1 + B'(T)p + C'(T)p^2 + \dots \infty$$

The new virial coefficients, B' , C' , \dots , can be calculated from the original virial coefficients, B , C , \dots . To do this we equate the two virial expansions,

$$(4) \quad \frac{pV}{nRT} = 1 + B(T) \frac{n}{V} + C(T) \frac{n^2}{V^2} + \dots \infty = 1 + B'(T)p + C'(T)p^2 + \dots \infty$$

Then we solve the original virial expansion for p ,

$$(5) \quad p = \frac{nRT}{V} \left(1 + B(T) \frac{n}{V} + C(T) \frac{n^2}{V^2} + \dots \infty \right)$$

and substitute this expression for p into the right-hand-side of equation (4),

(6a)

$$1 + B \frac{n}{V} + C \frac{n^2}{V^2} + \dots = 1 + B' \frac{nRT}{V} \left(1 + B \frac{n}{V} + C \frac{n^2}{V^2} + \dots \right) + C' \left(\frac{nRT}{V} \right)^2 \left(1 + B \frac{n}{V} + C \frac{n^2}{V^2} + \dots \right)^2 + \dots$$

(6b)

$$1 + B \frac{n}{V} + C \frac{n^2}{V^2} + \dots = 1 + B' RT \frac{n}{V} + B' RTB \frac{n^2}{V^2} + \dots + C' (RT)^2 \frac{n^2}{V^2} + \dots$$

Both sides of Equation (6b) are power series in n/V . (We have omitted third and higher powers of n/V because the second power is as high as we are going here.) Since the two power series must be equal, the coefficients of each power of n/V must be the same on both sides. The coefficient of $(n/V)^0$ on each side is 1, which gives the reassuring but not very interesting result, $1 = 1$. Equating the coefficient of $(n/V)^1$ on each side gives $B = B'RT$ and equating the coefficients of $(n/V)^2$ gives

$$(7) \quad C = B'RTB + C'(RT)^2$$

These equations are easily solved to give B' and C' in terms of B , C , and R .

$$(8) \quad B' = \frac{B}{RT}$$

$$C' = \frac{C - B^2}{(RT)^2}$$

Topics Covered: Discussion for Ideal gas : Internal energy, enthalpy, heat capacity at constant temperature and pressure. Isothermal, Isobaric & Isochoric process

Ideal Gases under Constant Volume, Constant Pressure, Constant Temperature, & Adiabatic Conditions

Note to the student: The following section is a reduction of college notes I made in introductory thermodynamics. It does not read as easily as the preceding sections. I include it here because, for me, it represented a significant unification of the ideas presented in the text and during lecture. The first year college student will certainly find it useful.

The equation of state for an ideal gas is

$$pV = nRT \quad 1.$$

where p is gas pressure, V is volume, n is the number of moles, R is the universal gas constant ($= 8.3144 \text{ J}/(^{\circ}\text{K mole})$), and T is the absolute temperature. The first law of thermodynamics, the conservation of energy, may be written in differential form as

$$dq = du + p dV \quad 2.$$

where dq is a thermal energy input to the gas, du is a change in the internal energy of the gas, and $p dV$ is the work done by the gas in expanding through the change in volume dV .

Constant Volume Process

If $V = \text{const.}$, then $dV = 0$, and, from 2, $dq = du$; i.e., all the thermal input to the gas goes into internal energy of the gas. We should expect a temperature rise. If the gas has a specific heat at constant volume of C_v ($\text{J}/(^{\circ}\text{K mole})$), then we may set $dq = C_v dT$. It follows, in this case, that

$$du = C_v dT \quad 3.$$

Since du was initially unspecified, we are free to choose its mathematical form. Equation 2 will be retained for du throughout the remainder of the cases.

Constant Pressure Process

If $p = \text{const.}$, then $dp = 0$, and, from 1, $p dV = R dT$; i.e., the work done by the gas in expanding through the differential volume dV is directly proportional to the temperature change dT . If the gas has a specific heat at constant pressure of C_p , then $dq = C_p dT$, and, from 2 (with 3),

$$C_p dT = C_v dT + R dT$$

Simplifying gives an important constitutive relationship between C_v , C_p , and R , namely:

$$C_p = C_v + R \quad 4.$$

Constant Temperature Process

If $T = \text{const.}$, then $dT = 0$, and, from 1, $d(pV) = 0$, i.e., pressure and volume are inversely proportional. Further, from 2, $dq = p dV$; i.e., there is no change in internal energy (from 3, $du = 0$), and all the thermal input to the gas goes into the work of expansion.

Adiabatic Process

If $q = \text{const.}$, then $dq = 0$, and, from 2 (with 3), $0 = C_v dT + p dV$; i.e., internal energy of the gas might be reduced in favor of expansion, or vice versa. This expression may be written in an equivalent form as

$$0 = (C_v/R)(dT/T) + dV/V \quad 5.$$

(division of the first term by RT , and the second term by pV). Further, from 1,

$$p dV + V dp = R dT$$

or, equivalently,
$$dp/p + dV/V = dT/T \quad 6.$$

(division of the Left Hand Side by pV , and the Right Hand Side by RT).

Equations 5 and 6 may be used to develop relationships between p and V , or p and T :

Case 1:

To eliminate T , use 6 in 5 for dT/T to obtain $0 = (C_v/R)(dp/p + dV/V) + dV/V$, or

$$-(C_v/R) dp/p = (1 + C_v/R) dV/V \quad 6a.$$

Using 4, we may write $C_v/R = C_v/(C_p - C_v) = 1/(\gamma - 1)$ where $\gamma = C_p/C_v$, the ratio of the specific heats (>1 ; in fact, approximately 1.4 for air at STP). Thus, equation 6a becomes (after simplification)

$$-dp/p = \gamma dV/V$$

which, upon integration, yields

$$p_0/p = (V/V_0)^\gamma \quad 7.$$

i.e., the pressure varies inversely as the volume raised to the power γ .

Case 2:

To eliminate V , use equation 6 to write $dV/V = dT/T - dp/p$, and substitute for dV/V in eq. 5

$$(C_v/R + 1) dT/T = dp/p$$

Proceeding as before produces the result that

$$p/p_0 = (T/T_0)^{\gamma/(\gamma - 1)} \quad 8.$$

Entropy changes may be calculated for each of the above thermodynamic processes. The definition of entropy is

$$dS = dq/T \quad 9.$$

where dS is the differential entropy change.

For constant volume processes, $dq = \mu C_v dT$, so that $dS = \mu C_v dT/T$, and

$$S = \mu C_v \ln(T/T_0) \quad 10.$$

For constant pressure processes, $dq = \mu C_p dT$, so that $dS = \mu C_p dT/T$, and

$$S = \mu C_p \ln(T/T_0) \quad 11.$$

For constant temperature processes, $dq = p dV$, so that $dS = p dV/T = R dV/V$, and

$$S = \mu R \ln(V/V_0)$$

12.

For adiabatic processes, $dq = 0$, so that $ds = 0$, and

$$S = \text{const.}$$

Fundamental Property Relations

The first law for a closed system undergoing reversible process with only PV work is given by

$$dU = \delta Q_{\text{rev}} + \delta W_{\text{rev}}$$

From the second law, $\delta Q_{\text{rev}} = TdS$, the first law can be written as

$$dU = TdS - pdV \quad (2.2-1)$$

We can write the change in internal energy in terms of two independent variables S and V , that is, $U = U(S, V)$

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad (2.2-2)$$

Comparing equations (2.2-1) and (2.2-2) we have

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad p = - \left(\frac{\partial U}{\partial V} \right)_S \quad (2.2-3)$$

The four functions U , H , A , and G are collectively called *thermodynamic potentials*. The expression represented by $U = U(S, V)$ results in the partial derivatives of the thermodynamic potentials

corresponding to thermodynamic properties T and p as defined in Eq. (2.2-3). While U can be a function of any two properties, no other grouping of independent properties x and y , $U = U(x, y)$, allows us to write partial derivatives in terms of thermodynamic properties as given by Eq. (2.2-3). The three properties $\{U, S, V\}$ form a **fundamental grouping**.

We have two more relations for the change in *Helmholtz free energy*, dA , and the change in

Gibbs free energy, dG ,

$$dA = -SdT - pdV$$

$$dG = -SdT + Vdp$$

The fundamental groupings $\{A, T, V\}$ and $\{G, T, p\}$ result in

$$S = - \frac{\partial A}{\partial T}_V \quad \text{and} \quad p = - \frac{\partial A}{\partial V}_T$$

$$S = - \frac{\partial G}{\partial T}_p \quad \text{and} \quad V = \frac{\partial G}{\partial p}_T$$

The grouping can be obtained from the following diagram where there properties at a corner form a fundamental grouping, for example $\{A, T, V\}$ and $\{G, T, p\}$.

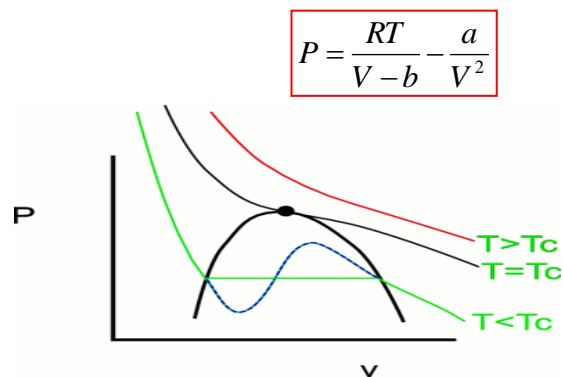
$$T = \frac{\partial H}{\partial S} \quad \text{and} \quad V = \frac{\partial H}{\partial p}$$

Lecture 5

Topics Covered: Cubic equation of state, Van der Waals equations of state, A generic cubic equations of state

Cubic Equations of State

- Simple equation capable of representing both liquid and vapor behavior.
- The van der Waals equation of state:
 - a and b are positive constants
 - unrealistic behavior in the two-phase region. In reality, two, within the two-phase region, saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor pressure.
 - Three volume roots, of which two may be complex.
 - Physically meaningful values of V are always real, positive, and greater than constant b .



In order to use the **van der Waals equation of state**, we need to determine the material- dependent constants, a and b .

a

Using the principle of corresponding states, we can argue that the constants for all materials may be obtained by recognizing that, at the critical point:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$$

We can then use three equations at the critical point to write a and b in terms of P_c and T_c :

$$P_c = \frac{RT_c}{v_c b} - \frac{a}{v_c^2}$$

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 = -\frac{RT_c}{(v_c b)^2} + \frac{2a}{v_c^3}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 = \frac{2RT_c}{(v_c b)^3} - \frac{6a}{v_c^4}$$

this approach leads to (i.e., solving the two equations -- above -- for the two unknowns

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}$$

-- a and b):

$$b = \frac{RT_c}{8P_c}$$

z_c

$$z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$$

doing a bit more algebra, we can write an expression for

which is higher than is typically observed experimentally.

A generic cubic equations of state: Soave-Redlick-Kwong (SRK) Equation

- General form:

- where b , θ , κ , λ and η are parameters depend on temperature and (mixture) composition.

- Reduce to the van der Waals equation when $\eta = b$, $\theta = a$, and $\kappa = \lambda = 0$.

- Set $\eta = b$, $\theta = a(T)$, $\kappa = (\epsilon + \sigma) b$, $\lambda = \epsilon \sigma b^2$, we have:

- where ϵ and σ are pure numbers, the same for all substances, whereas $a(T)$ and b are substance dependent.

$$P = \frac{RT}{V-b} - \frac{\theta(V-\eta)}{(V-b)(V^2 + \kappa V + \lambda)}$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V + \epsilon b)(V + \sigma b)}$$

Lecture 6

Topics Covered: Generalized correlations for gases : Pitzer correlations for the compressibility factor, concept of reduced temperature and pressure, Correlation for 2nd virial coefficient

Generalized correlations for gases:

- Pitzer correlations for the compressibility factor:

$$Z = Z^0 + \omega Z^1$$

- $Z^0 = F^0(T_r, P_r)$
- Simple linear relation between Z and ω for given values of T_r and P_r .
- Of the Pitzer-type correlations available, the Lee/Kesler correlation provides reliable results for gases which are nonpolar or only slightly polar (App. E).
- Only tabular nature (disadvantage)

Pitzer correlations for the 2nd virial coefficient:

- Correlation:
 - Validity at low to moderate pressures
 - For reduced temperatures greater than $T_r \sim 3$, there appears to be no limitation on the pressure.
 - Simple and recommended.

Most accurate for nonpolar species

$$Z = 1 + \frac{BP}{RT} = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r} \rightarrow Z = Z^0 + \omega Z^1$$

↑

$$Z^0 = 1 + B^0 \frac{P_r}{T_r}$$

$$Z^1 = B^1 \frac{P_r}{T_r}$$

↑

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Lecture 7

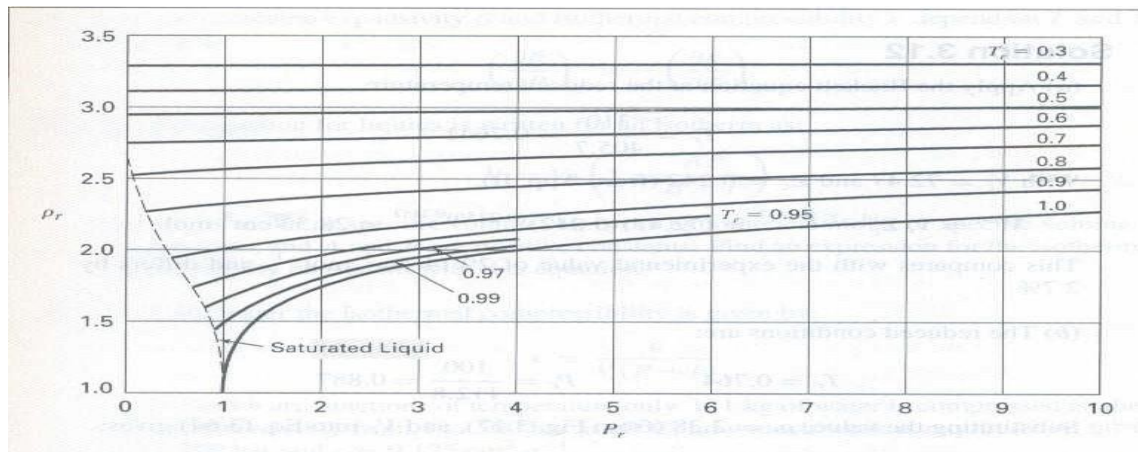
Topics Covered: Generalized correlations for liquids, Problem solving

Generalized correlations for liquids:

- The generalized cubic equation of state (low accuracy)
- The Lee/Kesler correlation includes data for subcooled liquids
 - Suitable for nonpolar and slightly polar fluids
- Estimation of molar volumes of saturated liquids
 - Rackett, 1970:
 - Generalized density correlation for liquid (Lydersen, Greenkorn, and Hougen, 1955):

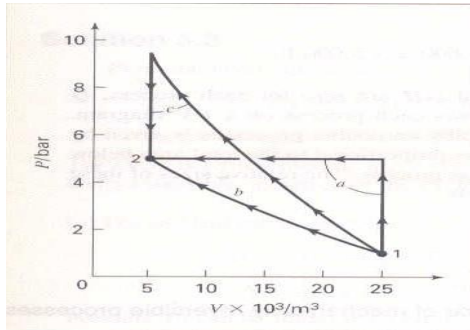
$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$



$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}}$$

Prob 1: Air is compressed from an initial condition of 1 bar and 25°C to a final state of 5 bar and 25°C by three different mechanically reversible processes in a closed system. (1) heating at constant volume followed by cooling at constant pressure; (2) isothermal compression; (3) adiabatic compression followed by cooling at constant volume. Assume air to be an ideal gas with the constant heat capacities, $C_V = (5/2)R$ and $C_P = (7/2)R$. Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air in each process.



Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement.

For $R = 8.314 \text{ J/mol.K}$, $C_V = 20.785$, $C_P = 29.099 \text{ J/mol.K}$

The initial and final molar volumes are: $V_1 = 0.02479 \text{ m}^3$ and $V_2 = 0.004958 \text{ m}^3$

The initial and final temperatures are identical: $\Delta U = \Delta H = 0$

(1) $Q = C_V\Delta T + C_P\Delta T = -9915 \text{ J}$; $W = \Delta U - Q = 9915 \text{ J}$

$$Q = -W = RT \ln\left(\frac{P_1}{P_2}\right) = -3990$$

adiabatic compression:

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 567.57 \text{ K}$$

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^{\gamma} = 9.52 \text{ bar}$$

$$W = C_v \Delta T = 5600 \text{ J}$$

cooling at constant V, $W = 0$.

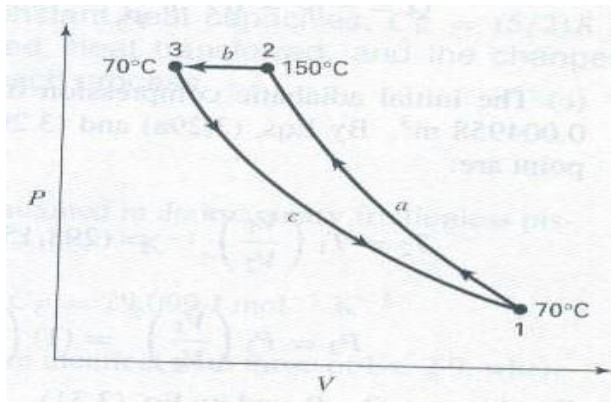
overall, $W = 5600 \text{ J}$, $Q = \Delta U - W = -5600 \text{ J}$.

Prob 2: An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system:

(1) From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150°C . (2) It is then cooled from 150 to 70°C at constant pressure.

(3) Finally, it is expanded isothermally to its original state.

Calculate W , Q , ΔU , and ΔH for each of the three processes and for the entire cycle. Take $C_v = (3/2)R$ and $C_p = (5/2)R$. If these processes are carried out irreversibly but so as to accomplish exactly the same changes of state (i.e. the same changes in P , T , U , and H), then different values of Q and W result. Calculate Q and W if each step is carried out with an efficiency of 80%.



Choose the system as 1 mol of air, contained in an imaginary frictionless piston /cylinder arrangement. For $R = 8.314 \text{ J/mol.K}$, $C_v = 12.471$, $C_p = 20.785 \text{ J/mol.K}$

For an ideal gas undergoing adiabatic compression, $Q = 0$

$$\Delta U = W = C_v \Delta T = 12.471(150 - 70) = 998 \text{ J}$$

$$\Delta H = C_p \Delta T = 20.785(150 - 70) = 1663 \text{ J}$$

$$P_2 = P_1 \left(\frac{T_2}{T_1} \right)^{\frac{\gamma}{\gamma-1}} = 1.689 \text{ bar}$$

For the constant-pressure process:

$$Q = \Delta H = C_p \Delta T = 20.785(70 - 150) = -1663 \text{ J}$$

$$\Delta U = C_v \Delta T = 12.471(70 - 150) = -998 \text{ J}$$

$$W = \Delta U - Q = 665 \text{ J}$$

Isotherm process, ΔU and ΔH are zero:

$$Q = -W = RT \ln \left(\frac{P_3}{P_1} \right) = 1495 \text{ J}$$

Overall:

$$Q = 0 - 1663 + 1495 = -168 \text{ J}$$

$$W = 998 + 665 - 1495 = 168 \text{ J}$$

$$\Delta U = 0$$

$$\Delta H = 0$$

Irreversible processes:

For 80% efficiency:

$$W(\text{irreversible}) = W(\text{reversible}) / 0.8 = 1248 \text{ J}$$

$$\Delta U(\text{irreversible}) = \Delta U(\text{reversible}) = 998 \text{ J}$$

$$Q(\text{irreversible}) = \Delta U - W = -250 \text{ J}$$

For 80% efficiency:

$$W(\text{irreversible}) = W(\text{reversible}) / 0.8 = 831 \text{ J}$$

$$\Delta U = C_v \Delta T = 12.471(70 - 150) = -998 \text{ J}$$

$$Q = \Delta U - W = -998 - 831 = -1829 \text{ J}$$

Isotherm process, ΔU and ΔH are zero:

$$W(\text{irreversible}) = W(\text{reversible}) \times 0.8 = -1196 \text{ J}$$

$$Q = \Delta U - W = 1196 \text{ J}$$

$$\text{Overall: } Q = -250 - 1829 + 1196 = -883 \text{ J}$$

$$W = 1248 + 831 - 1196 = 883 \text{ J}$$

$$\Delta U = 0$$

$$\Delta H = 0$$

Module 2

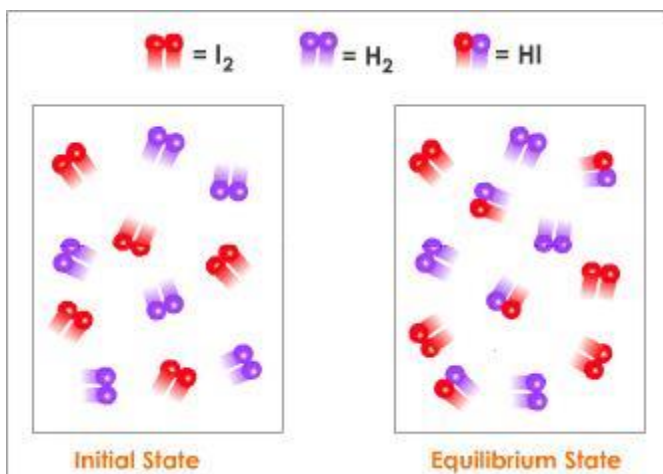
Lecture 8

Topics Covered: Explanation for nature of equilibrium, Measures of composition : molar concentration, mass or mole fraction

Dynamic nature of chemical equilibrium and its characteristics

The state of equilibrium is a state in which the measurable properties of the system do not undergo any noticeable change under a particular set of conditions.

We have seen that all observable properties of a system become constant at equilibrium. It may lead us to think that the reaction stops altogether at equilibrium. But this is not true. Actually at equilibrium the rate of forward reaction becomes equal to the rate of backward reaction so that there is no net change in the concentration of various species. In other words we can say that equilibrium state is a dynamic balance between the forward and backward reaction. This can be illustrated by considering the reaction between hydrogen and iodine to form hydrogen iodide.



Molar concentration, mass or mole fraction:

Concentration of Solutions

Objectives:

- 1. Measure the concentrations in terms of molarity, molality, and mole fraction.
- 2. Differentiate between saturated, unsaturated, and supersaturated solutions.

Key Terms:

- Concentration, molarity, molality, mole fraction, saturated, unsaturated, supersaturated

Concentration

- A measure of how much solute is dispersed throughout the solvent
- Molarity (M), molality (m), and mole fraction (χ), mass percent

$$\text{Molarity} = \frac{\text{moles solute}}{\text{liters solution}}$$

$$\text{Molality} = \frac{\text{moles solute}}{\text{kg solvent}}$$

$$\chi = \frac{\text{moles of component}}{\text{total moles of all components}}$$

$$\text{mass}\% = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \cdot 100$$

Lecture 9

Topics Covered: Introduction of Gibb's phase rule and explanation, Discussion of Duhem's theorem

Gibbs' Phase Rule provides the theoretical foundation, based in thermodynamics, for characterizing the chemical state of a (geologic) system, and predicting the equilibrium relations of the phases (minerals, melts, liquids, vapors) present as a function of physical conditions such as pressure and temperature. Gibbs' Phase Rule also allows us to construct phase diagrams to represent and interpret phase equilibria in heterogeneous geologic systems. In the simplest understanding of phase diagrams, stable phase (mineral) assemblages are represented as "fields" (see colored areas on the figure to the right) in "P-T space", and the boundaries between stable phase assemblages are defined by lines (or curves) that represent reactions between the phase assemblages. The reaction curves actually represent the condition (or the locus of points in P-T space) where $\Delta G_{\text{rxn}} = 0$; for more information on this point see Gibbs Free Energy. A solid understanding of Gibbs' Phase Rule is required to successfully master the applications of heterogeneous phase equilibria presented in this module.

Gibbs Phase Rule is expressed by the simple formulation:

$$F = 2 - \pi + N$$

π is the number of phases in the system

A phase is any physically separable material in the system. Every unique mineral is a phase (including polymorphs); igneous melts, liquids (aqueous solutions), and vapor are also considered unique phases. It is possible to have two or more phases in the same state of matter (e.g. solid mineral assemblages, immiscible silicate and sulfide melts, immiscible liquids such as water and hydrocarbons, etc.) Phases may either be pure compounds or mixtures such as solid or aqueous solutions—but they must "behave" as a coherent substance with fixed chemical and physical properties.

N is the *minimum* number of chemical components required to constitute all the phases in the system.

F is the number of degrees of freedom in the system

Duhem Theorem:

It is similar to the phase rule. It is applied to closed systems in equilibrium, in which intensive and extensive states are kept as constant. The system state is completely determined and characterized not only by the $2 + (N - 1) \pi$ intensive variables, obtained in the phase rule, if not also by the π extensive variables represented by the masses (or number of moles) of the phases. The total number of variables is.

$$2 + N \pi - \pi N = 2$$

For any closed system formed by the known masses of the chemical species prescribed, the equilibrium state is determined fully when two independent variables are set.

These two independent variables are intensive or extensive. However, the number of independent intensive variables are known by the phase rule. So, when $F=1$, one of the variables must be extensive, and when $F=0$, both must be it.

Lecture 10

Topics Covered: Multiple-Component Phase Equilibrium: Phase Diagrams, VLE curves

Phase Equilibrium

Many processes in chemical engineering do not only involve a single phase but a combination of two immiscible liquids, or a stream containing both gas and liquid. It is very important to recognize and

be able to calculate when these phases are in **equilibrium** with each other, and how much is in each phase. This knowledge will be especially useful when you study separation processes, for many of these processes work by somehow distorting the equilibrium so that one phase is especially rich in one component, and the other is rich in the other component.

More specifically, there are three important criteria for different phases to be in equilibrium with each other:

1. The **temperature** of the two phases is the same at equilibrium.
2. The **partial pressure** of every component in the two phases is the same at equilibrium.
3. The **Gibbs free energy** of every component in the two phases is the same at equilibrium.

The third criteria will be explored in more depth in another course; it is a consequence of the first two criteria and the second law of thermodynamics.

Single-Component Phase Equilibrium

If there is only a single component in a mixture, there is only a single possible temperature (at a given pressure) for which phase equilibrium is possible. For example, water at standard pressure (1 atm) can *only* remain in equilibrium at 100°C. Below this temperature, all of the water condenses, and above it, all of the water vaporizes into steam.

At a given temperature, the unique *atmospheric* pressure at which a pure liquid boils is called its **vapor pressure**. Students may benefit from conceptualizing vapor pressure as the minimum pressure required to keep the fluid in the liquid phase. If the atmospheric pressure is higher than the vapor pressure, the liquid will not boil. Vapor pressure is strongly temperature-dependent. Water at 100°C has a vapor pressure of 1 atmosphere, which explains why water on Earth (which has an atmosphere of about 1 atm) boils at 100°C. Water at a temperature of 20°C (a typical room temperature) will only boil at pressures under 0.023 atm, which is its vapor pressure at that temperature.

Multiple-Component Phase Equilibrium: Phase Diagrams

In general, chemical engineers are not dealing with single components; instead they deal with equilibrium of **mixtures**. When a mixture begins to boil, the vapor does **not**, in general, have the same composition as the liquid. Instead, the substance with the lower boiling temperature (or higher vapor pressure) will have a vapor concentration higher than that with the higher boiling temperature, though **both will be present in the vapor**. A similar argument applies when a vapor mixture condenses.

The concentrations of the vapor and liquid when the *overall* concentration and one of the temperature or pressure are fixed can easily be read off of a **phase diagram**. In order to read and understand a phase diagram, it is necessary to understand the concepts of *bubble point* and *dew point* for a mixture.

Bubble Point and Dew Point

In order to be able to predict the phase behavior of a mixture, scientists and engineers examine the *limits* of phase changes, and then utilize the laws of thermodynamics to determine what happens in between those limits. The limits in the case of gas-liquid phase changes are called the **bubble point** and the **dew point**.

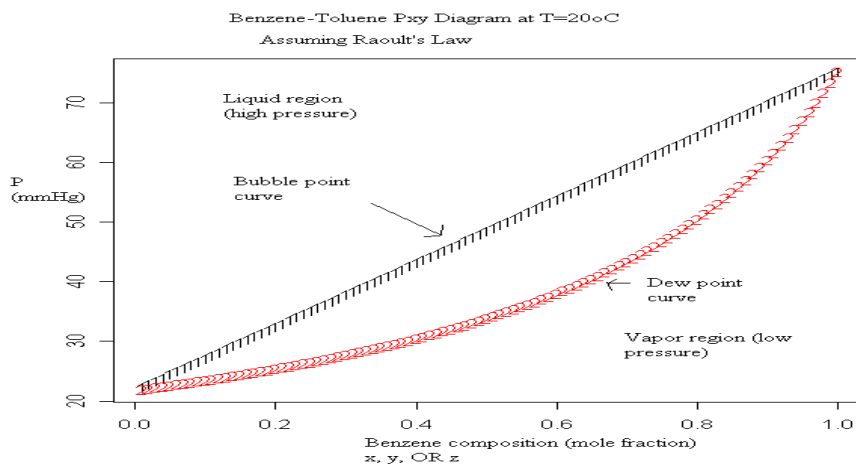
The names imply which one is which:

1. The bubble point is the point at which the first drop of a liquid mixture begins to vaporize.
2. The dew point is the point at which the first drop of a gaseous mixture begins to condense.

If you are able to plot both the bubble and the dew points on the same graph, you come up with what is called a **Pxy** or a **Txy** diagram, depending on whether it is graphed at constant temperature or constant pressure. The "xy" implies that the curve is able to provide information on both liquid *and* vapor compositions, as we will see when we examine the thermodynamics in more detail.

Txy and Pxy diagrams

The easier of the two diagrams to calculate (but sometimes harder to grasp intuitively) is the Pxy diagram, which is shown below for an idealized Benzene-Toluene system:



In order to avoid getting confused about what you're looking at, think: what causes a liquid to vaporize? Two things should come to mind:

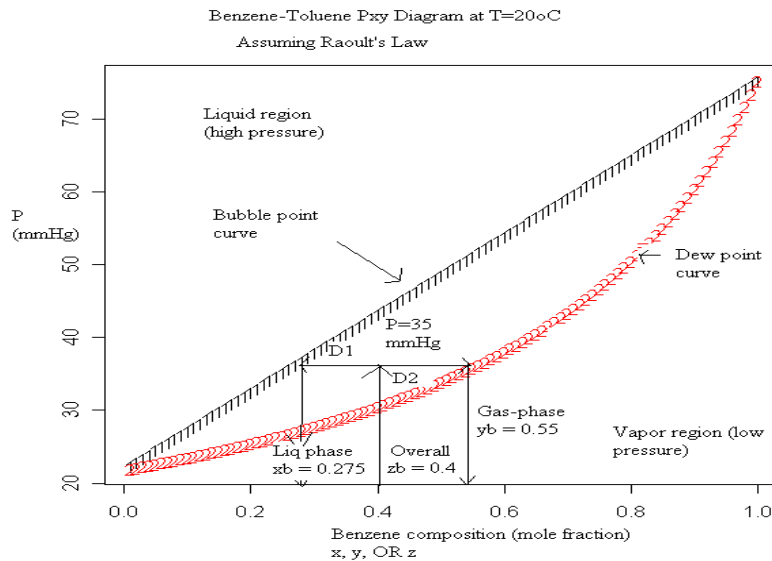
- Increasing the temperature

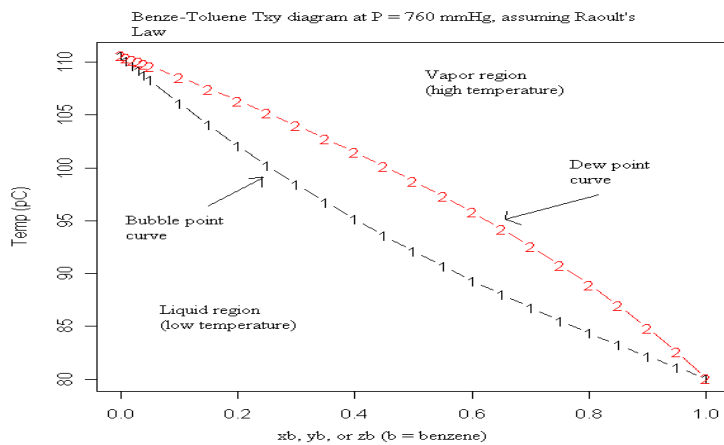
- *Decreasing* the pressure

Therefore, the region with the *higher* pressure is the liquid region, and that of *lower* pressure is vapor, as labeled. The region in between the curves is called the **two-phase region**.

We can determine, given the mole fraction of one component and a pressure, whether the system is gas, liquid, or two-phase, which is critical information from a design standpoint. For example, if the Benzene composition in the Benzene-Toluene system is 40% and the pressure is 25 mmHg, the entire mixture will be vapor, whereas if the pressure is raised to 50 mmHg it will all condense. The design of a flash evaporator at 20°C would require a pressure between about 30 and 40 mmHg (the 2-phase region).

We can also determine the composition of each component in a 2-phase mixture, if we know the overall composition and the vapor pressure. First, start on the x-axis at the overall composition and go up to the pressure you want to know about. Then from this point, go left until you reach the bubble-point curve to find the *liquid* composition, and go to the right until you reach the dew-point curve to find the *vapor* composition. See the below diagram.





Lecture 11

Topics Covered: Raoult's law, dew point and bubble point calculation with VLE, Henry's law

Raoult's Law

The simplest case (by far) to analyze occurs when an **ideal solution** is in equilibrium with an ideal gas. This is potentially a good approximation when two very similar liquids (the archetypal example is benzene and toluene) are dissolved in each other. It is also a good approximation for **solvent** properties (NOT solute properties; there is another law for that) when a very small amount of a solute is dissolved.

In an ideal liquid, the pressure exerted by a certain component on the gas is proportional to the vapor pressure of the *pure liquid*. The only thing that may prevent the liquid from exerting this much pressure is the fact that another component is present. Therefore, the partial pressure of the *liquid component* on the *gas component* is:

$$P_A = x_A \times P_A^*$$

where P_A^* is the vapor pressure of pure component A.

Therefore, since the partial pressures must be equal at equilibrium, we have the Raoult's Law equation for each component:

Recall that the partial pressure of an ideal gas in a mixture is given by:

$$P_A = y_A \times P$$

Raoult's Law for component A

$$y_A \times P = x_A \times P_A^*$$

Vapor Pressure Correlations

Unfortunately, life isn't that simple even when everything is ideal. Vapor pressure is not by any stretch of the imagination a constant. In fact, it has a very strong dependence on temperature. Therefore, people have spent a good deal of time and energy developing correlations with which to predict the vapor pressure of a given substance at any reasonable temperature.

One of the most successful correlations is called the **Antoine Equation**, which uses three coefficients, A, B, and C, which depend on the substance being analyzed. The Antoine Equation is as follows.

Antoine Equation

$$\log P_A^* = A - B/T + C$$

Bubble Point and Dew Point with Raoult's Law

When calculating either a bubble point or a dew point, one quantity is key, and this is the *overall composition*, denoted with the letter z. This is to distinguish it from the *single-phase composition* in either the liquid or the gas phase. It is necessary to distinguish between them because the composition of the two phases will almost always be different at equilibrium.

It is important to remember that the dew and bubble points of a multi-component mixture are *limits*. The bubble point is the point at which a very small amount of the liquid has evaporated - so small, in fact, that in essence, *the liquid phase composition remains the same as the overall composition*. Making this assumption, it is possible to calculate the composition of that single bubble of vapor that has formed.

Similarly, the dew point is the point at which a very small amount of the vapor has condensed, so that *the gas phase composition remains the same as the overall composition*, and thus it is possible to calculate the composition of the single bubble of liquid.

Bubble Point

Recall that the **dew point** of a solution is the set of conditions (either a temperature at constant pressure or a pressure at constant temperature) at which the first drops of a vapor mixture begin to condense.

Let us first consider how to calculate the bubble point (at a constant temperature) of a mixture of 2 components A and B, assuming that the mixture follows Raoult's Law under all conditions. To begin, write Raoult's Law for each component in the mixture.

$$y_A \times P = x_A \times P_A^*$$

$$y_B \times P = x_B \times P_B^*$$

Non-ideal VLE

Deviations from Raoult's Law occur because not all solutions are ideal, nor are all gas mixtures. Therefore, methods have been developed in order to take these nonidealities into account.

Henry's Law

The third non-ideal method, Henry's Law, is especially useful for **dilute solutions**, and states that at very low concentrations, the partial pressure of the dilute component over a liquid mixture is proportional to the concentration:

$$\text{For a dilute component A, } P_A = H_A \times x_A$$

This law is very similar to Raoult's Law, except that the proportionality constant is not the pure-component vapor pressure but is empirically determined from VLE data. Like the pure-component vapor pressure, the Henry's constant is dependent on temperature and the nature of component A. Unlike the pure-component vapor pressure, *it also depends on the solvent*, so when utilizing tables of Henry's constants, make sure that the solvents match.

Table 10.1: Henry's Constants for Gases Dissolved in Water at 25°C

Gas	\mathcal{H}/bar	Gas	\mathcal{H}/bar
Acetylene	1,350	Helium	126,600
Air	72,950	Hydrogen	71,600
Carbon dioxide	1,670	Hydrogen sulfide	550
Carbon monoxide	54,600	Methane	41,850
Ethane	30,600	Nitrogen	87,650
Ethylene	11,550	Oxygen	44,380

Lecture 12

Topics Covered: VLE by modified Raoult's law : activity coefficient, VLE from k-value correlations

VLE by Modified Raoult's Law

Deviation from solution ideality.

($i=1,2,\dots,N$)

Where γ_i = Activity coefficient.

It is function of T and liquid composition and based on experiments.

As a result, bubble point and dew point calculations are more complex.

In this chapter γ values are assumed known.

General solution:

$$\sum y_i = 1$$

Sum equation 10.5 becomes $P = \sum x_i \gamma_i P_i^{\text{sat}}$

Also you can solve for x_i as

$$\sum x_i = 1$$

$$P = 1 / \sum y_i \gamma_i P_i^{\text{sat}}$$

$$y_i P = x_i \gamma_i P_i^{\text{sat}}$$

VLE from K-value correlations

$$K_i = y_i/x_i$$

K -value measure the tendency of species to favor the vapor phase.

$K_i > 1$ Species I exhibit a higher concentration in the vapor phase.

$K_i < 1$ Species I exhibit a higher concentration in the liquid phase.

Allowing elimination of one set of mole fractions x or y , two types of calculations result:

Bubble point calculation: $y_i = K_i x_i$ and $\sum y_i = 1$

Then $\sum K_i x_i = 1$

Find the set of K -values that satisfies equation

Dew point calculation: $x_i = y_i / K_i$ and $\sum x_i = 1$

Then $\sum y_i / K_i = 1$ (10.14)

Find the set of K -values that satisfies equation

Figures 10.13 and 10.14 show monographs for the K -values of light hydrocarbons as function of T and P . They are prepared for average effect of compositions.

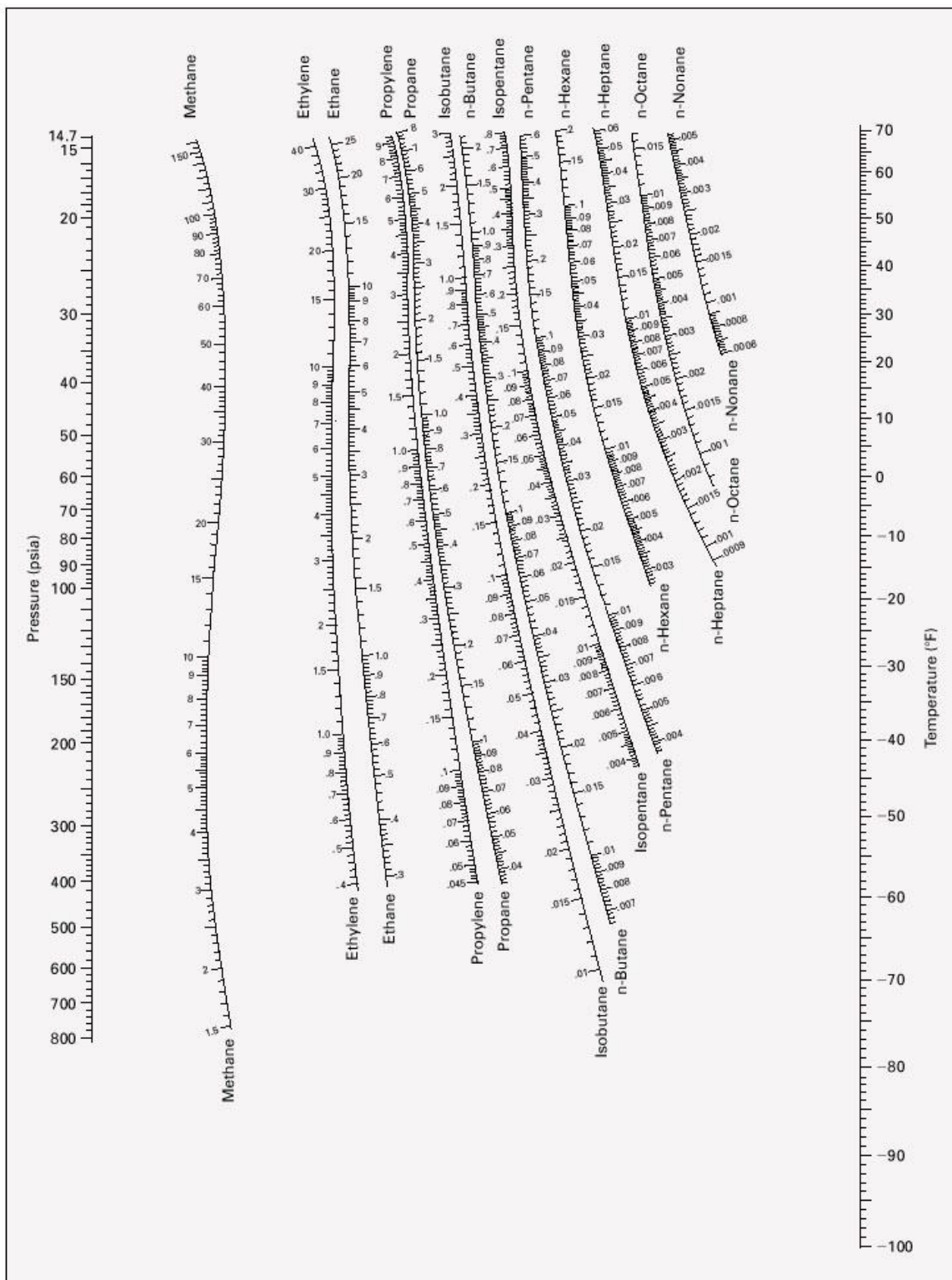


Figure 10.13: *K*-values for systems of light hydrocarbons. Low-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 41, 1953.)

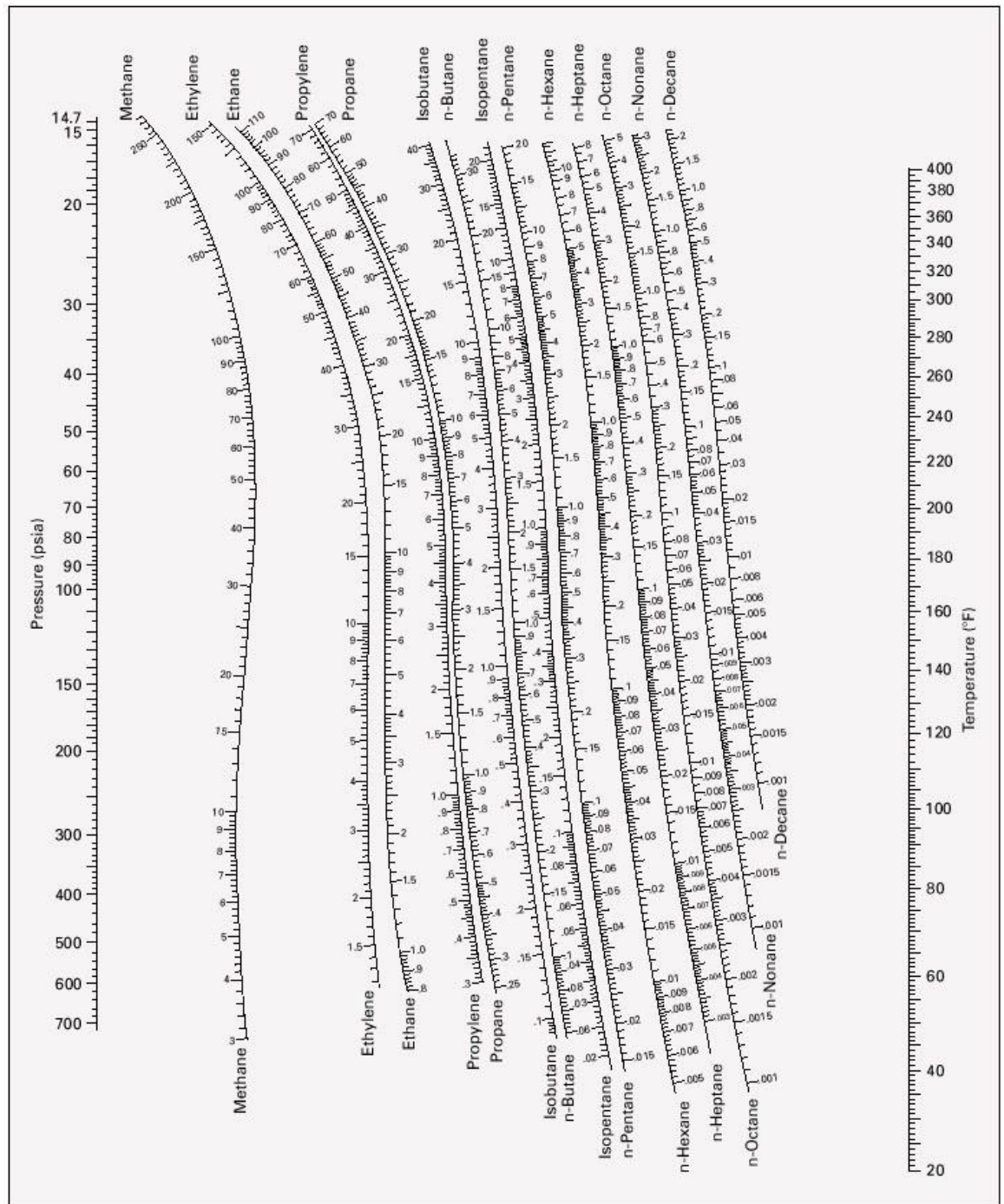


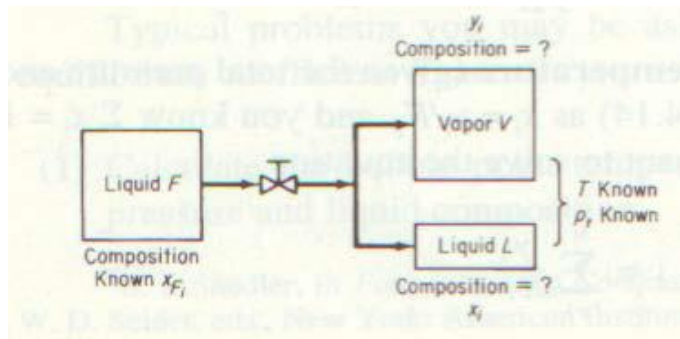
Figure 10.14: *K*-values for systems of light hydrocarbons. High-temperature range. (Reproduced by permission from C. L. DePriester, *Chem. Eng. Progr. Symp. Ser. No. 7*, vol. 49, p. 42, 1953.)

Lecture 13

Topics Covered: Flash calculations with Problem solving, Antoine equation : Problem solving

Flash Calculations

A liquid at a pressure equal to or greater than its bubble point pressure “flashes” or partially evaporates when the pressure is reduced producing a two phase system of vapor-liquid in equilibrium.



Flash vaporization with V and L in equilibrium

$L \equiv$ moles of liquid, with mole fraction $[x_i]$.

$V \equiv$ moles of vapor, with mole fraction $[y_i]$.

$Z_i \equiv$ over all mole fraction.

$$L + V = 1$$

$$Z_i = x_i L + y_i V$$

Combine equations to eliminate L and substitute with $x_i = y_i / k_i$ then solve for y_i

$$y_i = Z_i k_i / 1 + V(k_i - 1)$$

Since $\sum y_i = 1$, then

$$\sum Z_i k_i / 1 + V(k_i - 1) = 1$$

The initial step for solving a P-T flash problem is to find the value of V that satisfies this equation.

The **Antoine equation** is a class of semi-empirical correlations describing the relation between vapor pressure and temperature for pure components. The Antoine equation is derived from the Clausius–Clapeyron relation. The equation was presented in 1888 by the French engineer Louis Charles Antoine (fr) (1825–1897).

$$\text{Log}_{10}P = A - B/C + T$$

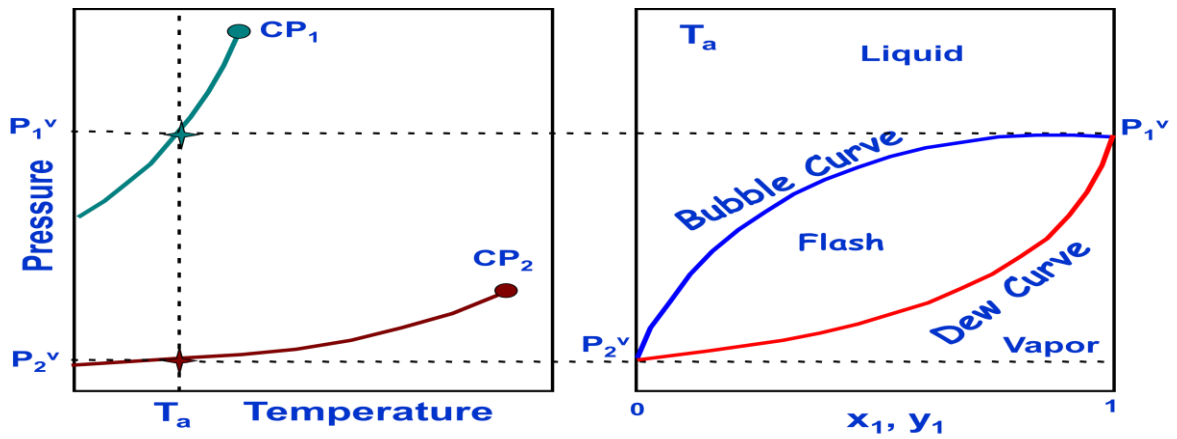
where p is the vapor pressure, T is temperature and A , B and C are component-specific constants.

Module 3

Lecture 14

Topics Covered: Overall discussion for Raoult’s law, Duhom’s theorem, VLE, Bubble point and Dew point calculations

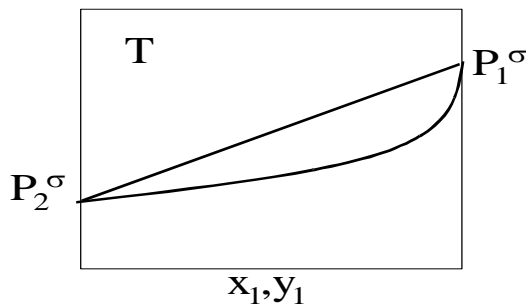
Types of VLE Calculations



- **Bubble Point Evaluation (Ideal Behavior Model)** : The bubble point pressure at a given T is

$$\sum y_i P_{bp} = \sum z_i P_i^\sigma \qquad P_{bp} = \sum z_i P_i^\sigma$$

Bubble Point from Raoult's law



Dew Point Calculation

At the dew point the overall fluid composition coincides with the gas composition. That is

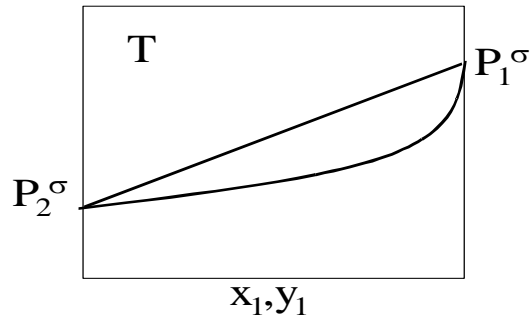
$$z_i = y_i$$

Dew Point Calculation (Ideal Behavior Model)

$$\begin{aligned} y_i P &= x_i P_i^\sigma \\ z_i P &= x_i P_i^\sigma \end{aligned} \quad \longrightarrow \quad \sum \frac{z_i}{P_i^\sigma} = \sum \frac{x_i}{P}$$

$$P_{dp} = \left[\sum_{i=1}^{N_c} \frac{z_i}{P_i^\sigma} \right]^{-1}$$

Dew Point from Raoult's law



Flash Calculations

- There are several equivalent expressions for the flash function

$$\sum y_i - 1 = 0$$

$$\sum x_i - 1 = 0 \qquad \sum y_i - \sum x_i = 0$$

Lecture 15

Topics Covered: Application of thermodynamics : Chemical potential, partial properties and fugacity definition.

The chemical potential of a pure substance

In this section we shall introduce the concept of **chemical potential** ' μ ' and we shall first consider the chemical potential of a pure substance and then, that of the particular case when the substance is a perfect gas.

The **chemical potential** ' μ ' of a pure substance is defined as:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p}$$

and describes how the Gibbs free energy of a system changes as a substance is added to it.

Thus for a pure substance, the Gibbs free energy is given by:

$$G = n \times G_m$$

where G_m is the molar Gibbs free energy. This means that the chemical potential of a pure substance is simply G_m since:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,p} = \left(\frac{\partial n G_m}{\partial n} \right)_{T,p} = G_m$$

Chemical potential for perfect gases

Let us now derive an expression for G_m for a perfect gas (pure substance) at a pressure p .

We have already seen that the fundamental equation of thermodynamics for a pure substance is given by:

$$dG = Vdp - SdT$$

that is at constant T :

$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

i.e.:

$$dG = V dp$$

Thus for n moles of a perfect gas, $pV=nRT$, i.e.:

$$dG = nRT \frac{dp}{p}$$

which for a change in pressure from p_0 (= 1 atm) to p , we have:

$$\Delta G = G(p) - G(p_0) = nRT \int_{p_0}^p \frac{dp}{p} = nRT \ln \left(\frac{p}{p_0} \right)$$

Thus, for one mole of pure gas ($n=1$), the molar Gibbs energy G_m is given by:

$$G_m = G_m^0 + RT \ln \left(\frac{p}{p_0} \right)$$

or in terms of the chemical potentials:

$$\mu = \mu^0 + RT \ln \left(\frac{p}{p^0} \right)$$

where μ^0 is the standard chemical potential, that is the molar Gibbs free energy of the pure gas at 1 bar ($=p^0$) of the pure gas

The fugacity may be written as:

$$f = \phi p$$

where ϕ is the dimensionless fugacity coefficient, and depends on the identity of the gas, temperature and pressure. In this case, the equation for the chemical potential for a real gas becomes:

$$\mu = \mu^0 + RT \ln \left(\frac{p}{p^0} \right) + RT \ln \phi$$

Lecture 16

Topics Covered: Explanation of chemical potential and phase equilibria, Proof of identity in chemical potential in different phases

Chemical potential for pure liquids

At equilibrium, the chemical potential of a substance present as a vapour is equal to its chemical potential in the liquid. This means that the chemical potential of a pure liquid is given once again by:

$$\mu = \mu^0 + RT \ln \left(\frac{p}{p^0} \right)$$

where μ^0 is the standard chemical potential, and p is now the vapour pressure of the liquid.

Chemical potential for real gases

Before we can discuss real gases, we need to introduce a new term, namely the **fugacity**, f , a property which will replace the true pressure of the gas by an effective property. We may then write:

$$\mu = \mu^0 + RT \ln \left(\frac{f}{p^0} \right)$$

Chemical potential for mixtures of ideal gases - partial molar Gibbs free energy, the fundamental equation of chemical thermodynamics

For a substance J in a mixture, the chemical potential μ_J is defined as the partial molar Gibbs free energy, i.e.:

$$\mu_J = \left(\frac{\partial G}{\partial n_J} \right)_{p, T, n_i \neq n_J}$$

It may be shown that the total Gibbs free energy of a mixture of k components is given by:

$$G = n_A \mu_A + n_B \mu_B + \dots + n_K \mu_K$$

where μ_A , μ_B , etc. are the chemical potentials at the composition of the mixture, whilst n_A , n_B , etc. are the number of moles of component A , B , etc. in the mixture (the composition). This means that G is dependent on the composition of the system.

This suggests that our fundamental equation of thermodynamics stating how G changes with T and p need to be updated to include this variation with composition. This new updated equation is given by:

$$\begin{aligned} dG &= Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots \\ &= Vdp - SdT + \sum_J \mu_J dn_J \end{aligned}$$

and is now called the **fundamental equation of chemical thermodynamics**.

At constant temperature and pressure, the fundamental equation of chemical thermodynamics reduces to:

$$dG = \sum_J \mu_J dn_J$$

Lecture 17

Topics Covered: Fugacity and fugacity coefficient for pure species, Introduction of residual properties : Residual Gibbs free energy, Residual volume.

Fugacity and Fugacity Coefficient of Species in Mixture

The definition of the fugacity of a species in a mixture is parallel to the definition of the pure species

fugacity. For an ideal gas mixture the chemical potential is given by eqn.:

$$\mu_i^{ig} \equiv G_i^{ig} + RT \ln y_i$$

$$\text{Or: } d\mu_i^{ig} = dG_i^{ig} + RT d \ln y_i \quad (\text{at const. T})$$

$$\text{But } dG_i^{ig} = V_i dP = RT d \ln P \quad (\text{at const. T})$$

$$\text{Thus: } d\mu_i^{ig} = RT d \ln P + RT d \ln y_i = RT d \ln(y_i P)$$

$$\text{Or: } d\mu_i^{ig} = RT d \ln p_i \quad (\text{where } p_i = \text{partial pressure of } i^{\text{th}} \text{ species})$$

Using the same idea implicit in eqn. 6.86, we extend eqn. 6.122 to define a similar expression for fugacity of species in a *real* mixture:

$$d\mu_i = RT d \ln \hat{f}_i$$

Residual Property

Residual property is the difference between the property in the real system with that of the corresponding ideal gas system. The residual property is a measure of deviation from the ideal gas system. For a property M:

$$M^R = M - M^{ig}$$

For example, the residual Gibbs free energy is useful for the phase equilibria calculation through the definition of fugacity coefficients:

$$R.T. \ln \phi_i = \{\partial G^R / \partial n_i\}_{T,P,n_j \neq i}$$

And also the relation between the compressibility factor and the residual Helmholtz free energy, which is very useful for EoS that is based on statistical mechanics such as SAFT:

$$Z^R = Z - 1 = (\rho/n.R.T) \{\partial A^R / \partial \rho\}_{T,n}$$

From this residual Helmholtz energy, many residual properties can be derived, for example:

- The residual entropy: (from the total differential of free energy)

$$S^R = -\{\partial A^R / \partial T\}_{V,n}$$

- The residual internal energy:

$$U^R = A^R + T.S^R$$

- The residual enthalpy:

$$H^R = U^R + P.V^R$$

- The residual Gibbs energy:

$$G^R = A^R + P.V^R$$

Note: $P.V^R = n.R.T.Z^R$. All residual properties listed above are calculated at constant V. However for some properties it is more common to use their values at constant P, so that an adjustment is needed due to different ideal-gas properties at those two different situations:

- The residual entropy: (at constant P)

$$S^R = -\{\partial A^R / \partial T\}_{V,n} + n.R.T.\ln Z$$

- The residual Gibbs energy: (at constant P)

$$G^R = A^R + P.V^R - n.R.T.\ln Z$$

Lecture 18

Topics Covered: Proof of identity in fugacity and fugacity coefficients in different phases, Fugacity of a pure liquid, Poyinting factor, Fugacity and fugacity coefficient for liquid.

Here, \hat{f}_i is the fugacity of species i in the mixture, replacing the partial pressure P_i . As we will demonstrate later, \hat{f}_i is a partial molar property, and is therefore denoted by a *circumflex* rather than by an *overbar*, as are partial properties. On integrating eqn. 6.113 between the any two multi-component phases α and ψ in equilibrium with each other:

$$\int_{\mu_i^\psi}^{\mu_i^\alpha} d\mu_i = RT \int_{\hat{f}_i^\psi}^{\hat{f}_i^\alpha} d \ln \hat{f}_i$$

Hence,
$$\mu_i^\alpha - \mu_i^\psi = RT \ln(\hat{f}_i^\alpha / \hat{f}_i^\psi)$$

But by eqn. 6.42, for equilibrium: $\mu_i^\alpha = \mu_i^\psi$

It follows, therefore,
$$\mu_i^\alpha - \mu_i^\psi = RT \ln(\hat{f}_i^\alpha / \hat{f}_i^\psi) = 0$$

Or:
$$\hat{f}_i^\alpha / \hat{f}_i^\psi = 1$$

That is:
$$\hat{f}_i^\alpha = \hat{f}_i^\psi$$

Thus for an arbitrary number of phases in equilibrium with each other:

$$\hat{f}_i^\alpha = \hat{f}_i^\psi = \dots = \hat{f}_i^\phi \quad (i = 1, 2, \dots, N)$$

Thus, eqn. 6.126 offers a criterion of equilibrium correspondent to that provided by eqn. 6.42. The great advantage this equivalence offers is that, the fugacity coefficients of species in a mixture can be related to the volumetric properties of the mixtures, which facilitates the solution of phase and chemical reaction

equilibria problems.

On comparing eqns. 6.122 and 6.123, the following limiting condition obtains:

$$\lim_{P \rightarrow 0} \hat{f}_i = y_i P$$

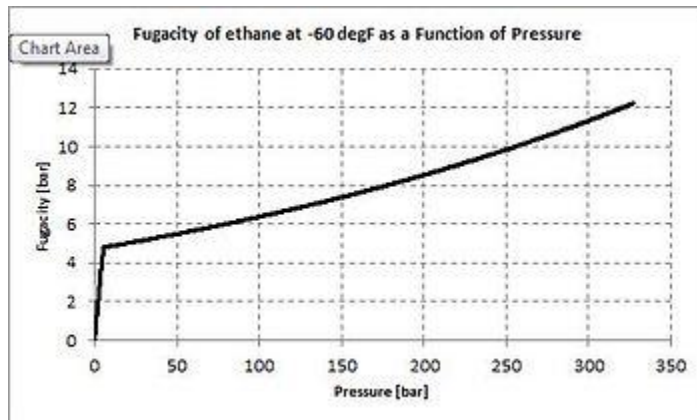
It follows that a *fugacity coefficient* $\hat{\phi}_i$ (dimensionless) of a species in a real gas mixture may be defined as:

$$\hat{\phi}_i^V \equiv \frac{\hat{f}_i^V}{y_i P}$$

Although the derivation above defines the fugacity coefficient with respect to gaseous mixture the definition may be extended to represent fugacity coefficient of a species in a real liquid solution. Accordingly, in that case it is defined in the following manner:

$$\hat{\phi}_i^L \equiv \frac{\hat{f}_i^L}{x_i P}$$

Of a pure liquid



Fugacity vs. pressure of ethane at -60°F (-51°C). Note the "breakpoint" at the saturation pressure and the curvature at higher pressures as the Poynting correction factor becomes important.

For a pure fluid in vapor–liquid equilibrium, the vapor phase fugacity is equal to the liquid phase fugacity. At pressures above the saturation pressure, the liquid phase fugacity is:

$$f_{\text{liq}}(T,P) = \phi_{\text{sat}} P_{\text{sat}} \exp\left[\int_{P_{\text{sat}}}^P \frac{V_{\text{liq}}}{RT} dP\right]$$

The fugacity correction factor for the vapor, ϕ_{sat} , should be evaluated at the saturation pressure and is unity when P_{sat} is low. The exponential term represents the Poynting correction factor and is usually near 1 unless pressures are very high. Frequently, the fugacity of the pure liquid is used as a reference state when defining and using mixture activity coefficients.

Lecture 19

Topics Covered: Generalized correlation for the fugacity coefficient, Introduction of Ideal solution, Definitions of excess properties : GE, HE, SE, VE

Generalized Correlations for the Fugacity Coefficient

The generalized correlation approach which has been presented earlier for calculation compressibility factor Z and the residual enthalpy and entropy of gases (section 5.7), can also be applied for computing fugacity coefficients for pure gases and gaseous mixtures. Equation (6.90) can be rewritten in a generalized form as follows:

$$P = P_c P_r; \text{ hence, } dP = P_c dP_r$$

$$\ln \phi = \int_0^{P_r} (Z - 1) \frac{dP_r}{P_r} \quad (\text{at const. } Tr)$$

Hence, an alternately,

Substitution for $Z = Z_0 + \omega Z_1$, gives :

$$\ln \phi = \int_0^{P_r} (Z^0 - 1) \frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

The last equation may be written in alternative form:

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1$$

$$\text{Or: } \phi = (\phi^0)(\phi^1)^\omega$$

$$\ln \phi^0 = \int_0^{P_r} (Z^0 - 1) \frac{dP_r}{P_r}$$

Where,

$$\ln \phi^1 = \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

For obtaining the values of the integrals in the last two equations, the tabulated data for Z^0 and Z^1 for various values of T_r and P_r may be used for numerical or graphical computations. Yet another approach is due to Lee-Kesler which employs a variant of the BWR-EOS (eqn. 2.17) to evaluate the expressions for $\ln \phi^0$ and $\ln \phi^1$ for a wide range of values of T_r and P_r , and are available in the form of extended tables.

Excess Properties

Unlike for real gases (pure or mixtures) the EOS based approach to calculation of thermodynamic properties of real liquid solutions have not proved very successful. However, as molar residual property is defined for real gases, for real liquid solutions one may formulate a different departure function called the molar excess property that quantify the deviation from ideal solution property. The mathematical formalism of excess properties is, therefore, analogous to that of the residual properties.

If M represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g., V, U, H, S, G , etc.), then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus:

$$M^E \equiv M - M^{id}$$

The excess property bear a relationship to the property change of mixing. One may take the example of excess Gibbs free energy to illustrate the point. Thus:

$$G^E = G - G^{id}$$

Or:

$$G^E = G - \left(\sum_i x_i G_i + RT \sum_i x_i \ln x_i \right)$$

$$G^E = \Delta G_{mix} - RT \sum_i x_i \ln x_i$$

Thus:

Other relations include:

$$H^E = H - H^{id} = \Delta H_{mix}$$

$$S^E = \Delta S_{mix} + R \sum_i y_i \ln y_i$$

Also: $G^E = H - TS^E$

The non-ideality of real liquid solutions are depicted well by use of excess properties, especially through the behaviour of G^E , H^E and S^E . The excess Gibbs energy is typically obtained from low pressure vapour-liquid equilibrium data, while H^E is obtained by measuring isothermal enthalpy change of mixing. Lastly S^E is derived using the following relation:

$$S^E = \frac{H^E - G^E}{T}$$

Lecture 20

Topics Covered: The Lewis-Randall Rule, Heats of solution

The Lewis/Randall Rule:

A simple equation for the fugacity of a species in an ideal solution follows from the following equations. In general, for any solution:

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

Applying to ideal solution, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}$

However we know (eqn. 6.77) that: $\mu_i^{id} = \bar{G}_i^{id} = G_i + RT \ln x_i$

Also, from eqn. 6.86: $G_i = \Gamma_i(T) + RT \ln f_i$

Thus, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$

On comparing eqns.: $\hat{f}_i^{id} = x_i f_i$

The last relation is known as the *Lewis/Randall rule*, and applies to each species in an ideal solution at all conditions of temperature, pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant is the fugacity of pure species *i* in the same physical state as the solution and at the same T and P.

One may write the same equation specifically for an ideal solution, whence:

$$d \left(\frac{G^u}{RT} \right) = \frac{V^u}{RT} dP - \frac{H^u}{RT^2} dT$$

Thus subtracting eqn. 6.165 from 6.164:

$$d \left(\frac{G^E}{RT} \right) = \frac{V^E}{RT} dP - \frac{H^E}{RT^2} dT$$

Thus we may write the following further *generative* relations:

$$\frac{V^E}{RT} = \left[\frac{\partial(G^E / RT)}{\partial P} \right]_T$$

$$\frac{H^E}{RT} = -T \left[\frac{\partial(G^E / RT)}{\partial T} \right]_P$$

$$\text{And further: } \frac{S^E}{RT} = \frac{H^E}{RT} - \frac{G^E}{RT}$$

Lecture 21

Topics Covered: Refrigeration and liquefaction, Carnot refrigeration; Problem solving, The vapour-compression cycle : graphical explanation, Problem solving

Basics of Refrigeration

The technique of preserving food and perishable goods is an idea of prehistoric times.

A system which produces cold or maintains such low temperatures is called as a Refrigerating System.

This process is called as Refrigeration.

A refrigerating system normally operates in a closed cycle system.

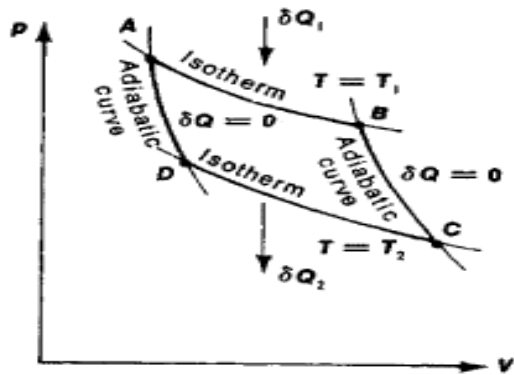
Carnot cycle

A hypothetical cycle consisting of four reversible processes in succession: an isothermal expansion and heat addition, an isentropic expansion, an isothermal compression and heat rejection process, and an isentropic compression.

The Carnot cycle was first examined by the French scientist N. L. S. Carnot (1824) as the ideal operating cycle of a heat engine. The conversion of heat into work is accompanied by the transfer of a certain amount of heat by the engine's working substance from the hotter body (the heater) to the cooler.

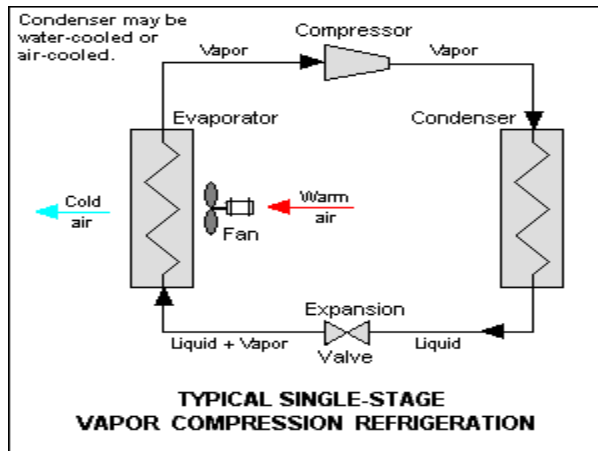
The Carnot cycle proceeds as follows: at a temperature T_1 the working substance (such as steam in a cylinder under a piston) is brought into contact with a heater that has a constant temperature T_1 and isothermally acquires from it an amount of heat δQ_1 (here the steam expands and performs work). In Figure 1 this process is represented by the segment AB of the isotherm. The working substance, expanding adiabatically (along the adiabatic curve BC), then cools to temperature T_2 . At this temperature, as it becomes isothermally compressed (segment CD), it gives off a quantity of heat δQ_2 to the cooler with temperature T_2 . The cycle ends with an adiabatic process (DA in Figure 1) that returns the working substance to its initial thermodynamic state. When the temperature difference ($T_1 - T_2$) between the heater and cooler is constant, the working substance performs the following amount of work in one cycle

$$A = \delta Q_1 - \delta Q_2 = \frac{T_1 - T_2}{T_1} \delta Q_1$$

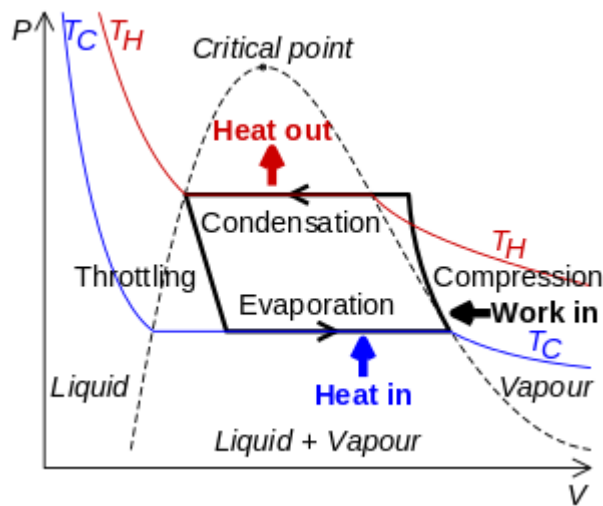


A Carnot cycle consists entirely of reversible processes; thus it can theoretically operate to withdraw heat from a cold body and to discharge that heat to a hot body. To do so, the cycle requires work input from its surroundings. The heat equivalent of this work input is also discharged to the hot body. Just as the Carnot cycle provides the highest efficiency for a power cycle operating between two fixed temperatures, so does the reversed Carnot cycle provide the best coefficient of performance for a device pumping heat from a low temperature to a higher one. *See Heat pump, Refrigeration cycle.*

The Vapour-Compression Cycle:



The vapor-compression uses a circulating liquid refrigerant as the medium which absorbs and removes heat from the space to be cooled and subsequently rejects that heat elsewhere. Figure 1 depicts a typical, single-stage vapor-compression system. All such systems have four components: a compressor, a condenser, a thermal expansion valve (also called a throttle valve or metering device), and an evaporator. Circulating refrigerant enters the compressor in the thermodynamic state known as a saturated vapor^[2] and is compressed to a higher pressure,^[2] resulting in a higher temperature as well. The hot, compressed vapor is then in the thermodynamic state known as a superheated vapor and it is at a temperature and pressure at which it can be condensed with either cooling water or cooling air flowing across the coil or tubes. This is where the circulating refrigerant rejects heat from the system and the rejected heat is carried away by either the water or the air (whichever may be the case).



A fictitious pressure-volume diagram for a typical refrigeration cycle

The condensed liquid refrigerant, in the thermodynamic state known as a saturated liquid, is next routed through an expansion valve where it undergoes an abrupt reduction in pressure. That pressure reduction results in the adiabatic flash evaporation of a part of the liquid refrigerant. The auto-refrigeration effect of the adiabatic flash evaporation lowers the temperature of the liquid and vapor refrigerant mixture to where it is colder than the temperature of the enclosed space to be refrigerated.

The cold mixture is then routed through the coil or tubes in the evaporator. A fan circulates the warm air in the enclosed space across the coil or tubes carrying the cold refrigerant liquid and vapor mixture. That warm air evaporates the liquid part of the cold refrigerant mixture. At the same time, the circulating air is cooled and thus lowers the temperature of the enclosed space to the desired temperature. The evaporator is where the circulating refrigerant absorbs and removes heat which is subsequently rejected in the condenser and transferred elsewhere by the water or air used in the condenser.

To complete the refrigeration cycle, the refrigerant vapor from the evaporator is again a saturated vapor and is routed back into the compressor.

Lecture 22

Topics Covered: Choice of refrigerants, Absorption refrigeration : Explanation, Problem solving

Choice of refrigerants:

A **refrigerant** is a substance or mixture, usually a fluid, used in a heat pump and refrigeration cycle. In most cycles it undergoes phase transitions from a liquid to a gas and back again. Many working fluids have been used for such purposes. Fluorocarbons, especially chlorofluorocarbons, became commonplace in the 20th century, but they are being phased out because of their ozone depletion

effects. Other common refrigerants used in various applications are ammonia, sulfur dioxide, and non-halogenated hydrocarbons such as propane.

The desired thermodynamic properties are a boiling point somewhat below the target temperature, a high heat of vaporization, a moderate density in liquid form, a relatively high density in gaseous form, and a high critical temperature. Since boiling point and gas density are affected by pressure, refrigerants may be made more suitable for a particular application by choice of operating pressures.

Types of Refrigerants

In the air conditioning and refrigeration industry, virtually all of the refrigerant experience has been limited to single-component ("pure") refrigerants; however, as we search for acceptable replacements for these compounds, refrigerant manufacturers have been unsuccessful in developing single-component replacements that meet all of the required or highly desirable characteristics for a widely used refrigerant.

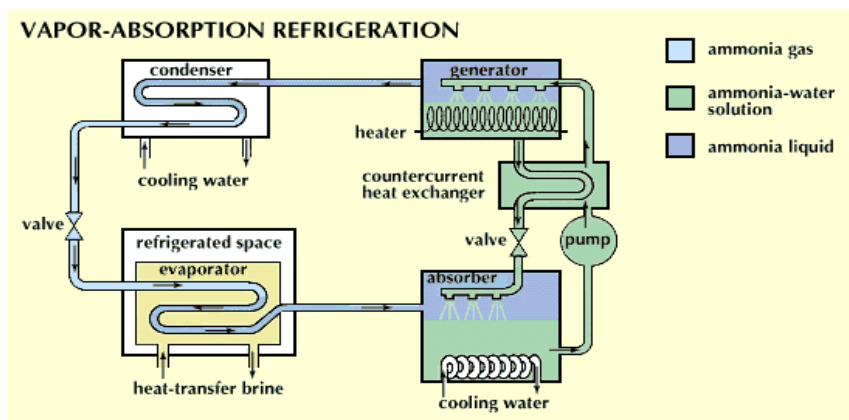
These requirements include:

- Environmental acceptability
- Chemical stability
- Materials compatibility
- Refrigeration-cycle performance
- Adherence to nonflammable and nontoxic
- Boiling point

Absorption refrigeration:

An **absorption refrigerator** is a refrigerator that uses a heat source (e.g., solar energy, a fossil-fueled flame, waste heat from factories, or district heating systems) to provide the energy needed to drive the cooling process.

Absorption refrigerators are often used for food storage in recreational vehicles. The principle can also be used to air-condition buildings using the waste heat from a gas turbine or water heater. Using waste heat from a gas turbine makes the turbine very efficient because it first produces electricity, then hot water, and finally, air-conditioning (called cogeneration/trigeneration).



Lecture 23

Topics Covered: Liquefaction processes : The Linde and Claude Liquefaction process; Explanation with flow diagram

The processes are used for scientific, industrial and commercial purposes. Many gases can be put into a liquid state at normal atmospheric pressure by simple cooling; a few, such as carbon dioxide, require pressurization as well. Liquefaction is used for analyzing the fundamental properties of gas molecules (intermolecular forces), for storage of gases, for example: LPG, and in refrigeration and air conditioning. There the gas is liquefied in the *condenser*, where the heat of vaporization is released, and evaporated in the *evaporator*, where the heat of vaporization is absorbed. Ammonia was the first such refrigerant, and is still in widespread use in industrial refrigeration, but it has largely been replaced by compounds derived from petroleum and halogens in residential and commercial applications.

Liquid oxygen is provided to hospitals for conversion to gas for patients with breathing problems, and liquid nitrogen is used in the medical field for cryosurgery, and by inseminators to freeze semen. Liquefied chlorine is transported for eventual solution in water, after which it is used for water purification, sanitation of industrial waste, sewage and swimming pools, bleaching of pulp and textiles and manufacture of carbon tetrachloride, glycol and numerous other organic compounds as well as phosgene gas.

Liquefaction of helium (^4He) with the precooled Hampson-Linde cycle led to a Nobel Prize for Heike Kamerlingh Onnes in 1913. At ambient pressure the boiling point of liquefied helium is 4.22 K ($-268.93\text{ }^\circ\text{C}$). Below 2.17 K liquid ^4He becomes a superfluid (Nobel Prize 1978, Pyotr Kapitsa) and shows characteristic properties such as heat conduction through second sound, zero viscosity and the fountain effect among others.

The liquefaction of gases is a complicated process that uses various compressions and expansions to achieve high pressures and very low temperatures, using, for example, turboexpanders.

The liquefaction of air is used to obtain nitrogen, oxygen, and argon and other atmospheric noble gases by separating the air components by fractional distillation in a cryogenic air separation unit.

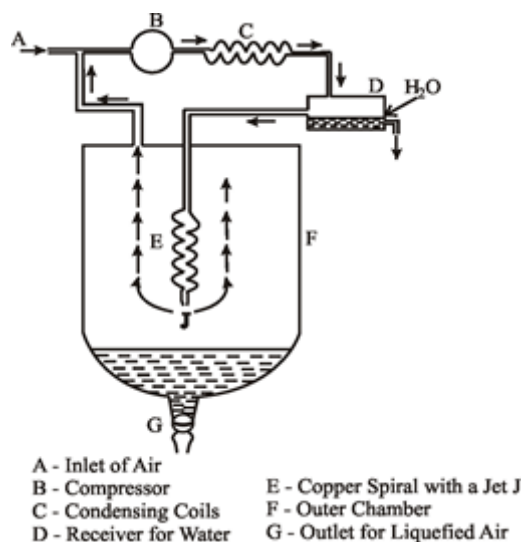
Linde's process is known as Adiabatic expansion of compressed gas.

Principle

The process is based upon *Joule – Thomson Effect*, which states,

“When a gas under high pressure is allowed to expand adiabatically through a fine hole into a region of low pressure, it is accompanied by cooling.

The term ‘adiabatically’ means that apparatus is perfectly insulated so that no heat is lost to or gained from the surroundings.



Procedure

The process based upon the above principle is known as **Linde's Process**. The apparatus used is shown in figure on side with names of different parts. This apparatus was used by **Linde** to liquefy air.

The air is first compressed to about 200 atmospheres in the compressor and then passed through the condensing coils. As a result, the air is cooled and the water vapours present condense to form the water which is removed from receiver. The dry air is then passed through the spiral copper tube which terminates into a jet. The air expands through the jet into the chamber where pressure is about 50 atmospheres. Thus, as a result of *Joule-Thomson effect*, the air is cooled. As this cooled air moves up, it further cools the incoming air. The cooled air is sent to the compressor again and the process is repeated a number of times till ultimately the air is cooled to such an extent that it liquefies. The liquefied air gets collected at the bottom of the outer chamber and can be drawn off. Any uncondensed air is recirculated.

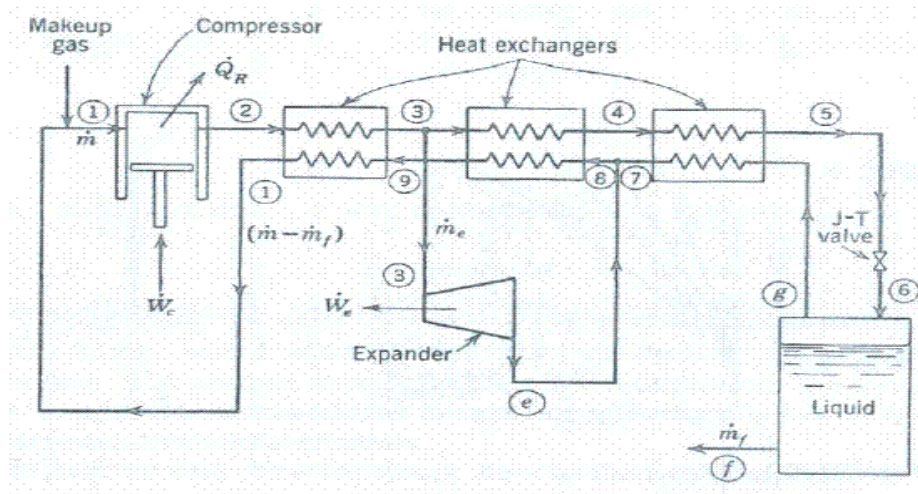
Claude's process

Principle

This process is based upon the principle that when a gas expands adiabatically against a piston in an engine, it does some external work, hence its internal energy falls and consequently the temperature of the gas falls. This principle combined with the Joule-Thomson effect, has been applied in the Claude's process for liquefaction of air.

Procedure

The purified air i.e. air free from CO₂ and water vapours is first compressed to about 200 atmospheres by compressor. The compressed air then passes through the tube which bifurcates the incoming gas part of the air goes into the cylinder fitted with an air tight piston and rest of the air passes through the spiral coil which ends in a jet. The air that goes into the cylinder pushes the piston and thus does some external work. As a result, the internal energy of air falls and hence temperature falls. The cooled air then enters the chamber at lower end. The air that passes through the spiral coil is cooled by *Joule-Thomson effect* as it comes out through the jet in low pressure region (50 atm) of chamber. The cooled air is circulated again and again with the incoming air till the air gets liquefied. The liquefied air collects in the chamber and is withdrawn.



Claude air liquefaction system

Lecture 24

Topics Covered: Equilibrium and stability; Criteria of stability; Problem solving

Thermodynamic equilibrium is an axiomatic concept of thermodynamics. It is an internal state of a single thermodynamic system, or a relation between several thermodynamic systems connected by more or less permeable or impermeable walls. In thermodynamic equilibrium there are no net macroscopic flows of matter or of energy, either within a system or between systems. In a system in its own state of internal thermodynamic equilibrium, no macroscopic change occurs. Systems in mutual thermodynamic equilibrium are simultaneously in mutual thermal, mechanical, chemical, and radiative equilibria. Systems can be in one kind of mutual equilibrium, though not in others. In

thermodynamic equilibrium, all kinds of equilibrium hold at once and indefinitely, until disturbed by a thermodynamic operation. In a macroscopic equilibrium, almost or perfectly exactly balanced microscopic exchanges occur; this is the physical explanation of the notion of macroscopic equilibrium.

A thermodynamic system in its own state of internal thermodynamic equilibrium has a spatially uniform temperature. Its intensive properties, other than temperature, may be driven to spatial inhomogeneity by an unchanging long range force field imposed on it by its surroundings.

In non-equilibrium systems, by contrast, there are net flows of matter or energy. If such changes can be triggered to occur in a system in which they are not already occurring, it is said to be in a metastable equilibrium.

Though it is not a widely named law, it is an axiom of thermodynamics that there exist states of thermodynamic equilibrium. The second law of thermodynamics states that when a body of material starts from an equilibrium state, in which portions of it are held at different states by more or less permeable or impermeable partitions, and a thermodynamic operation removes or makes the partitions more permeable and it is isolated, then it spontaneously reaches its own new state of internal thermodynamic equilibrium, and this is accompanied by an increase in the sum of the entropies of the portions.

Classical thermodynamics deals with states of dynamic equilibrium. The state of a system at thermodynamic equilibrium is the one for which some thermodynamic potential is minimized, or for which the entropy (S) is maximized, for specified conditions. One such potential is the Helmholtz free energy (A), for a system with surroundings at controlled constant temperature and volume:

$$A=U -TS$$

Another potential, the Gibbs free energy (G), is minimized at thermodynamic equilibrium in a system with surroundings at controlled constant temperature and pressure:

$$G=U-TS+PV$$

where T denotes the absolute thermodynamic temperature, P the pressure, S the entropy, V the volume, and U the internal energy of the system.

Thermodynamic equilibrium is the unique stable stationary state that is approached or eventually reached as the system interacts with its surroundings over a long time. The above-mentioned potentials are mathematically constructed to be the thermodynamic quantities that are minimized under the particular conditions in the specified surroundings.

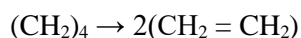
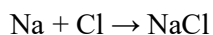
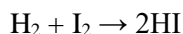
Module 4

Lecture 25

Topics Covered: Kinetics: Rate of chemical reaction

Chemical kinetics deals with the study of the rate of a reaction, its conditions and the mechanisms. Modern studies have distinguished the various types of reactions and classified as - i) Elementary reactions or single step reactions and ii) Complex reactions or multi step reactions. Reaction rate is the most important information about a chemical reaction, if that reaction is to be employed to serve any purpose. Every reaction has its own physical conditions as temperature, pressure, concentration of the reactants etc., optimization of these conditions are very important for obtaining maximum product.

Elementary reactions are those reactions where smaller numbers of chemical bonds are broken and formed. Isomerization, free radical reactions or second-order displacement reactions are common elementary reactions. The following are the few examples of elementary reaction :-



Cyclobutane Ethylene

Order of a Chemical Reaction.: If a reaction be : $p\text{A} + q\text{B} \rightarrow \text{Products}$ and if its observed Rate Law is : $\text{Rate} \propto [\text{A}]^\alpha \times [\text{B}]^\beta$ then the reaction is said to be of α -order with respect to A and β -order with respect to B, and $\alpha + \beta$ is the overall order of reaction.

Molecularity of a Chemical Reaction – Though no universal definition of molecularity is there, the following definition is the commonest one :

Molecularity is defined as the number of molecules taking part in the rate determining step of a complex chemical reaction.

So, the molecularity would be equal to either 1 or 2 and not necessarily equal either to the sum of the stoichiometric co-efficients or to the overall kinetic order.

DISTINCTION BETWEEN ORDER AND MOLECULARITY

ORDER	MOLECULARITY
<ol style="list-style-type: none"> 1. Kinetic order is a purely <i>experimental property</i> connected with the Rate equation. It is not necessary connected with the chemical equation of the reaction. 2. In a reaction $A + B + \dots = \dots$, if the observed Rate $\propto [A]^\alpha \times [B]^\beta \dots$, the order of the reaction = $\alpha + \beta + \dots$ 3. Physical condition, such as pressure may change the order of the reaction eg. order changes from 1 to 2 at low pressure for many gaseous reactions. 	<ol style="list-style-type: none"> 1. Molecularity is a theoretical property. In its definition it is connected with the mechanism. 2. Molecularity is defined as the number of Molecules taking part in the rate-determining step of its mechanism. 3. Molecularity is an invariant number for a given chemical reaction
<ol style="list-style-type: none"> 4. For elementary reactions, order is necessarily equal to molecularity. For complex reactions it may or may not, very often not. 	

Lecture 26

Topics Covered: First order reactions

INTEGRATED RATE LAW

Rate Law : Temperature, pressure, reactant concentration and catalyst are the principal speed limiters of any chemical reactions. The actual relationship between the rate of any reaction and reactant concentration is called the “Rate Law”

For example, the rate of decomposition of H_2O_2 at any instant is found to be proportional to its concentration at that instant. Therefore, its rate law is as follows :

Observed Rate : Rate of decomposition of $H_2O_2 \propto [H_2O_2]$

Therefore, *Rate Law :* Rate of decomposition, $-d[H_2O_2] / dt = k_1 [H_2O_2] \dots\dots\dots(1)$

(1) is called the Rate Law and k_1 , the rate constant or specific reaction rate.

The principal aim of chemical kinetics is to find the Rate Law for a given chemical reaction. Next aim is to suggest a mechanism consistent with the Rate Law. Ultimately the goal is to calculate the rate constants theoretically from the fundamental properties of the reactants.

Mathematical Formulation of a First-Order Reaction.-

In a first-order reaction, the reaction speed is proportional to the concentration of the substance at a given instant. Let the reaction be the decomposition of A, *i.e.*



If we start with 'a' moles of A and 'x' moles get decomposed in time 't' secs. Then (a - x) remains unchanged at that instant. The speed of the reaction at 't' is proportional to the concentration of A at that instant, $[A] \propto (a - x)$.

Therefore, Rate of decomposition of reactant A

$$-d[A] / dt \propto [A] \quad (= \text{conc. of A at any instant 't'}) \dots\dots\dots (i)$$

Since [A] is proportional to (a - x), we have,

$$-d(a - x) / dt \propto (a - x); \text{ or, } -d(a - x) / dt = -k_1(a - x) \dots\dots\dots (ii)$$

where k_1 is called the first-order rate constant.

As this equation involves infinitesimally small quantities and so need integration to obtain the Integrated Rate Law before this can be applied to experimental results. Integrating, we find,

$$\int d(a - x) / (a - x) = -k_1 \int dt \dots\dots\dots (iii)$$

or, $\ln(a - x) = -k_1 t + \text{constant.}$

Substituting $x = 0$ and $t = 0$ in the above equation taking into consideration the fact that at the beginning (at $t = 0$), there is no decomposition (*i.e.* $x = 0$). The equation then becomes, $\ln a = \text{constant}$

Substituting this value of the constant in equation (iii), we get

$$\ln(a - x) = -k_1 t + \ln a$$

$$\text{or, } \ln(a / a - x) = -k_1 t \dots\dots\dots (iv)$$

Then, *First Order Reaction* :

$$2.303 / t \log_{10} a / (a - x) = k_1 \dots\dots\dots (a)$$

But after putting $(a - x) = c$, that means, the initial concentration being $a = c_0$ and concentration at any time t , in the eqn. (iv), we get another form of (a):

$$k_1 t = \ln c_0 / c; \text{ or, } c = c_0 e^{-k_1 t} \dots\dots\dots (b)$$

$$\text{Linearity of } \log c \text{ vs time : therefore, } \log c = -k_1 / 2.303 t + \log c_0 \dots\dots\dots (c)$$

i.e. $\log c$ plotted against t gives a straight line of negative slope equal to $(-k_1 / 2.303)$

Lecture 27

Topics Covered: Second and Third order reactions

Mathematical Formulation of a Second-Order Reaction.-

When two molecules of same or different kinds take part in the reaction and rate of reaction is proportional to the concentration of each of them, then it is called second-order reactions.

If the reaction is $A + B \rightarrow C + D$ and initial concentration of A and B are a and b respectively and if x represents the number of moles of A or of B decomposed in time t , then the rate of disappearance of A or B (= rate of increase of C or D) is given by the second-order rate law.

$$\text{Rate Law : } -d(a-x)/dt = dx/dt = k_2(a-x)(b-x)$$

where k_2 is the reaction rate of the second-order equation. Upon integration by the method of fractional parts, the equation changes to :

$$\text{Second-order Rate Constant, } k_2 = 2.303 / t(a-b) \log b(a-x) / a(b-x) \dots \dots \dots (d)$$

If the initial concentration of A and B are equal, then we have $a = b$ and so the rate law becomes :- $2A \rightarrow \text{Product}$

$$\text{Rate Law : } dx/dt = k_2(a-x)^2, \text{ upon integration it yields,}$$

$$\text{Second Order Rate Constant, } k_2 = 1/t \cdot x / a(a-x) \dots \dots \dots (e)$$

As we know that $(a-x) = c$, the concentration of the substance decomposing, the reciprocal form of this equation is,

$$\text{Linearity of } 1/c \text{ vs. time : } 1/c = k_2 t + 1/a$$

It shows that $1/c$ increases linearly with time with $\text{slope} = k_2$

Unit of K_2

As k_2 is given by

$$K_2 = dx/dt \cdot 1/c^2 = \text{conc.} / \text{time} \times 1 / \text{conc}^2 = 1 / \text{Time} \times \text{Concentration}$$

Hence k_2 has the usual unit of litre per mole per second

Examples of Second Order Reaction.

1. Alkaline hydrolysis of ester.

2. Esterification of acids.
3. Decomposition of HI in gas phase.
4. Dimerisation of butadiene

Lecture 28

Topics Covered:

Half Decomposition Period (for 1st order reaction).

The time required for half decomposition, $\tau_{1/2}$, is obtained by putting $x = a / 2$ in the first order equation (a), when we get

$$\text{Half-Life period, } \tau_{1/2} = 2.303 \log 2 / k_1 = 0.693 / k_1 = \text{constant.}$$

Half Decomposition Period (for 2nd order reaction).

Half decomposition period can be obtained by putting $x = a/2$ in eqn. (e) –

$$\text{Half - Decomposition Period, } \tau_{1/2} = 1/k_2 \dots \dots \dots (f)$$

i.e. in a second order equation, half decomposition period is inversely proportional to the first power of initial concentration and is equal to $1/k_2$ provided $a = 1$.

Lecture 29

Topics Covered: Non Elementary Reactions

Elementary and Non-Elementary Reactions

Chemical Reaction rarely proceed in one step. In a conventional single step writing of the stoichiometric equation of a chemical reaction, only initial and final states of the reaction system are indicated. In case of multistep reactions the rate of overall reaction is determined primarily by the slowest step. It is customary in chemical kinetics to class all the reactions as the elementary and Non-elementary reactions

Elementary reaction The individual reaction steps which contribute to the overall reaction are termed as elementary reactions. (OR) The reaction in which the molecules react exactly as the stoichiometric equation written for a reaction, is called as an elementary reaction.

Non-Elementary Reaction The reactions in which formation of product from the original reactants occur through a series of steps are called as non- elementary reactions.

For non-elementary reactions there is difference between order and stoichiometric coefficient . We observe Non-Elementary reaction as a single reaction rather than elementary reactions in series because the amount of the intermediates formed is negligibly small and cannot be detected.

For the irreversible elementary reaction $aA + bB \rightarrow rR$ The rate equation is $-r_A = k C_A^\alpha C_B^\beta$ For the non elementary reaction $aA + bB \rightarrow rR$ The rate equation (rate law), by analogy with a true simple (or elementary) reaction may be written as $-r_A = k C_A^\alpha C_B^\beta$ Where α and β are the orders with respect to A and B and are found by experimental observations. NOTE: $\alpha \neq a$ and $\beta \neq b$

Difference between elementary and non- elementary reactions •Elementary reactions are single step reactions whereas non elementary reactions are multistep reactions , i.e , such reactions occur through a series of reaction steps. •Elementary reactions are simple in nature whereas the non elementary reactions are complex in nature.

For elementary reactions the order agrees with the stoichiometry whereas for non elementary reaction ,the order does not agrees with the stoichiometry(i.e., there is a difference between order and stoichiometric coefficient) •For an elementary reaction, the order of reaction must be an integer whereas for a non elementary reaction, the order of reaction may be an integer or have a fractional value

For an elementary reaction $2A \rightarrow R$, the rate law is $-r_A = k C_A^2$ whereas for a non elementary reaction $2B \rightarrow S$, the rate law may be $-r_B = k C_A^\alpha C_B$ where $\alpha \neq 2$. • An example of an elementary reaction: $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$ • Examples of non elementary reaction: $H_2 + Br_2 \rightarrow 2HBr$ $CH_3CHO \rightarrow CH_4 + CO$

Representation of Elementary reaction While writing a rate equation we may use any measure equivalent to concentration, e.g., partial pressure of the reacting materials in case of gas phase reaction in which case the rate is given by $-r_A = k p_A^{n_1} p_B^{n_2}$ Remember that the order with respect to a reacting component remains same/unchanged though we use any measure equivalent to concentration only thing is that it will change the numerical value and units of k.

Elementary reactions are represented by an equation showing the molecularity as well as the rate constant. For example, $2A \rightarrow 2S$ represents a bio molecular irreversible reaction with second-order rate constant k , implying that the rate of reaction is $-r_A = r_S = k C_A^2$

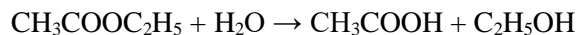
Representation of a non elementary reaction : A non-elementary reaction is the one whose stoichiometry does not match with its kinetics(i.e., for such a reaction there is no direct correspondence between reaction order and stoichiometry). For example, Stoichiometry : $H_2 + Br_2 \rightarrow 2HBr$ Rate : $r_{HBr} = k_1 C_{H_2} C_{Br_2}^{1/2} - k_2 (C_{HBr})^2$.

Topics Covered: Pseudo-first order reaction

Pseudo First Order Reaction.

Some reactions though apparently follow the first order reaction, actual order of these reactions are different from their rate equation. Such reactions are called pseudo first order reaction.

The acid catalyzed hydrolysis of ethyl ester in aqueous medium is first order with respect to ester.



This is a truly second order reaction.

So extrapolating eqn. (d)

$$\text{Therefore, } k = 2.303 / t(a - b) \log b(a - x) / a(b - x)$$

If conc. Of one of the reactants is very high compared to other.

i.e. $b \gg c$.

Therefore, $b - x \approx b$ and $a - b \approx -b$

$$\text{Therefore, } k_b = 2.303 / t(-b) \log b(a - x) / a X b$$

$$k_b = 2.303 / t \log a / a - x$$

$$\text{or, } k' = 1 / t \ln a / a - x$$

Therefore under these circumstances, the reaction will follow first order kinetics.

1. Show that for a first order reaction; the time required for 75% reaction is twice the time for 50% reaction.

Solution :

$$\text{For a first order reaction, } K = 1/t \ln a/(a - x)$$

$$\text{Or, } t = 1/K \ln a/(a - x)$$

$$\text{In the 1}^{\text{st}} \text{ case : } x = 75a/100 = 3/4a$$

$$\text{In the 2}^{\text{nd}} \text{ case : } x = 50a/100 = a/2$$

$$\therefore \text{Time in the 1}^{\text{st}} \text{ case (t}_1\text{)} = 1/K \ln a / a - (3/4a)$$

$$= 1/K \ln 4 = 1/K \ln 2^2 = 2 \ln 2/K$$

$$\begin{aligned} \therefore \text{Time in the 2}^{\text{nd}} \text{ case (t}_2\text{)} &= 1/K \ln a / a - (a/2) \\ &= 1/K \ln 2 = \ln 2/K \end{aligned}$$

Therefore, time for 75% reaction is twice that of 50% reaction.

2. A certain first order reaction is 20% complete in 45 minutes at 20°C. How long will it take to complete 40% of the reaction at 40°C (the energy of activation = 23.03 Kcal / mole)?

Solution :

The first order rate expression is : $K = 1/t \ln a/(a - x)$ [here, $t = \text{time} = 15$ min.]

As the reaction is 20% complete, so $x = 0.2a$

$$\text{Therefore, } K = 1/15 \ln a/(a - 0.2a) = 1/15 \ln a/0.8a = 1/15 \ln 1/0.8 = 1.5 \times 10^{-2} \text{ min}^{-1}$$

Therefore, rate constant at 20°C is $1.5 \times 10^{-2} \text{ min}^{-1}$

According to Arrhenius equation,

$\ln K_2/K_1 = -E/R (1/T_2 - 1/T_1)$ [K_1 & $K_2 =$ Rate constants at 20°C (T_1) & 40°C (T_2) respectively]

$$\begin{aligned} \text{Therefore, } \ln K_2/1.5 \times 10^{-2} &= -23.03 \times 1000/2 \{1/(40 + 273) - 1/(20 + 273)\} \\ &= 2.51 \end{aligned}$$

$$\text{Therefore, } K_2/1.5 \times 10^{-2} = 12.3$$

$$K_2 = 12.3 \times 1.5 \times 10^{-2} \text{ min}^{-1} \text{ at } 40^\circ\text{C}$$

Let the time taken for 40% completion of the reaction at 40°C is t'

$$\begin{aligned} \text{Therefore, } t' &= 1/K \ln a/(a - x) = 1/(1.8 \times 10^{-2}) \ln a/(a - 0.4a) \\ &= 28.4 \text{ minutes} \end{aligned}$$

Lecture 31

Topics Covered: Arrhenius equation, Collision Theory, Transition State Theory

Effect of Temperature on Reaction Rate : Arrhenius Theory

On limited range the rate constant of a reaction increase with increase in temperature and the dependence of rate constant on temperature is usually called Arrhenius equation:

$$k = A e^{-E_a/RT}, \quad d \ln k / dt = E_a / RT^2 \dots\dots\dots (g)$$

Where A = frequency factor which is constant for a particular reaction; E_a = Activation Energy ; R = Universal gas constant

On taking logarithm, it becomes,

$$\text{Log } k = \text{log } A - E_a / 2.303 RT \dots\dots\dots (h)$$

Here, k and T are experimental variables and A and E_a are constant parameters.

Eqn. (h) provides the method to determine E_a by plotting log k against 1/T in a graph where the slope is $E_a / 2.303R$ and so, from the observed slope, the Activation Energy is easily calculated.

Transition State Theory.

Lets take an example, as two reactants XY and Z have to make reaction and Z is forced to come so close to Y that Y can be confused of its origin. The *transition state* of indecision of Y, being attached to both X and Z, though somewhat loosely than before. This complex is called the *activated complex* and energy necessary to push Z to approach Y for creating this transition state or *activated complex* is the energy of activation E_a

Activation Energy.

According to Arrhenious, the molecules must reach up to a certain energy level before entering into chemical transformation. If average energy level of the reactant be E_a and that of product be E_b and even if $E_a > E_b$, then even the reactant molecules will not be transformed into the product unless those must be raised to a minimum energy level E_x for the reaction. The extra energy ($E_x - E_a$) must be acquired by the reactant to be transformed into product and that extra energy is called *activation energy*. Molecules having energy level of E_x are called activated complex and those molecules reside in active state. The following figure elucidates the plot of energy of the system in relation to the reaction coordinate which measures the proceedings of the reactant molecules towards transformation. The reaction co-ordinate is a measure of some physical variations like intermolecular distances, internal vibrations or structural orientations of the reactant molecules, which are involved energy changes in the system. Reaction co-ordinate only gives a qualitative description rather than quantitative value for the conversion of the reactant into products.

It is earlier said that reactant must acquire the energy $(E_x - E_a) = E_1$ to undergo any chemical reaction and after the chemical transformation the product will have the average energy of E_B , then $(E_x - E_B) = E_2$ amount of energy will come out. When $E_2 > E_1$, then the reaction is exothermic, and when $E_2 < E_1$, the reaction must be endothermic. Moreover, in case of reverse reaction the molecules of B must have energy of E_2 by reaching at the energy level of E_x then the activated complex

transformed into the molecules of A and the extra energy $(E_x - E_A) = E_1$ will be given by the activated species.

Lecture 32

Topics Covered: Mathematical problems

WORKED OUT NUMERICAL PROBLEMS

1. Show that for a first order reaction; the time required for 75% reaction is twice the time for 50% reaction.

Solution :

For a first order reaction, $K = 1/t \ln a/(a - x)$

Or, $t = 1/K \ln a/(a - x)$

In the 1st case : $x = 75a/100 = 3/4a$

In the 2nd case : $x = 50a/100 = a/2$

$$\begin{aligned}\therefore \text{Time in the 1}^{\text{st}} \text{ case (t}_1\text{)} &= 1/K \ln a / a - (3/4a) \\ &= 1/K \ln 4 = 1/K \ln 2^2 = 2 \ln 2/K\end{aligned}$$

$$\begin{aligned}\therefore \text{Time in the 2}^{\text{nd}} \text{ case (t}_2\text{)} &= 1/K \ln a / a - (a/2) \\ &= 1/K \ln 2 = \ln 2/K\end{aligned}$$

Therefore, time for 75% reaction is twice that of 50% reaction.

2. A certain first order reaction is 20% complete in 45 minutes at 20°C. How long will it take to complete 40% of the reaction at 40°C (the energy of activation = 23.03 Kcal / mole)?

Solution :

The first order rate expression is : $K = 1/t \ln a/(a - x)$ [here, $t = \text{time} = 15$ min.]

As the reaction is 20% complete, so $x = 0.2a$

Therefore, $K = 1/15 \ln a/(a - 0.2a) = 1/15 \ln a/0.8a = 1/15 \ln 1/0.8 = 1.5 \times 10^{-2} \text{ min}^{-1}$

Therefore, rate constant at 20°C is $1.5 \times 10^{-2} \text{ min}^{-1}$

According to Arrhenius equation,

$\ln K_2/K_1 = -E/R (1/T_2 - 1/T_1)$ [K_1 & K_2 = Rate constants at 20°C (T_1) & 40°C (T_2) respectively]

$$\begin{aligned}\text{Therefore, } \ln K_2/1.5 \times 10^{-2} &= -23.03 \times 1000/2 \{1/(40 + 273) - 1/(20 + 273)\} \\ &= 2.51\end{aligned}$$

$$\text{Therefore, } K_2/1.5 \times 10^{-2} = 12.3$$

$$K_2 = 12.3 \times 1.5 \times 10^{-2} \text{ min}^{-1} \text{ at } 40^\circ\text{C}$$

Let the time taken for 40% completion of the reaction at 40°C is t'

$$\begin{aligned}\text{Therefore, } t' &= 1/K \ln a/(a-x) = 1/(1.8 \times 10^{-2}) \ln a/(a-0.4a) \\ &= 28.4 \text{ minutes}\end{aligned}$$

Therefore, the time for 40% reaction at 40°C is 28.4 minutes.

3. Calculate activation energy of a reaction whose rate constant is doubled when T is increased from 300 K to 310 K.

Solution :

According to Arrhenius equation : $\ln K_2/K_1 = e - E/R(1/T_2 - 1/T_1)$

Suppose, the rate constant at 300K is K_1

So the rate constant at 310K is $2K_1$

Therefore, $\ln 2K_1/K_1 = -E/R(1/310 - 1/300)$

$$= E \times 10 / (1 \times 310 \times 300) \quad [R = 2 \text{ cal}]$$

Therefore, $\ln 2 = E / (2 \times 31 \times 300)$

$$\text{Or, } E = 0.693 \times 2 \times 31 \times 300$$

$$\text{Or, } E = 12889.8 \text{ cal} = 12.9 \text{ Kcal.}$$

Therefore, the activation energy of the reaction is 12.9 Kcal.

4. The rate constant of a certain reaction is found to be doubled when temperature is raised from 27°C to 37°C . What is the activation energy ?

Solution :

According to Arrhenius equation :

$$\ln K_2/K_1 = -E/R [1/T_2 - 1/T_1]$$

Suppose, the rate constant at 27°C is K₁

Therefore, the rate constant at 37°C is 2K₁

$$\therefore \ln 2K_1/K_1 = -E/R [1/310 - 1/300]$$

$$= E \times 10 / (2 \times 310 \times 300) \quad [R = 2 \text{ cal }]$$

$$\therefore \ln 2 = E / (2 \times 31 \times 300)$$

$$\text{Or, } 0.693 \times 2 \times 31 \times 300 = E$$

$$\therefore E = 12889.8 \text{ cal} = 12.9 \text{ Kcal}$$

\therefore The activation energy of the reaction is 12.9 Kcal

5. The specific rate constant for the second order neutralization of nitro propane by a base is given by $\log K = 11.899 - (3163/T)$, where concentration is in mole litre⁻¹ and time in minutes. Initial concentration of both reactant is 0.005 M. Calculate :

(i) The energy of activation.

(ii) $t_{1/2}$ at 25°C.

Solution :

According to Arrhenius equation, $K = Ae^{-E/RT}$

$$\text{Or, } \log K = \log A - E/2.303R \times 1/T$$

So, the given equation is $\log K = 11.899 - 3163/T$

Comparing these two equations, $E/2.303R = 3163$

$$\text{Therefore, } E = 14569 \text{ cal}$$

So, after putting $T = 25^\circ\text{C}$ in the given equation, $\log K = 11.899 - 3163/298 = 1.28$

Therefore, $K = 19.27 \text{ min}^{-1}$

Now the $t_{1/2}$ for a second order reaction when both the reactions have same initial concentration = $1/aK$

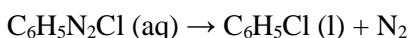
So, $t_{1/2} = 1/(0.005 \times 19.27) = 10.4 \text{ minutes.}$

Therefore, the activation energy is 14569 cal and $t_{1/2}$ at 25°C is 10.4 minutes.

MODEL QUESTIONS:

Multiple Choice Question (MCQ)

1. (i) Z, a Pitzer Correlation for compressibility factor is a function of
(a) temperature only, (b) reduced temperature and reduced pressure, (c) reduced pressure only, (d) pressure only.
- (ii) The dimensionless ratio fugacity coefficient is represented by
(a) f_i/P , (b) f_i/T , (c) f_i , (d) $f_i XP$.
- (iii) Work done in a reversible process is
(a) greater than (b) less than (c) equal to (d) not comparable to irreversible work done.
- (iv) Which of the following mathematical expression is true
(a) $G = U-TS$ (b) $G=H-PS$ (c) $G=H-TS$ (d) $G=H-VS$
- (v) In a pressure vs temperature diagram sublimation curve separates
(a) solid & liquid, (b) liquid & gas, (c) solid & gas, (d) solid, liquid & gas region.
- (vi) Hydrolysis of ethyl acetate follows the
(a) 1st order reaction kinetics, (b) 2nd order reaction kinetics, (c) zero order reaction kinetics, (d) pseudo 1st order reaction kinetics
- (vii) The order of a reaction is:
(a) experimentally determined quantity, (b) always a whole number, (c) theoretical concept, (d) obtained from balanced stoichiometric equations
- (viii) The decomposition of benzene diazonium chloride follows first order kinetics:



The rate constant for this reaction is 0.105 s^{-1} at 10°C . Starting with a concentration of 0.066 M of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, calculate its concentration after 15 seconds.

- (a) 0.0083 M , (b) 0.32 M , (c) $5.3 \times 10^{-7} \text{ M}$, (d) 0.014 M , (e) 0.037 M
- (ix) The time required to reduce the concentration of a reactant from 0.02 M to 0.01 M is 15 sec. and from 0.01 M to 0.005 M is also 15 sec. The order of the reaction is
(a) zero, (b) 1st, (c) 2nd, (d) 3rd
- (x) The expression for $t_{1/2}$ for 2nd order reaction, where the two reactants are same is:
(a) $t_{1/2} = 1/k$, (b) $t_{1/2} = a/k$, (c) $t_{1/2} = ka$, (d) $t_{1/2} = 1/ka$
- (xi) The unit of isothermal compressibility is (a) K^{-1} , (b) bar^{-1} , (c) $^\circ\text{C}$, (d) bar
- (x) For Isobaric process
(a) $G/\square T = P$ (b) $\square G/\square T = P$ (c) $\square G/\square T = S$ (d) $\square G/\square T = -S$
- (xi) Adiabatic process does not permit

- c) for molar solution
d) for normal solution
- (xxviii) At bubble point
- a) vapour phase ceases to exist
b) liquid phase ceases to exist
c) both liquid & vapour phases co-exist
d) none of these
- (xxix) Activity coefficients are functions of
- a) temperature
b) liquid phase composition
c) both a & b
d) none of these
- (xxx) K value for Raoult's law is
- a) P_1^{sat}/P
b) $\gamma_i P_1^{\text{sat}}/P$
c) y_i/x_i
d) both a & b

SHORT QUESTION

1. Explain the term energy of activation. How the energy of activation of a reaction is determined?
2+3
2. What do you understand by the term order of a reaction? Write an expression for the third order reaction. A first order reaction is 40 % complete at the end of 50 min. Calculate the value of rate constant. In what time will the reaction be 80% complete?
(1+1+3)
3. What is pseudo unimolecular reaction? By taking an example show that the specific reaction rate of a pseudo unimolecular reaction follows a first order kinetics. Give an example of zero order reaction.
(1+3+1)
4. Define coefficient of performance of a refrigeration cycle. Derive an expression for the amount of heat absorbed by the regenerator.
2+3
5. Determine the molar volume of n- butanol at 510K and 25 bar by
(a) Ideal gas equation
(b) Generalized compressibility factor correlation,
Given $Z^0=0.865$, $Z^1=0.038$, $\omega=0.2$ 5
6. For the system methanol (1)/ methyl acetate (2) the following equations provide a reasonable correlation for the activity coefficients :
 $\ln \phi_1 = Ax_2^2$, $\ln \phi_2 = Ax_1^2$, $A = 2.771 - 0.00523T$
Calculate P, $\{y_i\}$, for $T = 318.15K$, $x_1 = 0.25$, $P_1^{\text{sat}} = 44.51kPa$, $P_2^{\text{sat}} = 65.64 kPa$ 5
7. What are the assumptions of Raoult's law for VLE? What are the limitations of Raoult's law? How Henry's law overcomes the limitations of Raoult's law?
1.5+1.5+2
8. State and explain Arrhenius theory. (5)
9. In a 2nd order reaction the initial concentration of the reactant is 0.2 moles/ L. The reaction is found to be 30% complete in 50 min. Calculate:

- (i) the rate constant
(ii) half life period
(iii) the time required to complete 75% of the reaction. (5)

10. Explain Henry's law. Assuming that carbonated water contains CO₂ (1) and H₂O(2). Determine the composition of the vapour and liquid phases in a sealed can of "soda" and the pressure exerted on the can at 10 °C (283.15K). Henry's constant for CO₂ in water at 10°C is about 990 bar. 2+3

11. What is Reduced Temperature (T_r) and Reduced Pressure (P_r). Define Acentric factor (Z_c). How Z_c is related to T_r and P_r. 1+1+1+2=5

12. prove that C_p- C_v=R 5

13. A chemical reaction yielded the following concentration change with the time

Time(S)	0	184	319	526	867	1198	1877	2315	3144
Conc(mole /L)	2.33	2.08	1.91	1.67	1.36	1.11	0.72	0.55	0.34

Determine i) order of the reaction ii) rate constant of the reaction iii) time required for completion of 60 % reaction. 5

Long answer type questions (LQ)

1. State and explain Duhem's theorem. Binary system acetonitrile (1)/ nitromethane (2) conforms closely to Raoult's law. Vapour Pressures for the pure species are given by the following Antoine equations:

$$\ln P_1^{\text{Sat}}/\text{Kpa} = 14.2724 - 2945.47/T - 49.15$$

$$\ln P_2^{\text{Sat}}/\text{Kpa} = 14.2043 - 2972.64/T - 64.15$$

Prepare a graph showing P Vs. X₁ & P vs Y₁ for a temp of 348.15 K (75°C) 5+10

2. What is the difference between order and molecularity? Name the controlling factors of reaction rate.

(b) Show that for a first order reaction the time required for 75% reaction is twice the time required for 50% of the reaction.

(c) The optical rotations of sucrose in 0.5 (N) HCl at various time intervals are given below:

Time (mins.)	0	10	20	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+19.6	-11.1

Show that the reaction is of first order.

(4+2+4+5=15)

3. (a) Deduce the expression for first order kinetics. Show that the time for half decomposition of a first order reaction is independent of the initial concentration of the reactant. Explain the transition state theory for a reaction.

(b) A certain substance R_1 is mixed with an equal moles of another substance R_2 . At the end of 30 seconds, R_1 , is 25% reacted. How much of R_1 and R_2 be left untreated at the end of 35 seconds, if the reaction is-

(i) First order in R_1 and independent of R_2 ;

(ii) First order in both R_1 and R_2 .

(4+2+4+5)

4. (a) The specific reaction rates of a chemical reaction at 25°C and 30°C are 4×10^{-5} and $14 \times 10^{-5} \text{ s}^{-1}$ respectively.

(i) Find the activation energy of this reaction

(ii) Calculate Arrhenius frequency factor.

(b) A first order chemical reaction is found to have an activation energy (E_A) of 250 kJ/ mole and a pre-exponential (A) of $1.7 \times 10^{14} \text{ S}^{-1}$.

Determine: i) the rate constant at 750°C , ii) What fraction of reaction will be completed at 600°C in a period of 10 minutes?

(7+8=15)

5. Explain with diagram the Linde and Claude Liquefaction process. Write short note on choice of refrigerants.

(5+5+5)

6. Explain vapour compression refrigeration cycle with diagram. What is the difference between vapour compression and absorption refrigeration cycle?

Consider refrigeration at temperature level of $T_C=263.15\text{K}$ with a heat source available at atmospheric pressure ($T_H=373.15\text{K}$). Calculate COP of absorption refrigeration cycle if surroundings temperature is 303.15K .

(7+5+3)

7. Prove that $dV/V = \beta dT - \kappa dP$

For acetone at 293.15K (20°C) and 1 bar

$$\beta = 1.487 \times 10^{-3} \text{ K}^{-1}$$

$$\kappa = 62 \times 10^{-6} \text{ bar}^{-1}$$

$$V = 1.287 \times 10^{-3} \text{ m}^3/\text{kg}$$

Find:

(i) The value of $(\partial P / \partial T)_V$

(ii) The pressure generated when acetone is heated at constant volume from 293.15K (20 °C) and 1 bar to 303.15K (30 °C).

(iii) The volume change when acetone is changed from 293.15K (20 °C) and 1 bar to 273.15K (0 °C) and 10 bar. 3+(4+4+4)=15

8. Write two forms of Virial equations. Write also those equations truncated to two terms.

Reported values for the virial coefficients of isopropanol vapor at 473 K (200 °C) are : B= -0.388 m³/kmol, C= -26x 10⁻³ m⁶/kmol. Calculate V and Z for isopropanol vapor at 473 K (200 °C) and 10 bar by :

(a) Ideal gas equation

(b) First virial equation truncated to two terms

(C) Second virial equation truncated to two terms (1.5+1.5)+3+3+3=15

9. (a) State the condition of stability for a single- Phase binary system.

(b) Develop equations that apply to the limiting case of binary LLE for which the α-Phase is very dilute in species 1 & the β-Phase is very dilute in species 2.

(a) Show by stability analysis that LLE is predicted by the expression:

$$G^E/RT = AX_1.X_2 \quad A \geq 2 \quad \text{3+6+6}$$