CH365 Chemical Engineering Thermodynamics

Lesson 31
Two-Phase Systems, Thermodynamic Diagrams, and Property Tables

Lessons 28-30 Recap

- Mathematical structure of thermodynamics from Maxwell using Gibbs Energy "generating function."

- Developed residual (departure) properties G^R, H^R, and S^R and how to calculate them.

- Discussed how to combine residual (departure) properties G^R, H^R, and S^R with ideal properties G^{ig}, H^{ig}, and S^{ig} to generate real properties G, H, and S.

- Generalized methods – Lee-Kesler Tables and Virial Equation

Today's Agenda

- Phase equilibria and how to handle liquids.

- Where does "Antoine equation" come from?

P^{sat} is vapor pressure in kPa and T is temperature in °C

$$\ln P^{sat} = A - \frac{B}{T + C}$$ (Eq. 6.76)

A, B, and C are constants in Table B.2 on page 682

Used in flash and distillation calculations – Raoult's Law

Fundamental Property Relations

Property relations for a homogenous fluid of constant composition:

$dU = TdS - PdV$ (Eq.6.8)	$dH = TdS + VdP$ (Eq. 6.9)
$dA = -PdV - SdT$ (Eq. 6.10)	$dG = VdP - SdT$ (Eq. 6.11)

- consider a closed 2-phase system
- phases are α and β
- constant T and P
- Gibbs energy is the "driving force" for phase change

$dG = 0$ for the system $\alpha + \beta$

$dG^{\alpha} = dG^{\beta}$

$G^{\alpha} = G^{\beta}$ (Eq. 6.83)

$\Delta H = Q$

$\Delta S = \dfrac{Q}{T} = \dfrac{\Delta H}{T}$

$\Delta G = \Delta H - T\Delta S = \Delta H - T\dfrac{\Delta H}{T} = 0$

- **Postulate: $G^{\alpha} = G^{\beta}$ is the fundamental condition for equilibrium**

A vapor initially in equilibrium with its liquid undergoes a differential amount of evaporation.

$$dG = VdP - SdT$$

(Eq. 6.11)

$$dG^\alpha = dG^\beta$$

$$V^\alpha dP - S^\alpha dT = V^\beta dP - S^\beta dT$$

For a differential amount of evaporation, dP and dT approach zero but are not zero

$$V^\alpha dP^{sat} - S^\alpha dT = V^\beta dP^{sat} - S^\beta dT$$

$$V^\alpha dP^{sat} - V^\beta dP^{sat} = S^\alpha dT - S^\beta dT$$

$$\left(V^\alpha - V^\beta\right)dP^{sat} = \left(S^\alpha - S^\beta\right)dT$$

$$\frac{dP^{sat}}{dT} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

$$dH = TdS + VdP$$

(Eq. 6.9)

Consider for transition from α to β
Integrate at constant T and P
(pressure term goes away).

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \quad \text{(Eq. 6.84)}$$

Benoit Clapeyron, 1799-1864
(image from Wikipedia)

$$\Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \quad \text{(Eq. 6.84)}$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

Clapeyron Equation

(Eq. 6.85)

Transition from liquid l to vapor v
(change α and β to l and v)

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \Rightarrow \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$ (Eq. 6.86)

$$Z \equiv \frac{PV}{RT}$$ ⟹ $$\Delta Z^{lv} = \frac{P^{sat}\Delta V^{lv}}{RT}$$ ⟹ $$\Delta V^{lv} = \frac{RT}{P^{sat}}\Delta Z^{lv}$$ $$\Delta Z^{lv} = \text{change in Z on vaporization}$$

(P^{sat} and T are constant in phase change)

(from roots of cubic EOS)

$$\frac{dP^{sat}}{dT} = \frac{P^{sat}\Delta H^{lv}}{RT^2\Delta Z^{lv}}$$

$$\frac{dP^{sat}}{dT}\frac{1}{P^{sat}} = \frac{\Delta H^{lv}}{RT^2\Delta Z^{lv}}$$

$$d\ln P^{sat} = \frac{1}{P^{sat}}dP^{sat}$$ $$\frac{d\ln P^{sat}}{dT} = \frac{\Delta H^{lv}}{RT^2\Delta Z^{lv}}$$ (Eq. 6.87)

$$d(1/T) = -\frac{1}{T^2}dT$$ $$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}}$$ (Eq. 6.88)

T-Dependence of Vapor Pressure

(Eq. 6.88)

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}}$$

(Eq. 6.89)

Integrate: $$\ln P^{sat} = A - \frac{B}{T}$$

- Plot of $\ln P^{sat}$ vs $1/T$ is straight line
- A and B are constants determined from regression.
- Valid from triple point to critical point

(Eq. 6.90)

$$\ln P^{sat} = A - \frac{B}{T+C}$$

- Antoine Equation
- Addition of constant "C"
- Constants in Table B.2

(Eq. 6.91)

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau}$$

$$\tau = 1 - T_r$$

- Wagner Equation
- Best available
- Constants in Reid, Prausnitz, and Poling, *The Properties of Liquids and Gases*, 4th ed., McGraw-Hill, 1987

Total Properties from Δ's

Two-Phase Liquid/Vapor Systems

For any extensive property, such as total volume nV:

$$nV = n^{liquid}V^{liquid} + n^{vapor}V^{vapor} = n^l V^l + n^v V^v$$

V = molar volume

$$n = n^l + n^v$$

$$\frac{n}{n} = \frac{n^l}{n} + \frac{n^v}{n}$$

$$\frac{nV}{n} = \frac{n^l V^l}{n} + \frac{n^v V^v}{n}$$

$$1 = x^l + x^v$$

$$V = x^l V^l + x^v V^v$$

$$V = \left(1 - x^v\right)V^l + x^v V^v$$

$$x^v \equiv \text{quality of vapor}$$

$$M \equiv V, U, H, S, \text{etc.}$$

$$M = \left(1 - x^v\right)M^l + x^v M^v \qquad \text{(Eq. 6.96a)}$$

$$M = M^l + x^v \Delta M^{lv} \qquad \text{(Eq. 6.96b)}$$

Homework

Problem 6.14

Estimate the entropy changes of vaporizations of benzene at 50 deg C. The vapor pressure of benzene is given by the equation

$$\ln\left(P^{sat}/kPa\right)=13.8858-\frac{2788.51}{\left(t/degC\right)+220.79}$$

(a) Use Eq. 6.86 with an estimated value of ΔV^{lv}.
(b) Use the Clausius-Clapeyron equation from Example 6.6.

Report your answers in J/(mol-K).

Problem 6.28

What is the mole fraction of water vapor in air that is saturated with water at 25 deg C and 101.33 kPa?

At 50 deg C and 101.33 kPa?

Problem 6.83

(mixtures)

An equimolar mixture of methane and propane is discharged from a compressor at 5,500 kPa and 90 deg C at a rate of 1.4 kg/sec. If the velocity in the discharge line is not to exceed 30 m/sec, what is the minimum diameter of the discharge line?

Use pseudocritical parameters from equations 6.78-6.82 along with the SRK equation. (Don't use the API method.)

Problem 6.25

Steam at 2,100 kPa and 260 deg C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

Study example 6.9 closely first

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Interpolation of points in steam tables

(x,y) is between (x_1,y_1) and (x_2,y_2)

$$\frac{y - y_1}{x - x_1} = \frac{y_2 - y_1}{x_2 - x_1}$$ (x_1,y_1) and (x_2,y_2) are known

$$\frac{x - x_1}{x_2 - x_1} = \frac{y - y_1}{y_2 - y_1}$$ either x or y is known and the other is calculated

Remember slope is constant between two points