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

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

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 $\alpha + \beta$

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

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

$$\Delta H = Q$$

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

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

- **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)

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

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

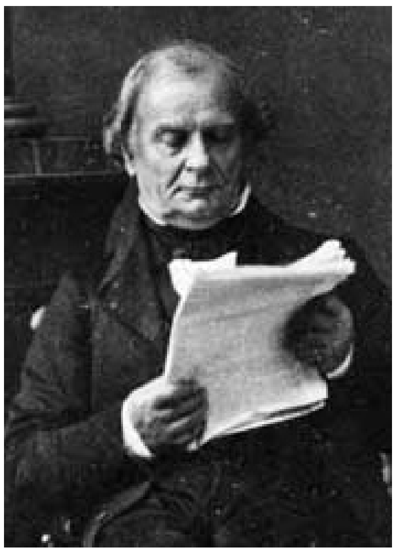
For a differential amount of evaporation, dP and dT approach zero but are not zero

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

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

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

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



Benoit Clapeyron, 1799-1864
(image from Wikipedia)

$$dH = TdS + VdP$$

(Eq. 6.9)

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

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

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

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

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)

$$Z \equiv \frac{PV}{RT} \Rightarrow \Delta Z^{lv} = \frac{P^{sat}\Delta V^{lv}}{RT} \Rightarrow \Delta V^{lv} = \frac{RT}{P^{sat}}\Delta Z^{lv}$$

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

ΔZ^{lv} = change in Z on vaporization
(from roots of cubic EOS)

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

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

$$\frac{1}{P^{sat}}dP^{sat} = d\ln P^{sat}$$

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

$$d(1/T) = -\frac{1}{T^2}dT$$

$$dT = -T^2 d(1/T) = -\frac{1}{T^2}dT$$

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}}$$ (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**
- Improved version.
- Addition of constant "C"
- Constants in Table B.2

Total Properties from Δ’s

Two-Phase Liquid/Vapor Systems

For any extensive property, such as total volume nV:

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

V = molar volume

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

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

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

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

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

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

$x^v \equiv$ quality of vapor

$M \equiv$ V, U, H, S, etc.

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

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

Questions?