ENGG 201

What is Going On with Vapours + Liquids?
(A Brief Outline of What is Important in Ch 7)

Chapter 7 – Liquids

Main Concepts:

1. Volumetric Behaviour of Liquids (Section 7.2)
   a. How are the VOLUME, TEMPERATURE and PRESSURE related for Liquids?

*** 2. Energy Effects in Liquids (Section 7.3)
   a. How are the VAPOR PRESSURE, LATENT HEAT OF VAPORAZATION and TEMPERATURE related for Liquids?

Things to Remember:

Volumetric Behavior of Liquids

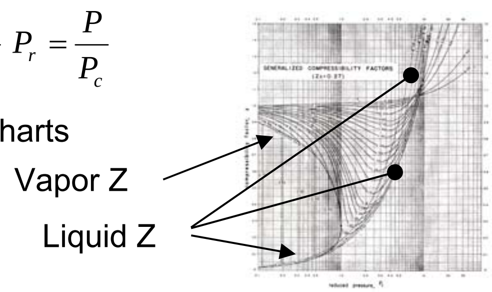
1. Effect of Pressure and Temperature (Individually) on Volume
   a. Isothermal Compressibility $\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\Delta V/V}{\Delta P}$
   b. Effect of Temperature $V_T = V_{T_o}\left(1 + A\theta + B\theta^2 + C\theta^3\right)$ (Table 7-2)
   c. Effect of Pressure (Tait's Law)

   $$\beta_T = \frac{c}{P+d} \qquad \frac{V_o - V}{V_o} = c\ln\left[\frac{P+d}{d}\right]$$ (Table 7-1)

   d. WATCH UNITS (1 Pa = 1 N/m^2)
2. van der Waals equation of State
   a. Liquid volume is smallest of 3 positive roots ($T<T_c$).
3. Corresponding States $PV_m = ZRT$ and $T_r = \frac{T}{T_c}$ $P_r = \frac{P}{P_c}$
   a. Z from Generalized Compressibility Charts

(arrows = vapor and liquid in equilibrium $P_r<1$)

(circles = liquid alone) (mostly $P_r>1$)



Energy Effects in Liquids (Vapor Pressure)

4. Specific Heat (C_p or C_v) can be used to calculate changes in temperature or energy added or removed (<u>no phase change</u>) with $\Delta E = mC\Delta T$ or $\Delta E = nC\Delta T$ (watch units).
5. Latent Heat of Vaporization (ΔHv) can be used to calculate energy added or removed (<u>phase change</u>) with $\Delta E = m\Delta H_v$ or $\Delta E = n\Delta H_v$ (watch units).
6. Vapor Pressure changes with Temperature
7. Latent Heat of Vaporization changes with Temperature
8. Normal boiling point means that P_v = 101.325 kPa
9. Vapor Pressure Correlations
   a. (Clausius Clapeyron) (if given V_g and V_l) $\frac{dP}{dT} = \frac{\Delta Hv}{T(V_g - V_l)}$
   b. Low Pressure (Ideal Gas Assumption) (P_v < 2 atm)
   $$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta Hv}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
   c. High Pressure (No Ideal Gas) (P_v > 2 atm)
   $\ln(P) = -\frac{A}{T} + C$ and A = $\frac{\Delta Hv}{R}$ only if T_1 and T_2 are close together

10. Trouton's Rule – Last resort to relate Normal Boiling Point to Latent Heat of Vaporization $\frac{\Delta Hv}{T_b} = 88 kJ/kmol$
11. Liquid composition given by x_i and vapor composition given by y_i
12. Mixtures – Raoult's Law $Pv_i x_i = Py_i = \overline{p}_i$
13. <u>Bubble Point Pressure above a Liquid Mixture</u>
    a. Known x_i values → Perform a ∑ y_i = 1.0 where $y_i = \frac{Pv_i x_i}{P}$ and solve for P
    b. Can then calculate vapor composition using $y_i = \frac{Pv_i x_i}{P}$

14. <u>Dew Point Pressure of a Vapor Mixture</u>
    a. Known y_i values → Perform a ∑ x_i = 1.0 where $x_i = \frac{y_i P}{Pv_i}$ and solve for P
    b. Can then calculate liquid composition using $x_i = \frac{y_i P}{Pv_i}$
15. Mixtures – Henry's Law (for gases dissolved in liquids) $H_i x_i = \overline{p}_i$
    a. Binary mixtures $H_1 x_1 + Pv_2(1 - x_1) = P$

<u>Examples of Typical Problems:</u>

Volumetric Behavior of Liquids

1. Given P, T, calculate V. (If using Tait's Law – always do effect of T first (low P), then effect of P) – you will be given c, d for Tait's law
2. After calculating V, may have to further calculate dimensions of container or mass/moles of substance in container.
3. More … (See old finals).

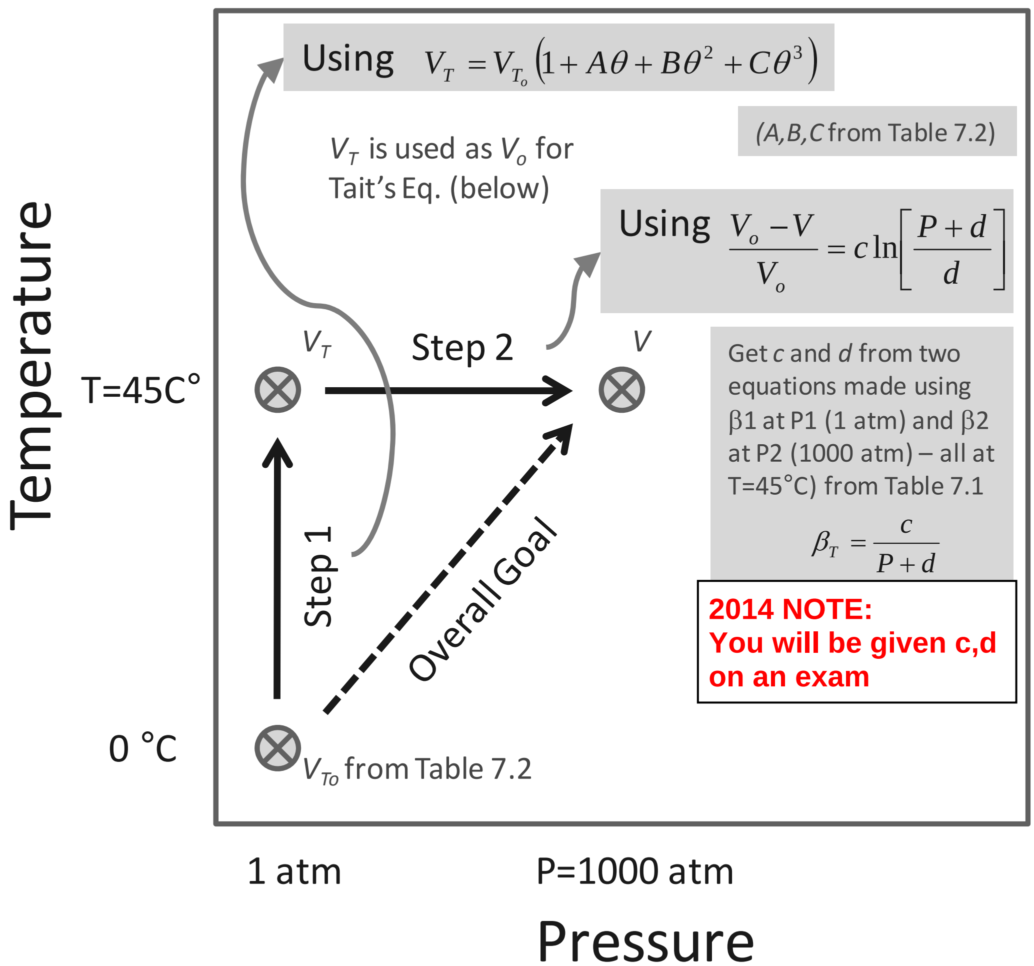
Energy Effects in Liquids (Vapor Pressure)

4. Given P_1, T_1, and P_2, T_2 derive equation for vapor pressure as a function of temperature.
5. Given P_1, T_1, and ΔHv derive equation for vapor pressure as a function of temperature.
6. Use correlations (given or derived) to calculate P at a certain temperature.
7. Use correlations (given or derived) to calculate ΔHv at a certain temperature.
8. Given liquid mixture, calculate bubble point pressure and corresponding vapor composition.
9. Given vapor mixture, calculate dew point pressure and corresponding liquid composition.
10. Given fixed amount of liquid, and energy input, calculate change in temperature or amount of phase change.
11. Given change in temperature or amount of phase change, calculate energy input.
12. More … (See old finals).

ENGG 201 – Example 7.2

Main Concept: Given P, T, calculate V (specific volume) of a liquid. If using Tait's Law, this is done by using a reference volume, and then correcting for how different the temperature and pressure are from the reference conditions (always do effect of T first (low P), then effect of P). Watch the units (1 Pa = 1 N/m^2).

Example 7.2: Calculate V at T and P. Only V we are given is in Table 7.2 at 1 atm and 0°C. First we correct the V to 45°C using $V_T = V_{T_o}\left(1 + A\theta + B\theta^2 + C\theta^3\right)$ and Table 7.2, and then we correct for P using Tait's law $\frac{V_o - V}{V_o} = c\ln\left[\frac{P+d}{d}\right]$ and Table 7.1 (getting c,d at T by using two β_T values (at the correct T) at 1 atm and 1000 atm).



Example Problem 7-2

Calculate the specific volume of liquid benzene at 45°C and 1000 atm.

Solution

In Table 7-1, two values for β_T are known at 45°C. At 1 atm pressure, $$\beta_1 = 11.32 \times 10^{-10}\ \frac{m^2}{N} \text{ or } 1.147 \times 10^{-4}\ atm^{-1}$$ and at 1000 atm pressure, $$\beta_2 = 5.5 \times 10^{-10}\ \frac{m^2}{N} \text{ or } 0.5572 \times 10^{-4}\ atm^{-1} \quad .$$ We can evaluate the parameters c and d at 45°C from Equations 7.15 and 7.16. Equation 7.8 then becomes $$\beta_{45°C} = \frac{0.1083}{P + 942.8}$$	**2014 NOTE: You will be given c,d on an exam and will not have to do this step (getting c,d from two values of P and β)**

where P is in atmospheres and $\beta_{45°C}$ is in atm^{-1}. The Tait equation of state for benzene at 45°C can now be expressed as

$$V = V_o \left[1 - 0.1083 \ln \frac{942.8 + P}{942.8}\right]$$

where the liquid volume at low pressure and 45°C, V_o, has yet to be determined. From the data in Table 7-2 and from Equation 7.7,

$$V_o = 1.1109 \times 10^{-3}\,(1.000 + 1.17626 \times 10^{-3}\,\theta + 1.27755 \times 10^{-6}\,\theta^2 + 0.80648 \times 10^{-8}\,\theta^3) \quad .$$

When $\theta = 45°C$,

$$V_o = 1.1109 \times 10^{-3}\,(1.000 + 0.0529 + 0.0026 + 0.0007) m^3/kg$$
$$= 1.173 \times 10^{-3}\ m^3/kg \quad .$$

(Note that the specific volume of liquid benzene at 0°C is $1.1109 \times 10^{-3}\ m^3/kg$. A 45°C change in temperature produces a 5.62% change in specific volume at 1 atm pressure.)

On substitution for V_o in Tait's equation,

$$V = 1.173 \times 10^{-3} \left[1 - 0.1083 \ln \frac{942.8 + P}{942.8}\right] \quad .$$

From this expression, V is calculated to be $1.081 \times 10^{-3}\ m^3/kg$ at 1000 atm pressure.

It is interesting to note that a 45°C increase in temperature at 1 atm causes a volume increase of 5.6 percent while an increase in pressure from 1 to 1000 atm effects a 7.8 percent decrease in volume at 45°C. The net effect is therefore a 2.7 percent decrease in volume from the original conditions.

Table 7-1 Isothermal Compressibilities of Selected Liquids

Liquid	Temperature °C	$\beta \times 10^{10}$, m^2/N 1 atm	1000 atm
Benzene	25	9.67	5.07
	35	10.43	5.28
	45	11.32	5.50
	55	12.29	5.73
	65	13.39	5.98
Carbon-tetrachloride	25	10.67	5.30
	35	11.95	5.52
	45	12.54	5.75
	55	13.63	5.97
	65	14.87	6.22
n Hexane	0	13.04	5.92
	25	16.06	6.51
	40	18.31	6.89
	60	21.93	8.87
Mercury	20	0.40	0.39
Water	25	4.57	3.46
	35	4.48	3.42
	45	4.44	3.40
	55	4.44	3.42
	65	4.48	3.47

Table 7-2 Coefficients of Cubical Expansion of Liquids at 1 atm, $T_o = 0°C$

	$A \times 10^3$	$B \times 10^6$	$C \times 10^8$	$V_{T_o} \times 10^3$ m^3/kg
Acetone	1.324	3.809	−0.87983	1.230
Benzene	1.17626	1.27755	0.80648	1.1109
Carbon-tetrachloride	1.18384	0.89881	1.35135	0.6126
Mercury	0.18169	0.00295	0.01146	0.07356
Water	−0.05325	7.6153	−4.3722	1.00013
n - Pentane	1.50697	3.435	0.975	1.549