# 7. Liquids

## Sections covered in detail

## Sections omitted

## Sections covered very briefly

## *7.1 Liquid State*

So far we have examined the properties of gases, both ideal gases and real gases. Gas molecules, in general enjoy complete freedom to move around. Early on we touched on crystalline solids, which involve fixed geometric patterns with virtually no mobility of molecules.  The liquid state is in between the gaseous state and the solid state. Liquid molecules can move, but their movement is strongly influenced by forces exerted by other molecules.  Gas molecules are like a few skaters on a large ice surface, they can move freely at high speed.  Liquid molecules are like pedestrians on a crowded street, they can move but, often they are slowed down by other pedestrians.  Molecules in a solid are like people packed tightly into a small room. They really have to work hard to move around.

**Triple Point** -- where V, L, and S can co-exist

**Critical Point** -- where L and V are "indistinguishable"

A critical point for solid and liquid, i.e. where the solid and liquid properties would be indistinguishable, has not located even at very high pressures.  We can assume that such a point does not exist.

## 7.1.1 Models for the Liquid State

Liquid state can be viewed as a modified gaseous state, because of many gross similarities.  However, there are significant differences in terms of molecular packing, which is closer to that in solids.  Also over a very short time span, some form of structural patterns may be found in liquid state, but none in gaseous state.

Thus, in some ways liquids are like solids, but for most situations, liquids are similar to gases.

## 7.1.2 The Glassy State and Liquid Crystals

**Glassy State** -- a metastable state that has liquid like structure but solid like properties.

- Like solids, glasses hold their shape and do not flow.
- There is no crystalline structure -- no clevage planes.
- Glasses do not melt at a constant temperature, they gradually soften with increase in temperature.

Glass Point  -- below this transition temperature, a glassy substance may accomplish a transition to crystalline structure.

**Liquid Crystals** -- behave neither as true liquids nor as true solids.

Liquid crystals are large complex molecules (mostly organic) that can pack together in sheets or cylinders.  Such materials have become industrially important only recently with widespread application in display devices, such as watches, calculators, computer screens etc.

The packing arrangement of liquid crystals can change with application of small amounts of external stimulation in the form of electromagnetic potential or heat. It is this property of liquid crystals that makes them useful in display applications.  The change in packing arrangement results in change of optical properties that may be reflected in a change of colour or change of light absorption characteristics.

## *7.2 Volumetric Behaviour of Liquids.*

Compared to gases, liquids are a lot harder to compress, but their volume does change with pressure.

### **Isothermal Compressibility, $\mathbf{b}_T$**

Isothermal compressibility is defined as the fractional change in volume per unit change in pressure at constant temperature. The volume of a given mass of liquid is a function of temperature and pressure, i.e. $V = f(P,T)$

At constant temperature, the volume is a function of pressure alone.

$V = f(P)$     when $T = $ Constant.

The functional relationship shown above, i.e. $V = f(P)$, can be differentiated with respect to P to obtain the rate of change of volume with pressure. This differential divided by the volume is equal to the isothermal compressibility.

$$b_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

The negative sign reflects the fact that volume decreases with increasing pressure (without the negative sign, compressibility will be negative).

The units of $\beta_T$ are $Pa^{-1}$ or $m^2/N$. Typical values of liquid compressibility are listed in Table 7-1.

Note that this table lists values of $\beta$ multiplied by $10^{10}$. The actual compressibility values are very small. Compressibility of benzene at 25 $^{\circ}C$ and 1 atm. Pressure is listed as

$\beta_T = 9.67 \times 10^{-10}$ $Pa^{-1}$ or $m^2/N$

If you increase the pressure from 1 atm to 2 atm, the change in volume will be given by

$$\frac{\Delta V}{V} = -b_T \,\Delta P$$

The change in pressure is 1 atm = 101.325 kPa.

**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 |

Therefore the fractional change in volume is

$$\frac{\Delta V}{V} = -b_T \, \Delta P = -9.67 \, x10^{-10} \, x101.325 x10^3$$

$$= 0.98 x10^{-4}$$

$$or \approx 0.0001$$

An ideal gas would have shrunk by 50% with same increase in pressure!

## Effect of Temperature on Liquid Volume

At constant pressure, liquid volume increases with increasing temperature. The isobaric coefficient of thermal expansion, $\alpha_P$ is defined as

$$a_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \approx \left(\frac{\Delta V / V}{\Delta T}\right)_P$$

For many liquids, $\alpha_P$, remains constant over a range of temperatures. When this is the case, the volume of liquid at any temperature can be related to its volume at a reference temperature by

$$V(T) = V_o\left[1 + a_P(T - T_o)\right]$$

Where,
V(T) = Volume at temperature T
$V_o$ = Volume at temperature $T_o$
$T_o$ = Reference temperature

Note that [V(T) -$V_o$) = $\Delta V$] and [(T-$T_o$) = $\Delta T$]. Therefore the above relationship is equivalent to

$$\Delta V = V_o a_P \Delta T$$

## Effect of Temperature on Pressure at Constant Volume

When temperature is increased at constant volume, i.e. in a situation where the volume increase is not allowed, the temperature increase causes the pressure to go up. The pressure coefficient is defined as,

$$g_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \approx \left(\frac{\Delta P / P}{\Delta T}\right)_V$$

The three parameters defined above are related by

$$g_V = \frac{a_P}{P b_T}$$

## 7.2.1 Thermal Expansion of Liquids

We earlier saw a simple equation for volume of liquid at any temperature in terms of its volume at a reference temperature, which was based on the assumption of constant coefficient of thermal expansion. However, the coefficient of thermal expansion is often not constant over a wide range of temperatures.  It is common to express the volume as a function of temperature in the more general case as,

$$V(T) = V_o \left[ 1 + Aq + Bq^2 + Cq^3 \right] \qquad (7.7)$$

Where,

$V_o$ is the specific volume at $T_o$ and $\theta = (T - T_o)$.

Table 7-2 lists typical values of constants A, B and C for several liquids.

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

|  | A x $10^3$ | B x $10^6$ | C x $10^8$ | $V_{T_o}$ x $10^3$ $m^3/kg$ |
|---|---|---|---|---|
| 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 |

This table is used with Equation 7.7, to calculate the specific volume of a liquid at any temperature.  Its use is illustrated in Example 7-1.

## 7.2.3 Compressibility; Tait's Equation

Tait's observation (1889)

$$b_T = \frac{c}{P + d}$$

Where, c and d remain constant for many liquids.

Combine with the definition of compressibility,

$$b_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{c}{P + d}$$

At constant temperature,

$$-\frac{dV}{V} = \frac{cdP}{P+d}$$

Integrating both sides we get

$$-\int \frac{dV}{V} = \int \frac{cdP}{P+d}$$

*or*

$$-\ln V = c\ln(P+d) + Const.$$

At P= $P_o$, V = $V_o$, therefore

The constant of integration is given by
Const. = -ln($V_o$) – c.ln($P_o$+d).

Hence,

$$-\ln V = c\ln(P+d) - \ln(V_o). - \ln(P_o + d)$$

or

$$-\ln \frac{V}{V_o} = c.\ln \frac{P+d}{P_o + d}$$

Since $P_o$ is arbitrary, we can chose a value much smaller than d, which allows us to drop $P_o$ from the equation.

Now, V = $V_o$ + $\Delta V$, but $\Delta V$ is very small compared to $V_o$. Therefore, using the approximation ln(1+x) = x,  for very small x, we can write

$$\ln\left(\frac{V}{V_o}\right) = \ln\left(\frac{V_o + \Delta V}{V_o}\right) = \ln\left(1 + \frac{\Delta V}{V_o}\right) \approx \frac{\Delta V}{V_o}$$

Hence

$$-\frac{\Delta V}{V_o} = \frac{V_o - V}{V_o} = c\ln\frac{P+d}{d}$$

This equation can be considered an equation of state for liquids at constant T.

Values of c and d can be evaluated by measuring the compressibility at two different pressures at constant temperature.
Let these be $\beta_1$ at $P_1$ and $\beta_2$ at $P_2$.
From Tait's equation at constant temperature

$$b_1 = \frac{c}{P_1+d} \quad \text{and} \quad b_2 = \frac{c}{P_2 + d}$$

$$c = b_1(P_1 + d) = b_2(P_2 + d)$$
*and*
$$d = \frac{P_1 b_1 - P_2 b_2}{b_2 - b_1}$$

Plug these two numbers into the constant temperature equation of state,

$$\frac{V_o - V}{V_o} = c \ln \frac{P + d}{d}$$

Now with c and d known, the equation can be used to calculate V for every P at constant temperature. For other temperatures, $V_o$ can be obtained from data given in Table 7-2.
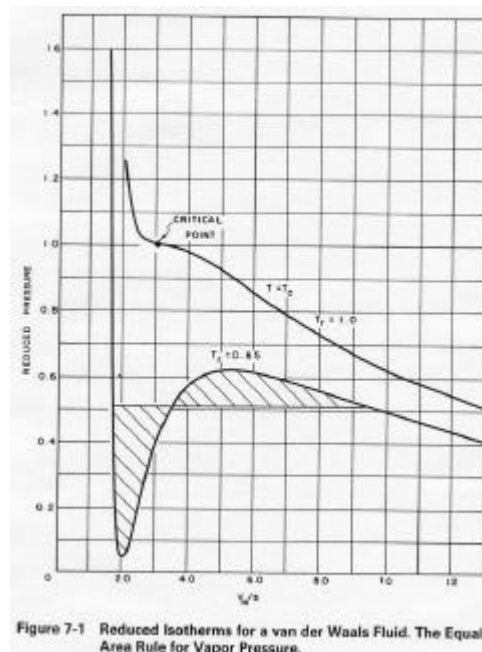
## 7.2.3 The van der Waals Equation



Figure 7-1 Reduced Isotherms for a van der Waals Fluid. The Equal Area Rule for Vapor Pressure.

The van der Waals equation of state in its cubic form is.

$$v_m^3 - \left( b + \frac{RT}{P} \right) v_m^2 + \frac{a}{P} v_m - \frac{ab}{P} = 0$$

We have also seen that this equation gives 3 real roots for $V_m$ for any P and T in the two-phase region.

For a given temperature, the vapour pressure is defined as the pressure that divides the regions such that the two areas formed by the isotherm and a constant pressure line are equal.

At a pressure greater than this value, the substance would exist as liquid, and its specific volume would be given by the smallest value of specific volume in the EOS.

This "Equal Area Rule," when applied to vdW EOS, gives liquid densities that are somewhat inaccurate → right order of magnitude though.  There are better EOS for predicting liquid density.

## 7.2.4 The Corresponding States

The compressibility charts, such as those in appendix-C could be used for calculating liquid densities. However, for liquids, we often have $T_r < 1.0$ ($T < T_c$) and $P_r > 1.0$ ($P > P_c$)

Other charts are available and can be used to get Z for liquids.

Then,

$$Z = \frac{PV_m}{RT}$$

can be used to calculate $V_m$ for liquids.