

### 7.3 Energy Effects in Liquids

We will look at the thermal properties of liquids. The energy that is supplied to a liquid can result in two consequences.

- (a) an increase in temperature (if  $P > P_v$ )
- (b) conversion of liquid into vapour (if  $P = P_v$ )

#### 7.3.1 Heat Capacity

This is related to the first effect of energy input, i.e. increase in temperature. The definition of heat capacity is identical to that used for gases, i.e. energy required to raise the temperature of one mole (or one kg) of a liquid by one Kelvin. The units are J/(kmol. K) or J/(kg.K). The first is the molar heat capacity the second is on mass basis.

The energy supplied to a liquid results in an increase in the kinetic and intermolecular potential energy of liquid molecules.

Table 7-3 gives typical values for some liquids.

Table 7-3 Heat Capacities at Constant Pressure  
for Liquids and Their Vapors

Substance	$C_p$ , kJ/kg K		Temperature °C
	Liquid	Vapor	
Acetic Acid	2.19	1.20	20-25
Aceton	2.25	1.30	24-49.4
Benzene	2.02	1.21	65
Bromine	0.448	0.226	1-32
Carbon-tetrachloride	0.837	0.549	30
Ethanol	2.85	1.503	0-98
Ethyl ether	2.18	1.420	0
Water	4.19	1.879	0-100
n-Hexane	2.51	1.823	20-100

#### 7.3.2 Latent Heat of Vapourization ( $\Delta H_v$ or $\lambda$ )

Suppose energy is added to a pure liquid at its vapour pressure. Some of the pure liquid would convert into vapour, but the temperature of the liquid (or vapour) will not change.

Phase Rule:  $F = C + 2 - P = 1 + 2 - 2 = 1$  ( $P$  = vapour pressure,  $P_v$ )

Since the addition of heat does not result in an increase in the temperature of the system, the energy supplied to convert liquids into vapour is called **Latent Heat,  $\Delta H_v$**

$$\Delta H_v = f(T \text{ or } P)$$

Table 7-4 Equilibrium Vapor Pressure and Latent Heats of Vaporization of n-Hexane and Water

Temperature °C	n-Hexane		Water	
	Vapor Pressure kPa	Heat of Vaporization $\Delta H_v \times 10^{-3}$ kJ/kmol	Vapor Pressure kPa	Heat of Vaporization $\Delta H_v \times 10^{-3}$ kJ/kmol
0	6.04	32.66	0.61	45.06
20	16.16	31.74	2.34	44.21
40	37.26	30.69	7.37	43.36
60	76.36	29.56	19.92	42.49
68.74	101.325	29.05	—	—
80	142.39	29.35	47.36	41.60
100	246.00	26.84	101.325	40.67
150	746.80	22.03	475.97	38.09
200	1802.00	15.32	1555.10	34.93

$\Delta H_v$  decreases as the temperature increases. At the limit of  $T \rightarrow T_c$ ,  $\Delta H_v = 0$ . There is little distinction between vapour and liquid.

### Trouton's Rule for Estimating $\Delta H_v$ at 1 atm.

$$\frac{\Delta H_v}{T_b} \approx 88 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}}$$

where,  $T_b$  is the normal boiling point, K.

Table 7-5 shows that this rule is only approximate ( $\pm 5\%$ ) for most liquids. Not bad as a first approximation.

Table 7-5 Molar Heats of Vaporization of Various Liquids at the Normal Boiling Point

Substance	Normal Boiling Point $T_b$ , °C	Heat of Vaporization $\Delta H_v \times 10^{-3}$ kJ/kmol	Ratio $\Delta H_v/T_b$ kJ/kmol K
Acetic acid	118.1	24.33	62.2
Acetone	56.2	30.27	92.0
Benzene	80.1	30.78	87.2
Bromine	58.8	30.01	90.4
Carbon-tetrachloride	76.8	29.89	85.4
Ethanol	78.4	39.40	112.3
Ethyl ether	34.6	26.03	84.5
Water	100.0	40.67	109.0
n-Hexane	68.74	29.05	85.0

### Heating of a Liquid to Convert it into Vapour

When a liquid is heated to convert it into a vapour heated to a temperature higher than its dew point, the process proceeds in three steps:

- (1) The temperature of the liquid increases as it absorbs sensible heat.
- (2) The liquid to vapour phase change occurs at constant temperature while the system absorbs latent heat.
- (3) The temperature of vapour then increases as the vapour absorbs sensible heat.

The total energy needed to convert one mole (or unit mass) of liquid at  $T_o$  to its vapour at  $T_1$  is given by:

$$E = C_{pl}(T_b - T_o) + \Delta H_v + C_{pv}(T_1 - T_b)$$

Note: both heat capacities and the latent heat should be on the same basis (i.e. either per kmol or per kg).

### ***The Clausius – Clapeyron Equation***

The slope of vapour pressure curve

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

$P$  = vapour pressure,  $T$  = temperature,  $\Delta H_v$  = latent heat of vapourization,  $V_g$  = sp. volume of vapour and  $V_l$  = specific volume of liquid.

We also have similar equations for other phase changes [melting/freezing; sublimation/desublimation]

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)} \quad \text{for freezing/melting}$$

and

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)} \quad \text{for sublimation/desublimation.}$$

### 7.2.3 Correlating Vapour Pressure Data

Vapour pressure data can be used to calculate  $\Delta H_v$  with help of the Clausius-Clapeyron equation.

Assumptions:

- (i) Pressure is low, so that the vapour can be assumed to be an ideal gas.
- (ii)  $V_g \gg V_l$

These assumptions are not bad if  $T \ll T_c$ .

Then  $V_g - V_l \approx V_g$

The Clausius- Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)} \approx \frac{\Delta H_v}{TV_g} \approx \frac{\Delta H_v}{T(RT/P)} = \frac{\Delta H_v}{RT^2} P$$

or

$$\frac{dP}{P} = \frac{\Delta H_v}{R} \frac{dT}{T^2}$$

Integrating both sides

$$\int \frac{dP}{P} = \frac{\Delta H_v}{R} \int \frac{dT}{T^2} + C_o$$

or

$$\ln P = \frac{\Delta H_v}{R} \left( \frac{-1}{T} \right) + C_o$$

If  $P = P_1$  at  $T = T_1 \rightarrow$  known vapour pressure at one temperature, then:

$$\ln P_1 = \frac{\Delta H_v}{R} \left( \frac{-1}{T_1} \right) + C_o$$

From these two equations

$$\ln \frac{P}{P_1} = \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right)$$

If vapour pressures are known at two different temperatures, we can solve for  $\Delta H_v$

$$\Delta H_v = \frac{R \ln \left( \frac{P_2}{P_1} \right)}{\left[ \frac{1}{T_1} - \frac{1}{T_2} \right]}$$

This equation gives average value of  $\Delta H_v$  between  $T_1$  and  $T_2$ .

In terms of  $\log_{10}$ ,

$$\Delta H_v = \frac{2.303 R \log_{10} \left( \frac{P_2}{P_1} \right)}{\left[ \frac{1}{T_1} - \frac{1}{T_2} \right]}$$

The above equation assumes that  $\Delta H_v$  is constant over  $T_1$  and  $T_2$ . But in Table 7-4, we saw that this is not quite true.

If  $\Delta H_v = A + BT$

then

$$\frac{dP}{dT} = \frac{A + BT}{RT^2} \cdot P$$

When this equation is integrated , we get

$$\ln P = -\frac{A}{RT} + B \ln T + C_o$$

If ideal gas law is not applicable to  $V_g$ , then the following empirical equation can be used.

$$\ln P = \frac{C_1}{T} + C_2$$

Values of  $C_1$  and  $C_2$  can be determined from known values of vapour pressures at two different temperatures. This equation gives good results, even though it is purely empirical.

$C_1 = -\Delta H_v/R$  is true only if  $C_1$  and  $C_2$  are evaluated from  $T_1$  and  $T_2$  that do not differ by much and the vapour pressure is low, i.e. ideal gas assumption can be used.