

### 3.7 GENERALIZED CORRELATIONS FOR LIQUIDS

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy.

In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by **Rackett** is an example:

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{0.2857}} \quad (3.72)$$

An alternative form of this equation is sometimes useful:

$$Z^{\text{sat}} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]} \quad (3.73)$$

Lydersen, Greenkorn, and Hougen developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density  $\rho_r$ , as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V} \quad (3.74)$$

where  $\rho_c$  is the density at the critical point. The generalized correlation is shown by Fig. 3.17. This figure may be used directly with Eq. (3.74) for determination of liquid volumes if the value of the critical volume is known. A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} \quad (3.75)$$

where  $V_2$  = required volume

$V_1$  = known volume

$P_{r1}$ ,  $\rho_{r2}$  = reduced densities read from Fig. 3.17

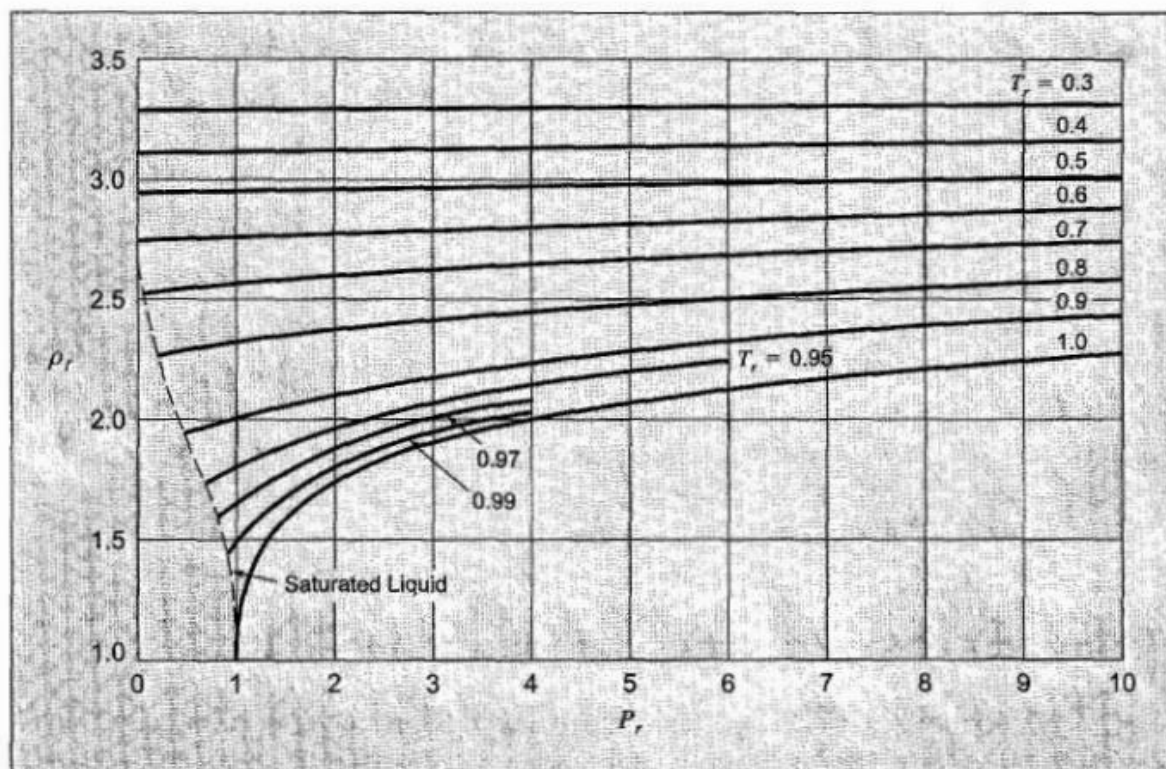


Figure 3.17 Generalized density correlation for liquids

### Example 3.13

For ammonia at 310 K, estimate the density of:

- (a) The saturated liquid; (b) The liquid at 100 bar.

### Solution 3.13

(a) Apply Eq. (3.72) at the reduced temperature,  $T_r = 310/405.7 = 0.7641$ . With  $V_c = 72.47$  and  $Z_c = 0.242$  (from Table B.1),

$$V^{\text{sat}} = V_c Z_c^{(1-T_r)^{2/3}} = (72.47)(0.242)^{(0.2359)^{2/3}} = 28.33 \text{ cm}^3 \text{ mol}^{-1}$$

For comparison, the experimental value is  $29.14 \text{ cm}^3 \text{ mol}^{-1}$ , a 2.7% difference.

(b) The reduced conditions are:

$$T_r = 0.764 \quad P_r = \frac{100}{112.8} = 0.887$$

Substituting the value,  $\rho_r = 2.38$  (from Fig. 3.16), and  $V_c$  into Eq. (3.74) gives:

$$V = \frac{V_c}{\rho_r} = \frac{72.47}{2.38} = 30.45 \text{ cm}^3 \text{ mol}^{-1}$$

In comparison with the experimental value of  $28.6 \text{ cm}^3 \text{ mol}^{-1}$ , this result is higher by 6.5%.

If we start with the experimental value of  $29.14 \text{ cm}^3 \text{ mol}^{-1}$  for saturated liquid at 310 K, Eq. (3.75) may be used. For the saturated liquid at  $T_r = 0.764$ ,  $\rho_{r1} = 2.34$  (from Fig. 3.16). Substitution of known values into Eq. (3.75) gives:

$$V_2 = V_1 \frac{\rho_{r1}}{\rho_{r2}} = (29.14) \left( \frac{2.34}{2.38} \right) = 28.65 \text{ cm}^3 \text{ mol}^{-1}$$

This result is in essential agreement with the experimental value.

Direct application of the Lee/Kesler correlation with values of  $Z^0$  and  $Z^1$  interpolated from Tables E.1 and E.2 leads to a value of  $33.87 \text{ cm}^3 \text{ mol}^{-1}$ , which is significantly in error, no doubt owing to the highly polar nature of ammonia.

## Chapter 4

### Heat Effects

Heat transfer is one of the most common operations in the chemical industry.

#### 4.1 SENSIBLE HEAT EFFECTS

Heat transfer to a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes the temperature of the system to change. Our purpose here is to develop relations between the quantity of heat transferred and the resulting temperature change.

When the system is a homogeneous substance of constant composition, the phase rule indicates that fixing the values of two intensive properties establishes its state. The molar or specific internal energy of a substance may therefore be expressed as a function of two other state variables. These may be arbitrarily selected as temperature and molar or specific volume:

$$U = U(T, V)$$

Whence,

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

As a result of Eq. (2.16) this becomes:

$$dU = C_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

The final term may be set equal to zero in two circumstances:

- For any constant-volume process, regardless of substance.
- Whenever the internal energy is independent of volume, regardless of the process. This is exactly true for ideal gases and incompressible fluids and approximately true for low- pressure gases.

In either case,  $dU = C_V dT$

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (4.1)$$

For a mechanically reversible constant-volume process,  $Q = \Delta U$ , and Eq. (2.19) may be rewritten:

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT$$

Similarly, the molar or specific enthalpy may be expressed as a function of temperature and pressure:

$$H = H(T, P)$$

Whence,

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

As a result of Eq. (2.20) this becomes:

$$dH = C_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

Again, two circumstances allow the final term to be set equal to zero:

- For any constant-pressure process, regardless of the substance.
- Whenever the enthalpy of the substance is independent of pressure, regardless of the process. This is exactly true for ideal gases and approximately true for low-pressure gases.

In either case,

$$dH = C_P dT$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (4.2)$$

Moreover,  $Q = \Delta H$  for mechanically reversible, constant-pressure, closed-system processes [Eq. (2.23)] and for the transfer of heat in steady-flow exchangers where  $\Delta E_P$  and  $\Delta E_K$  are negligible and  $W_s = 0$ . [Eq. (2.33)] In either case,

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \quad (4.3)$$

The common engineering application of this equation is to steady-flow heat transfer.

### Temperature Dependence of the Heat Capacity

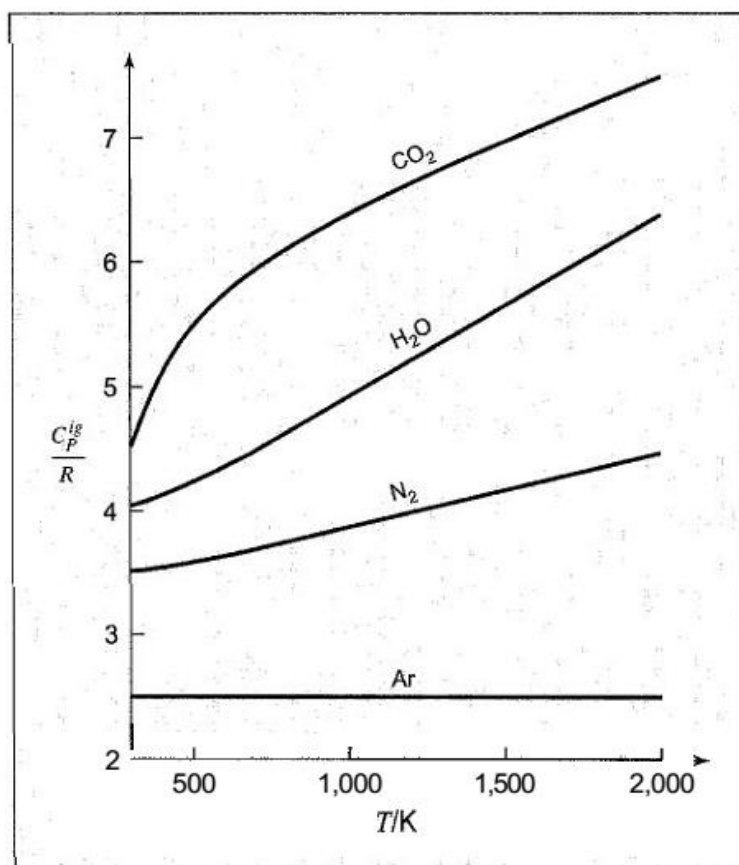
$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2} \quad (4.4)$$

where either C or D is zero, depending on the substance considered. Since the ratio  $C_p/R$  is dimensionless, the units of  $C_p$  are governed by the choice of R.

Ideal-gas heat capacities (designated by  $C_p^{ig}$  and  $C_v^{ig}$ ) are therefore different for different gases; although functions of temperature, they are independent of pressure.

**Figure 4.1 Ideal-gas heat capacities of argon, nitrogen, water, and carbon dioxide**

The influence of temperature on  $C_p^{ig}$  for argon, nitrogen, water, and carbon dioxide is illustrated in Fig. 4.1.



Temperature dependence is expressed analytically by equations such as Eq. (4.4), here written:

$$\frac{C_p^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

Values of the parameters are given in Table C. 1 of App. C for a number of common organic and inorganic gases. More accurate but more complex equations are found in the literature.

As a result of Eq. (3.19), the two ideal-gas heat capacities are related:

$$\frac{C_v^{ig}}{R} = \frac{C_p^{ig}}{R} - 1 \quad (4.5)$$

Although ideal-gas heat capacities are exactly correct for real gases only at zero pressure, the departure of real gases from ideality is seldom significant at pressures below several bars, and here  $C_p^{ig}$  and  $C_v^{ig}$  are usually good approximations to their heat capacities.

### Example 4.1

The parameters listed in Table C.1 require use of Kelvin temperatures in Eq. (4.4). Equations of the same form may also be developed for use with temperatures in °C, (R), and (°F), but the parameter values are different. The molar heat capacity of methane in the ideal-gas state is given as a function of temperature in kelvins by:

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}T - 2.164 \times 10^{-6}T^2$$

where the parameter values are from Table C.1. Develop an equation for  $C_P^{ig}/R$  for temperatures in °C.

### Solution 4.1

The relation between the two temperature scales is:

$$T \text{ K} = t^{\circ}\text{C} + 273.15$$

Therefore, as a function of  $t$ ,

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}(t + 273.15) - 2.164 \times 10^{-6}(t + 273.15)^2$$

or 
$$\frac{C_P^{ig}}{R} = 4.021 + 7.899 \times 10^{-3}t - 2.164 \times 10^{-6}t^2$$

Gas mixtures of constant composition may be treated in exactly the same way as pure gases.

Thus one calculates the ideal-gas heat capacity of a gas mixture as the mole-fraction-weighted sum of the heat capacities of the individual species. Consider 1 mol of gas mixture consisting of species A, B, and C, and let  $y_A$ ,  $y_B$ , and  $y_C$  represent the mole fractions of these species. The molar heat capacity of the mixture in the ideal-gas state is:

$$C_{P_{\text{mixture}}}^{ig} = y_A C_{P_A}^{ig} + y_B C_{P_B}^{ig} + y_C C_{P_C}^{ig} \quad (4.6)$$

where  $C_{p_A}^{ig}$ ,  $C_{p_B}^{ig}$  and  $C_{p_C}^{ig}$  are the molar heat capacities of pure A, B, and C in the ideal-gas state.

As with gases, the heat capacities of solids and liquids are found by experiment. Parameters for the temperature dependence of  $C_p$  as expressed by Eq. (4.4) are given for a few solids and liquids in Tables C.2 and C.3 of App. C. Correlations for the heat capacities of many solids and liquids are given by Perry and Green and by Daubert et al.

## 4.2 LATENT HEATS OF PURE SUBSTANCES

When a pure substance is liquefied from the solid state or vaporized from the liquid at constant pressure, no change in temperature occurs; however, the process requires the transfer of a finite amount of heat to the substance. These heat effects are called the latent heat of fusion and the latent heat of vaporization. Similarly, there are heats of transition accompanying the change of a substance from one solid state to another;

Thus the latent heat accompanying a phase change is a function of temperature only, and is related to other system properties by an exact thermodynamic equation:

$$\left[ \Delta H = T \Delta V \frac{dP^{\text{sat}}}{dT} \right] \quad (4.11)$$

where for a pure species at temperature T,

$\Delta H$  = latent heat

$\Delta V$  = volume change accompanying the phase change

$P^{\text{Sat}}$  = vapour pressure

There are many empirical methods to calculate the heat of vaporization, the method proposed by Watson<sup>8</sup> has found wide acceptance:

$$\frac{\Delta H_2}{\Delta H_1} = \left( \frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad (4.13)$$

### Example 4.4

Given that the latent heat of vaporization of water at 100°C is 2,257 J g<sup>-1</sup>, estimate the latent heat at 300°C.



**Solution 4.4**

Let  $\Delta H_1 = \text{latent heat at } 100^\circ\text{C} = 2,257 \text{ J g}^{-1}$

$\Delta H_2 = \text{latent heat at } 300^\circ\text{C}$

$$T_{r1} = 373.15/647.1 = 0.577$$

$$T_{r2} = 573.15/647.1 = 0.886$$

Then by Eq. (4.13),

$$\Delta H_2 = (2,257) \left( \frac{1 - 0.886}{1 - 0.577} \right)^{0.38} = (2,257)(0.270)^{0.38} = 1,371 \text{ J g}^{-1}$$

The value given in the steam tables is  $1,406 \text{ J g}^{-1}$ .