

Internal Energy and Entropy as Functions of T and V

$$\boxed{dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV} \quad (6.32)$$

$$\boxed{dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T} \right)_V dV} \quad (6.33)$$

These are general equations relating the internal energy and entropy of homogeneous fluids of constant composition to temperature and volume.

Equation (3.4) applied to a change of state at constant volume becomes:

$$\frac{dV}{V} = \beta dT - \kappa dP \quad (3.4)$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa} \quad (6.34)$$

Alternative forms of Eqs. (6.32) and (6.33) are therefore:

$$dU = C_V dT + \left(\frac{\beta}{\kappa} T - P \right) dV \quad (6.35)$$

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad (6.36)$$

For an incompressible β and $\kappa = 0$, Equations (6.28) and (6.29) become:

$$dH = C_P dT + V dP$$

$$dS = C_P \frac{dT}{T}$$

6.2 RESIDUAL PROPERTIES:

Unfortunately, no experimental method for the direct measurement of numerical values of G or G/RT is known, and the equations which follow directly from the Gibbs energy are of little practical use.

Thus, by definition the residual Gibbs energy is: $G^R \equiv G - G^{ig}$

where G and G^{ig} are the actual and the ideal-gas values of the Gibbs energy at the same temperature and pressure. Other residual properties are defined in an analogous way. The residual volume, for example, is:

$$V^R \equiv V - V^{ig} = V - \frac{RT}{P}$$

Since $V = ZRT/P$, the residual volume and the compressibility factor are related:

$$V^R = \frac{RT}{P}(Z - 1)$$

The definition for the generic residual property is:

$$\boxed{M^R \equiv M - M^{ig}} \quad (6.41)$$

where M is the molar value of any extensive thermodynamic property, e.g., V , U , H , S , or G . Note that M and M^{ig} , the actual and ideal-gas properties, are at the same temperature and pressure.

Enthalpy and Entropy from residual properties

Applied to the enthalpy and entropy, Eq. (6.41) is written:

$$H = H^{ig} + H^R \quad \text{and} \quad S = S^{ig} + S^R$$

Thus, H and S follow from the corresponding ideal-gas and residual properties by simple addition. General expressions for H^{ig} and S^{ig} are found by integration of Eqs. (6.23) and (6.24) from an ideal-gas state at reference conditions T_0 and P_0 to the ideal-gas state at T and P

$$H^{ig} = H_0^{ig} + \int_{T_0}^T C_P^{ig} dT \quad S^{ig} = S_0^{ig} + \int_{T_0}^T C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0}$$

Substitution into the preceding equations gives:

$$H = H_0^{ig} + \int_{T_0}^T C_P^{ig} dT + H^R \quad (6.50)$$

$$S = S_0^{ig} + \int_{T_0}^T C_P^{ig} \frac{dT}{T} - R \ln \frac{P}{P_0} + S^R \quad (6.51)$$

Equations (6.50) and (6.51) may be expressed alternatively to include the mean heat capacities introduced in Secs. 4.1 and 5.5:

$$H = H_0^{ig} + \langle C_P^{ig} \rangle_H (T - T_0) + H^R \quad (6.52)$$

$$S = S_0^{ig} + \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0} - R \ln \frac{P}{P_0} + S^R \quad (6.53)$$

$$\boxed{\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} \quad (\text{const } T)} \quad (6.46)$$

$$\boxed{\frac{S^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P} \quad (\text{const } T)} \quad (6.48)$$

6.4 TWO-PHASE SYSTEMS

The exception is the molar or specific Gibbs energy, which for a pure species does not change during a phase transition such as melting, vaporization, or sublimation. Consider a pure liquid in equilibrium with its vapor in a piston/cylinder arrangement at temperature T and the corresponding vapor pressure P^{sat} . When a differential amount of liquid is caused to evaporate at constant temperature and pressure, Eq. (6.6) applied to the process reduces to $d(nG) = 0$. Since the number of moles n is constant, $dG = 0$, and this requires the molar (or specific) Gibbs energy of the vapor to be identical with that of the liquid. More generally, for two phases α , and β of a pure species coexisting at equilibrium,

$$G^\alpha = G^\beta \quad (6.69)$$

where G^α and G^β are the molar or specific Gibbs energies of the individual phases.

If the temperature of a two-phase system is changed, then the pressure must also change in accord with the relation between vapor pressure and temperature if the two phases continue to coexist in equilibrium. Since Eq. (6.69) applies throughout this change,

$$dG^\alpha = dG^\beta$$

Substituting expressions for dG^α and dG^β as given by Eq. (6.10) yields:

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

which upon rearrangement becomes:

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

The entropy change $\Delta S^{\alpha\beta}$ and the volume change $\Delta V^{\alpha\beta}$ are changes which occur when a unit amount of a pure chemical species is transferred from phase α to phase β at the equilibrium temperature and pressure. Integration of Eq. (6.8) for this change yields the latent heat of phase transition:

$$\Delta H^{\alpha\beta} = T \Delta S^{\alpha\beta} \quad (6.70)$$

Thus, $\Delta S^{\alpha\beta} = \Delta H^{\alpha\beta} / T$, and substitution in the preceding equation gives:

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}} \quad (6.71)$$

which is the Clapeyron equation.

For the particularly important case of phase transition from liquid l to vapor v , Eq. (6.71) is written:

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta H^{lv}}{T \Delta V^{lv}} \quad (6.72)$$

But

$$\Delta V^{lv} = \frac{RT}{P^{\text{sat}}} \Delta Z^{lv}$$

Where ΔZ^{lv} is the compressibility factor change of vaporization, combination of last two equations gives on rearrangement

$$\frac{d \ln P^{\text{sat}}}{dT} = \frac{\Delta H^{lv}}{RT^2 \Delta Z^{lv}} \quad (6.73)$$

or

$$\frac{d \ln P^{\text{sat}}}{d(1/T)} = - \frac{\Delta H^{lv}}{R \Delta Z^{lv}} \quad (6.74)$$

Equations (6.72) through (6.74) are equivalent, exact forms of the Clapeyron equation for pure species vaporization

Example 6.5

The Clapeyron equation for vaporization may be simplified by introduction of reasonable approximations, namely, that the vapor phase is an ideal gas and that the molar volume of the liquid is negligible compared with the molar volume of the vapor. How do these assumptions alter the Clapeyron equation?

Solution 6.5

The assumptions made are expressed by:

$$\Delta V^{lv} = V^v = \frac{RT}{P^{\text{sat}}} \quad \text{or} \quad \Delta Z^{lv} = 1$$

Equation (6.74) yields:
$$\Delta H^{lv} = -R \frac{d \ln P^{\text{sat}}}{d(1/T)}$$

This approximate equation, known as the Clausius/Clapeyron equation, relates the latent heat of vaporization directly to the vapor-pressure curve. Specifically, it shows that ΔH^{lv} is proportional to the slope of a plot of $\ln P^{\text{sat}}$ vs. $1/T$. Such plots of experimental data produce lines for many substances that are nearly straight. According to the Clausius/Clapeyron equation, this implies that ΔH^{lv} is almost constant, virtually independent of T . This is not true; ΔH^{lv} decreases monotonically with increasing temperature from the triple point to the critical point, where it becomes zero. The assumptions on which the Clausius/Clapeyron equation are based have approximate validity only at low pressures.

Temperature Dependence of the Vapor Pressure of Liquids:

As noted in Ex. 6.5, a plot of $\ln P^{\text{sat}}$ vs. $1/T$ generally yields a line that is nearly straight:

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad (6.75)$$

where A and B are constants for a given species. **This equation gives a rough approximation of the vapor-pressure relation for the entire temperature range from the triple point to the critical point.** Moreover, it provides an excellent basis for interpolation between values that are reasonably spaced.

The Antoine equation, which is more satisfactory for general use, has the form:

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

The constants A, B, and C are readily available for a large number of species. Each set of constants is valid for a specified temperature range, and should not be used outside of that range. Values of Antoine constant for selected substances are given in Table B2 in APP. B.

The accurate representation of vapor-pressure data over a wide temperature range requires an equation of greater complexity. The Wagner equation is one of the best available; it expresses the reduced vapor pressure as a function of reduced temperature:

$$\ln P_r^{\text{sat}} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1 - \tau} \quad (6.77)$$

where $\tau = 1 - T_r$

and A, B, C, and D are constants. Values of the constants either for this equation or for Eq. (6.76) are given by Reid, Prausnitz, and Poling⁶ for many species.

⁶ R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., App. A, McGraw-Hill

Corresponding-States Correlations for Vapor Pressure

A number of corresponding-state, correlation are available for the vapor pressure of non-polar, non-associating liquid. One of the simplest is that of Lee and Kesler, it is a Pitzer type correlation of the form:

$$\ln P_r^{\text{sat}}(T_r) = \ln P_r^0(T_r) + \omega \ln P_r^1(T_r) \quad (6.78)$$

$$\text{where} \quad \ln P_r^0(T_r) = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (6.79)$$

$$\ln P_r^1(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \quad (6.80)$$

Lee and Kesler recommend that the value of ω used with Eq. (6.78) be found from the correlation by requiring that it reproduce the normal boiling point. In other words, to for a particular substance is determined from:

$$\omega = \frac{\ln P_r^{\text{sat}} - \ln P_r^0(T_{r_n})}{\ln P_r^1(T_{r_n})} \quad (6.81)$$

where T_{r_n} is the reduced normal boiling point and P_{r_n} is the reduced vapor pressure corresponding to 1 standard atmosphere (1.01325 bar).

Example 6.6

Determine the vapor pressure (in kPa) for liquid *n*-hexane at 0, 30, 60, and 90°C:

- (a) With constants from App. B.2. (b) From the Lee/Kesler correlation for P_r^{sat} .

Solution 6.6

- (a) With constants from App. B.2, the Antoine equation for *n*-hexane is:

$$\ln P^{\text{sat}}/\text{kPa} = 13.8193 - \frac{2696.04}{t/^{\circ}\text{C} + 224.317}$$

Substitution of temperatures yields the values of P^{sat} under the heading "Antoine" in the table below. We take these to be equivalent to good experimental values.

- (b) We first determine ω from the Lee/Kesler correlation. At the normal boiling point of *n*-hexane (Table B.1),

$$T_{r_n} = \frac{341.9}{507.6} = 0.6736 \quad \text{and} \quad P_{r_n}^{\text{sat}} = \frac{1.01325}{30.25} = 0.03350$$

Application of Eq. (6.81) then gives the value of ω for use with the Lee/Kesler correlation: $\omega = 0.298$. With this value, the correlation produces the P^{sat} values shown in the table. The average difference from the Antoine values is about 1.5%.

$t/^{\circ}\text{C}$	$P^{\text{sat}}/\text{kPa}$ (Antoine)	$P^{\text{sat}}/\text{kPa}$ (Lee/Kesler)	$t/^{\circ}\text{C}$	$P^{\text{sat}}/\text{kPa}$ (Antoine)	$P^{\text{sat}}/\text{kPa}$ (Lee/Kesler)
0	6.052	5.835	30	24.98	24.49
60	76.46	76.12	90	189.0	190.0