Properties at Saturation

Phase change is possible at subcritical conditions. Phase equilibrium is characterized by the same temperature, pressure and chemical potential of a compound in all coexisting phases. Saturation curves describe the relation between equilibrium pressure and temperature (e.g. for vapor-liquid behavior this is the dependence of boiling temperature on pressure…).

Clapeyron Equation

Clapeyron equation relates temperature and pressure at two-phase equilibrium

$$\frac{dp^{\otimes}}{dT} = \frac{S^{(2)} - S^{(1)}}{V^{(2)} - V^{(1)}} = \frac{H^{(2)} - H^{(1)}}{T\left[V^{(2)} - V^{(1)}\right]} = \frac{\Delta H}{T\Delta V} \qquad\qquad \frac{d \ln p^{\otimes}}{dT} = \frac{\Delta H}{RT^2\left[z^{(2)} - z^{(1)}\right]} = \frac{\Delta H}{RT^2\Delta z}$$

where $S^{(2)}$, $S^{(1)}$, $H^{(2)}$, $H^{(1)}$, $z^{(2)}$, … $V^{(1)}$ are entropy, enthalpy, compressibility factor and volume in the respective phases. This equation is generally valid and can be applied on any two phases. Its parameters are molar volumes or compressibility factors of coexisting phases (available from EOS) and the enthalpy of phase change. All these properties are temperature dependent.

Clausius-Clapeyron Equation

If one of the equilibrium phases is gaseous, some simplifications may apply (at lower pressures):

a) $V_m^{(g)} = RT/p$

b) $V_m^{(cond)} << V_m^{(g)}$

where $V_m^{(cond)}$ is molar volume of condensed phase (liquid or solid). Using these approximations, the Clapeyron equation can be rearranged to so-called Clausius-Clapeyron equation

$$\frac{d \ln p^{\otimes}}{dT} = \frac{\Delta H}{RT^2}$$

(Saturated) Vapor Pressure

Vapor pressure is relatively easy to measure, its temperature dependence is often described by empirical relationships.

Antoine Equation

$$\ln p^{\otimes} = A - \frac{B}{T + C}$$

where A, B, C are parameters adjusted to experimental data and valid only in a temperature interval coved by the data. The equation is applied at pressures $1 - 200$ kPa (maximum range).

Wagner Equation

$$\ln p_r^{\otimes} = \frac{1}{T_r}\left(a_1 + a_2\tau^{1,5} + a_3\tau^{2,5} + a_4\tau^5\right)$$

$p_r^{\otimes} = p^{\otimes} / p_k$, $\tau = 1-T_r$.

Cox Equation

$$\ln\left(p^{\otimes} / p_0^{\otimes}\right) = \left(1 - \frac{T_0}{T}\right) \cdot \exp\left[\sum_{i=0}^{2} a_i T^i\right]$$

where $p_0^{\otimes}$, T_0 are vapor pressure and temperature at reference conditions. The usual choice of reference is normal boiling point or critical point, depending on the range of conditions we wish to cover.

Data Sources: Webbook (http://webbook.nist.gov/chemistry/)
Boublík T., Fried V., Hála E.: The Vapour Pressures of Pure Substances, Elsevier, Amsterdam, 1984.

Heat of Vaporization/Sublimation

Heat of vaporization is decreasing with temperature (similarly the heat of sublimation). At triple point

$$\Delta H_{subl} = \Delta H_{tání} + \Delta H_{výp}$$

Heat of vaporization is zero at the critical point, where the difference between liquid and gaseous phases disappears. Heat of vaporization/sublimation can be evaluated from the known vapor pressure equation using the Clapeyron equation.

Data Sources: Webbook

Majer V., Svoboda V.: Enthalpies of Vaporization of Organic Compounds, Critical Review and Data Compilation, Blackwell, Oxford, 1985.

Heat Capacity of Liquids

Heat capacity at saturation is practically equal to the isobaric heat capacity (atmospheric pressure). At temperatures above normal boiling point the difference can be obtained from the EOS and vapor pressure equation

$$C_p - C_{sat} = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_{sat}$$

Data Sources: Webbook

Wagman D.D. et al.: J. Phys. Chem. Ref. Data, 11, 1982.

Zábranský M., Růžička V., Majer V., Domalski E.S.: Heat Capacities of Liquids. Critical Review and Recommended Values. J. Phys. Chem. Ref. Data Monograph No. 6, 1996.

Homework 3: Calculate the heat of vaporization for (water; ethanol; benzene; phenol; acetone; 1-butanol; diethylether; chlorobenzene) at 25°C using the Clapeyron equation and Antoine equation for vapor pressure. The properties of liquid and gas phases calculate from the Redlich-Kwong EOS. Find appropriate experimental value and compare.