CHEME 3130: Equations of state for pure substances

Jeffrey D. Varner[*]

[*]Robert Frederick Smith School of Chemical and Biomolecular Engineering
Cornell University, Ithaca NY 14853

Recall

Previously we introduced the energy balance equation for an open and closed system. An open system allows both mass and energy transfer to occur between a system and its surroundings:

$$\frac{d}{dt}\Big[m\left(u + e_K + e_P\right)\Big]\Big|_{sys} = \dot{Q} + \dot{W} + \sum_{s=1}^{\mathcal{S}} \nu_s \left(u_s + gz_s + \frac{1}{2}s_s^2\right)\dot{m}_s + \sum_{r=1}^{\mathcal{R}} \dot{E}_r$$

$$\frac{dm}{dt} = \sum_{s=1}^{\mathcal{S}} \nu_s \dot{m}_s$$

On the other hand, in a closed system no mass transfer is allowed between the systems and the surroundings:

$$\frac{d}{dt}\Big[m\left(u + e_K + e_P\right)\Big]\Big|_{sys} = \dot{Q} + \dot{W} + \sum_{r=1}^{\mathcal{R}} \dot{E}_r$$

Lastly, we introduced pressure expansion work, and shaft work in the energy balance equations. In this lecture, we'll discuss the relationship between state variables and the physical composition of a system. In particular, we discuss:

- The phase behavior of a pure substance, and the Gibbs Phase Rule

- The Virial equation of state

- Cubic equations of state and van der Waals equation

- Data driven equations of state

Introduction

Equations of state *model* the behavior of pure materials, or mixture of materials as a function of physical conditions. This is critically important for a variety of reasons, not the least of which is that we harness the power of phase change in many technologies that are common place today. The physical knobs that can be adjusted for any system are the temperature T, pressure P and volume V. However, these three properties are *not* independent; we typically write a single property, for example the volume of system, as a function of the other two, where the temperature T and the pressure P are independent parameters that can be adjusted for some technological benefit.

Consider a typical pressure temperature (PT)-diagram shown above for a pure substance. This is an example of a phase diagram. As we move around the (P,T) space, pure substances assume different physical forms (phases) ranging from a solid, liquid or gas to a fourth regime called the supercritical phase which has fluid like properties. The solid lines, which are borders between these phases, demarcate phase transitions e.g., changing from a solid to a gas (sublimation curve) or a liquid to a gas (vaporization curve). At (P,T) points far away from these transitions, substances exists as a pure phase e.g., only a liquid or gas phase; however, directly on these curves both phases exist. At a special point called the triple point (P_{tp}, T_{tp}) all three phases coexist. If we continue to walk up the vaporization curve, we eventually arrive at the critical point (P_{cr}, T_{cr}). When the temperature and pressure exceed the critical values, the differences between the liquid and gas phases disappear, leading to a homogeneous supercritical fluid phase. Supercritical fluids have many industrial applications, mostly centered around extraction technologies [REF].
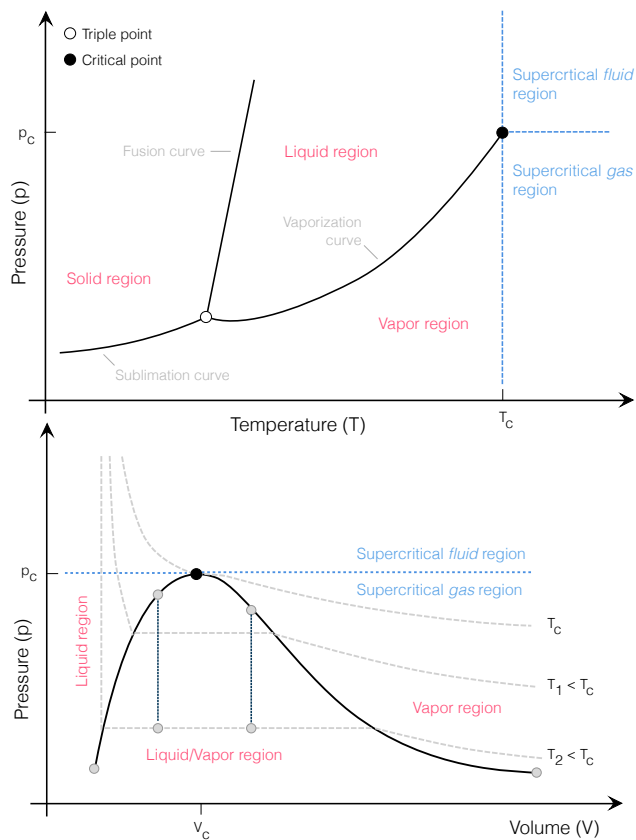

Fig. 1: Schematic of a general system and its surroundings. $\mathcal{S}$ streams enter or exit from the system which can transfer both heat and work with the surroundings. $\mathcal{R}$ chemical reactions can act a source or sink of heat for the system.

Equation of state models.

An equation of state is a function $f(\cdot)$ that relates the state variables, temperature T, pressure P and volume V of a system such that:

$$f(P, T, V) = 0 \tag{1}$$

Thus, equations of state are mathematical models of the physical behavior of pure substances or mixtures. In theory, we should be able to formulate an equation of state that describes all phases of a pure substance (or a mixture). However, in practice this is not often the case; most equations of state describe only single phase behavior.

Ideal Gas Law and Virial Equations of State. One of the simplest equations of state is the ideal gas law (IGL) (in standard form):

$$Pv - RT = 0 \tag{2}$$

The IGL ignores both the volume of the molecules in the gas, and all electrostatic interactions between them (hard-sphere model). While this makes the IGL simple to use, these assumptions do not allow the IGL to describe realistic gases and pressures; IGL describes gas phase behavior in the limit of low pressure. One way to correct the IGL for higher pressures, is to use a correction in the form of a Virial equation of state.

Suppose we define a dimensionless constant Z, called the compressibility factor, as $Z \equiv Pv/RT$. Then, by definition the compressibility factor for an ideal gas is Z=1. As the behavior of the gas deviates from the IGL, the compressibility factor can be used a correction. The model for how the compressibility changes with pressure (or alternatively with molar volume) is called the Virial equation of state. In particular, the Virial equation of state is the power-series of either pressure P or inverse powers of the molar (or specific) volume v:

$$Z \equiv \frac{Pv}{RT} = \sum_{i=0}^{\infty} \alpha_i v^{-i} \qquad Z \equiv \frac{Pv}{RT} = \sum_{i=0}^{\infty} \alpha_i' P^i \tag{3}$$

where α_i, α_i' denotes Virial coefficients. The Virial coefficients α_i and α_i' (which are related with one another and are strong functions of temperature) describe the strength of intermolecular interactions (interactions between molecules) in the fluid. These coefficients can be estimated from data for each material of interest, or they can be derived from first-principle statistical mechanical calculations given a potential function which describes the strength of interactions between molecules. In all cases, $\alpha_0 = \alpha_0' = 1$, however beyond the first coefficient in the series the coefficients are given by:

$$\alpha_1' = \frac{\alpha_1}{RT}$$

$$\alpha_2' = \frac{\alpha_2 - \alpha_1^2}{(RT)^2}$$
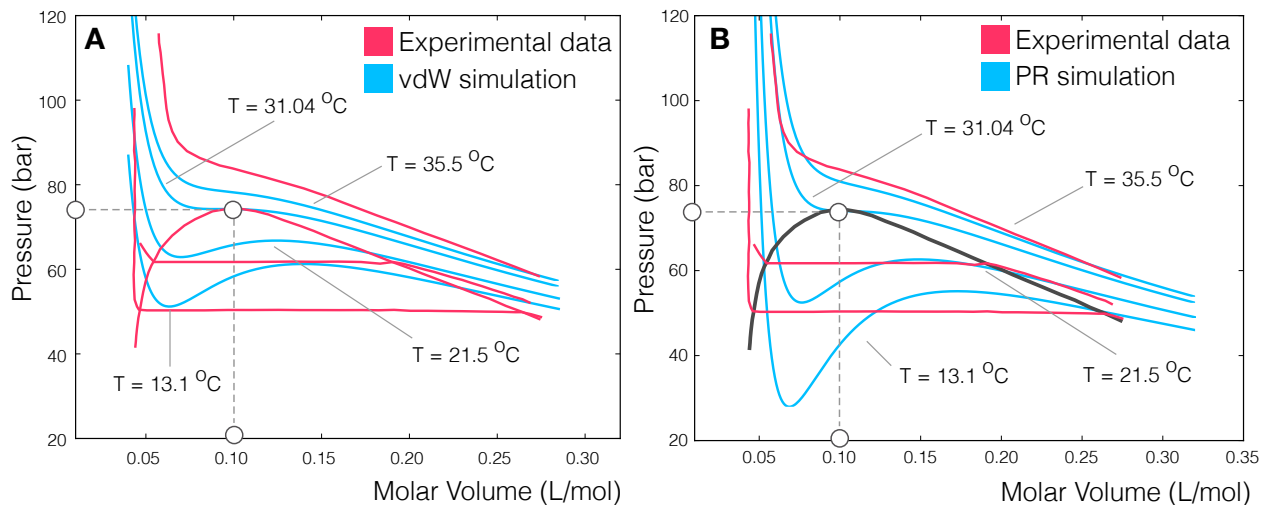
$$\vdots$$

Fig. 2: Schematic of a general system and its surroundings. $\mathcal{S}$ streams enter or exit from the system which can transfer both heat and work with the surroundings. $\mathcal{R}$ chemical reactions can act a source or sink of heat for the system.

> **Example**: Estimate the second and Virial coefficient (α_1) for CH_4 from compressibility data.
>
> **Solution.**

Cubic Equations of State Polynomials equations that are cubic in molar (or specific) volume v are the simplest equations of state that can describe both liquid and vapor behavior. The general form for this class of model is given by:

$$v^3 + f_1(T,P)v^2 + f_2(T,P)v + f_3(T,P) = 0 \qquad (4)$$

where $f_j(T,P)$ are specific functions of temperature T and pressure P for each instance of cubic state equation. Arguably, the best known cubic equation of state is van der Waals (vdW) equation:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (5)$$

The vdW equation of state was proposed by the Dutch physicist Johannes Diderik van der Waals in his Ph.D thesis published in 1873 at the University of Leiden [1]. He later won the Nobel prize for this work in 1910. The first term in the vdW equation of state describes the mechanical repulsion between molecules in the material, while the second term describes the attraction between molecules. The most significant advancements of the vdW equation was its description of molecular interactions; its parameters describe the volume occupied by fluid particles (excluded volume), and the interactions between particles (both features ignored by the ideal gas law). In particular, the van der Waals parameters a and b are associated with the van der Waal force, and the size of the molecules in the fluid (excluded volume), respectively. The vdW parameters can be estimated directly from data (as van der Waals himself did), potentially from first-principles statis-

tical mechanical calculations, or from analytical expressions derived based upon the behavior of the fluid near the critical point.

Estimate van der Waals parameters from critical point data At the critical point P=P_{cr}, T=T_{cr} and v=v_{cr}; all three roots of the vdW equation must equal v_{cr}:

$$(v - v_{cr})^3 = 0 \tag{6}$$

After we expand the term in parenthesis we get:

$$v^3 - (3v_{cr}) v^2 + (3v_{cr}^2) v - v_{cr}^3 = 0 \tag{7}$$

The vdW equation in standard form is given by:

$$v^3 - \left(b + \frac{RT_{cr}}{P_{cr}}\right) v^2 + \frac{a}{P_{cr}} v - \frac{ab}{P_{cr}} = 0 \tag{8}$$

Term by term comparison of the powers of the molar volume gives three equations:

$$3v_{cr} = b + \frac{RT_{cr}}{P_{cr}} \qquad 3v_{cr}^2 = \frac{a}{P_{cr}} \qquad v_{cr}^3 = \frac{ab}{P_{cr}} \tag{9}$$

Solving these three equations for v_{cr}, a and b in terms of P_{cr} and T_{cr} gives:

$$v_{cr} = \frac{3}{8} \frac{RT_{cr}}{P_{cr}} \qquad a = \frac{27}{64} \frac{R^2 T_{cr}^2}{P_{cr}} \qquad b = \frac{1}{8} \frac{RT_{cr}}{P_{cr}} \tag{10}$$

Although these estimates for v_{cr}, a and b may not be optimal, they can be estimated from tabulated critical values that are often available (in contrast to PVT data which is not as abundant).

Modifications to vdW equation of state

vdW was considered one of the most significant contributions to Thermodynamics since Boyle's work in the 17th century [Boyle-Ref]. However, it does not correctly predict gas-liquid behavior for most applications. Towards this issue, there have been many modifications to the vdW equation to correct its performance [2]. These modifications can all be generated from the generic cubic equation of state model:

$$P = \frac{RT}{(v - b)} - \frac{a(T)}{(v + \epsilon b)(v + \sigma b)} \tag{11}$$

For a given equation of state, ϵ and σ are constants (the same for all substances), while $a(T)$ and b are substance specific. The temperature dependence model, $a(T)$, is specific to each equation of state. Similar to vdW, we can derive analytical expressions for the $a(T)$ and b in terms the critical temperature and pressure:

$$a(T) = \Psi \left[\frac{\alpha(T_r) R^2 T_{cr}^2}{P_{cr}} \right] \qquad b = \Omega \left[\frac{RT_{cr}}{P_{cr}} \right] \tag{12}$$

Eq. of State	$\alpha\left(T_r\right)$	σ	ϵ	Ω	Ψ
vdW (1873)	1	0	0	1/8	27/64
RK (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK (1972)	$\alpha_{SRK}\left(T_r, \omega\right)$	1	0	0.08664	0.42748
PR (1976)	$\alpha_{PR}\left(T_r, \omega\right)$	$1+\sqrt{2}$	$1 - \sqrt{2}$	0.07779	0.45724

Data driven equations of state Suppose we know the molar (or specific) volume of a pure substance (in either the liquid, gas or solid phase) at some temperature T_o and pressure P_o, denoted by $v_o(T_o, P_o)$. Instead of developing a model for how the molar or specific volume changes as we move around the entire PT-space (which is complicated by phase transitions), lets develop an expression for $v(T, P)$ in the neighborhood of (T_o, P_o) by a Taylor expansion of $v(T, P)$:

$$dv \simeq \left(\frac{\partial v}{\partial T}\right)\Big|_P dT + \left(\frac{\partial v}{\partial P}\right)\Big|_T dP \tag{13}$$

Dividing both sides of the Taylor approximation by the molar (or specific volume) and then integrating:

$$\int_{v_o}^{v} \frac{dv}{v} = \int_{T_o}^{T} \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)\Big|_P dT + \int_{P_o}^{P} \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)\Big|_T dP \tag{14}$$

gives (after some algebraic rearrangement):

$$v \simeq v_o \exp\left(\beta\Delta T - \kappa\Delta P\right) \tag{15}$$

where $\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)\Big|_P$ and $\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)\Big|_T$ are referred to as the volume expansivity and the isothermal compressibility, respectively and $\Delta P = P - P_o$ and $\Delta T = T - T_o$.

Example: For liquid acetone at 20°C and 1 bar:

$$\beta = 1.5 \times 10^{-3}\ {}^{\circ}\text{C}^{-1} \qquad \kappa = 62 \times 10^{-6}\ \text{bar}^{-1} \qquad V = 1.3\ \text{ml g}^{-1}$$

For acetone estimate:

(a) The value of $\left(\partial P/\partial T\right)\Big|_V$

(b) The pressure generated by heating at constant volume from 20°C and 1 bar to 30°C

(c) The change in volume for a change from 20°C and 1 bar to 0°C and 10 bar

Generalized correlation models

Generalized correlation models find widespread industrial use. The most popular of these models are those developed by Pitzer and coworkers for the compressibility factor Z and the second virial coefficient [REF].

References

1. van der Waals, J D (1873) On the Continuity of the Gaseous and Liquid States. Ph.D. thesis, Universiteit Leiden, Leiden, The Netherlands.
2. Jose O Valderrama (2003) The State of the Cubic Equations of State. Ind Eng Chem Res 42: 1603-1618.