CHEME 3130: Equations of state for pure substances

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Previously:

We introduced the energy balance for an open and closed system. An open system allows both mass and energy transfer between the system and its surroundings:

$$\frac{d}{dt}\left[m\left(u + \frac{1}{2}\bar{v}_s^2 + gz\right)\right]_{sys} = \dot{Q} + \dot{W}_{sh} + \sum_{s=1}^{\mathcal{S}}\nu_s\left(h_s + gz_s + \frac{1}{2}\bar{v}_s^2\right)\dot{m}_s + \sum_{r=1}^{\mathcal{R}}\dot{e}_r$$

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

While no mass transfer is allowed between the system and the surroundings for a closed system. We derived the differential forms for the closed energy balances (closed first law):

$$\delta Q = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

$$\delta Q = C_P dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

where C_P and C_V denote the constant pressure and constant volume heat capacities, respectively. Mechanical work in a closed system was given by $\delta W = -P_e dV$, where P_e denotes the external pressure (of the surroundings). The external pressure $P_e \simeq P$ (external pressure equals the system pressure) for reversible expansion or contraction operations.

Student outcomes:

At the end of this lecture module, you will be able to:

O_1 Describe the assumptions associated with, and the similarities and differences between the ideal gas law, cubic equations of state, and the Virial equation of state

O_2 Use the ideal and cubic equations of state to calculate the reversible work for isothermal and adiabatic expansion/contraction of gases

O_3 Describe pressure-temperature (PT) and pressure-volume (PV) phase diagrams, the triple and critical points.

Introduction

Equations of state are mathematical models of the behavior of pure materials, or mixture of materials as a function of physical conditions and composition. Equations of state are critically important because the physical knobs that we can adjust for chemical engineering processes are the temperature T, pressure P and volume V of the system. However, these three properties are not independent; we typically write a single property, for example the volume of system, as a function of the temperature T and the pressure P, which are independent parameters that can be adjusted for some technological benefit. Thus, we rely on an equation of state to *predict* properties e.g., the volume from the independent parameters.
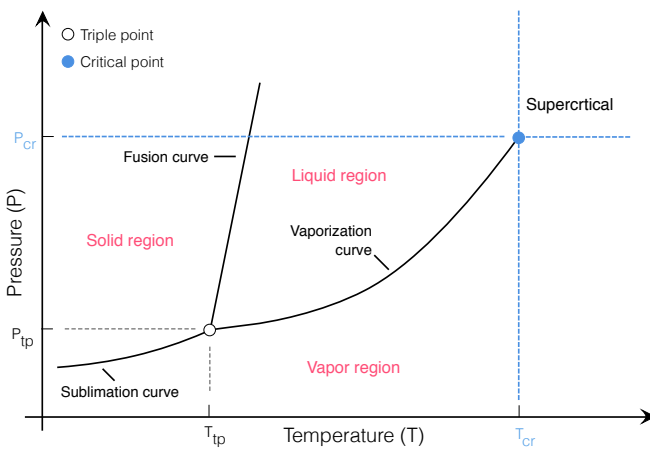
Fig. 1: Hypothetical pressure temperature (PT) phase diagram for a pure material.

Consider a typical pressure temperature (PT) phase diagram for a pure substance (Fig. 1, top). 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, the supercritical phase which has fluid like properties. The solid lines on the PT-diagram are borders which 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., a liquid or gas only; however, directly on these curves both phases exist in a mixture. At a special point called the triple point (P_{tp},T_{tp}) all three phases coexist. Continuing up the vaporization curve, we arrive at the critical point (P_{cr},T_{cr}). When temperature and pressure exceed the critical values, the differences between liquid and gas phases disappear, leading to a homogeneous supercritical fluid. Supercritical fluids have many industrial applications [1].

Equation of state models

An equation of state is a function $\mathcal{F}(\cdot)$ that described how the state variables, temperature T, pressure P, volume V and composition n of a system are related, such that:

$$\mathcal{F}(P, T, V, n) = 0 \tag{1}$$

Thus, equations of state are mathematical models of the physical behavior of pure substances, or mixtures with a few modifications. The structure of an equation of state can be motivated by our understanding of the physics of the molecules in a system, or can also be data driven mathematical constructs. Ultimately, the origin of an equation of state is irrelevant; given that their

primary purpose is the prediction of system properties, if predictions are good it does not matter how we arrived at the particular functional form for an equation of state. Let's discuss are few common equations of state that you likely use in process calculations.

Ideal Gas Law (IGL). One of the simplest equations of state is the ideal gas law (IGL):

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

The IGL ignores both the volume of the molecules in the gas, and all interactions between them (hard-sphere model) other than collisions with the wall of the container and each other. The attractiveness of the ideal gas law comes from our ability to derive it from first principles; the functional form for the ideal gas law can be derived from the kinetic theory of gases (discussed in almost every physical chemistry textbook). However, the IGL does not accurately describe gas phase behavior at realistic pressures, not does it describe phase transitions. Despite this, the IGL is often used for *quick and dirty* process calculations, even though it is technically valid in only in the limit of zero pressure.

The compressibility factor Z as a correction to the IGL. Suppose we wanted to fix the IGL so that we could use it under realistic process conditions. One strategy to do this would be to formulate a dimensionless correction factor that added back intermolecular forces, (and the volume of molecules making up a material) to the IGL. Lets give this correction factor the symbol Z, and call it the compressibility factor defined as $Z \equiv Pv/RT$. It's easy to see that the compressibility factor can act as correction to the IGL if we re-arrange the definition:

$$Pv = ZRT \tag{3}$$

where if $Z = 1$ we recover the IGL. However, we have not formulated what Z is; let's define the compressibility factor as:

$$Z \equiv \sum_{i=0}^{\infty} \alpha_i v^{-i} \qquad \text{or} \qquad Z \equiv \sum_{i=0}^{\infty} \alpha_i' P^i \tag{4}$$

These models for Z are called the Virial equations of state, where α_i, α_i' denotes Virial coefficients. The Virial coefficients α_i and α_i' which are related with one another:

$$
\begin{aligned}
\alpha_0 = \alpha_0' &= 1 \\
\alpha_1' &= \frac{\alpha_1}{RT} \\
\alpha_2' &= \frac{\alpha_2 - \alpha_1^2}{(RT)^2} \\
&\vdots
\end{aligned}
$$

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 can be derived from first-principle statistical mechanical calculations given a potential function which describes the
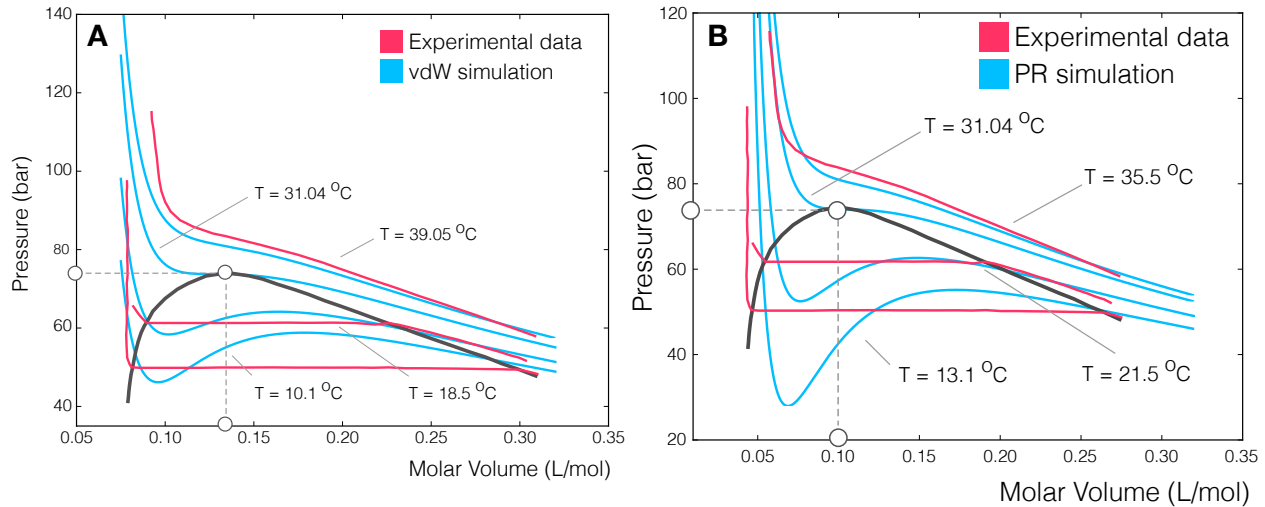
Fig. 2: Pressure volume behavior of CO_2. A: vdW equation prediction of the PV behavior of CO_2 for different temperatures versus data. B: Peng-Robinson equation prediction of the PV behavior of CO_2 for different temperatures versus data.

strength of interactions between molecules. The first Virial coefficient is always defined as unity, while the second Virial coefficient describes two-body interactions, the third describes three-body interactions and so on.

Cubic Equations of State. Cubic equations of state were developed to address the limitations of the ideal gas law. The general form for this class of equation of state is given by:

$$v^3 + f_1(T,P)v^2 + f_2(T,P)v + f_3(T,P) = 0 \tag{5}$$

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:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{6}$$

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 [2]; he later won the Nobel prize for this work in 1910. The first term in the vdW equation is the volume-corrected ideal gas law; the parameter b describes the volume occupied by the molecules of the gas. Thus $v - b$ describes the molar volume that is not occupied by the gas moleculues. The second term in the vdW equation describes the attraction between molecules; this term describes how potential energy interactions between molecules influences the pressure and is parameterized by the vdW parameter a. The vdW parameters can be estimated directly from data (as van der Waals himself did), potentially from first-principles statistical mechanical calculations, or from analytical expressions derived based upon the behavior of the fluid near the critical point.

Example. 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}:

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

After we expand the term in parenthesis we get:

$$v^3 - (3v_{cr})\, v^2 + \left(3v_{cr}^2\right) v - v_{cr}^3 = 0 \tag{8}$$

The vdW equation in standard form is given by:

$$v^3 - \left(b + \frac{RT_{cr}}{P_{cr}}\right) v^2 + \frac{a}{P_{cr}} v - \frac{ab}{P_{cr}} = 0 \tag{9}$$

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

$$3v_{cr} = b + \frac{RT_{cr}}{P_{cr}} \qquad 3v_{cr}^2 = \frac{a}{P_{cr}} \qquad v_{cr}^3 = \frac{ab}{P_{cr}} \tag{10}$$

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

$$v_{cr} = \frac{3}{8}\frac{RT_{cr}}{P_{cr}} \qquad a = \frac{27}{64}\frac{R^2 T_{cr}^2}{P_{cr}} \qquad b = \frac{1}{8}\frac{RT_{cr}}{P_{cr}} \tag{11}$$

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). vdW using a and b defined by the critical values has good performance near the critical point, but fails to capture the correct behavior away from the critical region (Fig. 2A).

Reduced vdW and principle of corresponding states. van der Waals hypothesized that all fluids, when compared at the same *reduced* temperature and reduced pressure, have approximately the same *compressibility factor*, and all deviate from ideal gas behavior to about the same degree. This hypothesis is called the *principle of corresponding states*. The utility of the principle of corresponding states is that it removes the material dependence from material specific constants; material specific constants that vary for each type of substance are eliminated in the *reduced* form of the equation of state. To begin this discussion, we first define what we mean by *reduced*. The reduced form for an equation state is the dimensionless form written with respect to:

$$T_r = T/T_{cr} \qquad P_r = P/P_{cr} \qquad v_r = v/v_{cr} \tag{12}$$

The reduced temperature T_r, pressure P_r and molar volume v_r are dimensionless quantitates that collapse the temperature, pressure and volume of all materials onto the same scale. Starting with the vdW equation, and the closed forms of a and b in terms of the critical temperature and pressure we can substitute the pressure, temperature and the molar volume in terms of the reduced

Table 1: Common cubic equations of state. The α functions for the SRK and Peng-Robinson (PR) are given by: $\alpha_{SRK}(T_r, \omega) = \left(1 + \left(0.480 + 1.574\omega - 0.176\omega^2\right)\left(1 - \sqrt{T_r}\right)\right)^2$ where ω is called the accentric factor and $\alpha_{PR}(T_r, \omega) = \left(1 + \kappa\left(1 - \sqrt{T_r}\right)\right)^2$ where $\kappa = 0.37464 + 1.54336\omega - 0.26992\omega^2$.

Eq. of State	year	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
van der Waals (vdW)	1873	1	0	0	1/8	27/64
Redlich-Kwong (RK)	1949	$T_r^{-1/2}$	1	0	0.08664	0.42748
Soave-Redlich-Kwong (SRK)	1972	$\alpha_{SRK}(T_r, \omega)$	1	0	0.08664	0.42748
Peng-Robinson (PR)	1976	$\alpha_{PR}(T_r, \omega)$	$1+\sqrt{2}$	$1 - \sqrt{2}$	0.07779	0.45724

variables to arrive at (after some algebra):

$$P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \tag{13}$$

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's law, published in 1662, see [3]). 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 [4]. These modifications can all be generated from the generic cubic equation of state model:

$$P = \frac{RT}{(v - b)} - \frac{a(T)}{(v + \epsilon b)(v + \sigma b)} \tag{14}$$

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:

$$a(T) = \Psi\left[\frac{\alpha(T_r) R^2 T_{cr}^2}{P_{cr}}\right] \qquad b = \Omega\left[\frac{RT_{cr}}{P_{cr}}\right] \tag{15}$$

Example: Estimate the second Virial coefficient α_1 as a function of temperature from CH_4 compressibility data.

Solution: Keeping up to first order term, the compressibility factor as a function of pressure gives:

$$Z = 1 + \alpha_1' P \tag{16}$$

We can estimate α_1' from the derivative of the power series expansion. The coefficient α_1' is the slope of the compressibility versus pressure; differentiating the Z pressure power series with respect to pressure gives:

$$\frac{dZ}{dP} = \sum_{i=0}^{\infty} i \cdot \alpha_i' P^{i-1} \tag{17}$$

from which:

$$\frac{dZ}{dP} = \alpha_1' = \frac{\alpha_1}{RT} \tag{18}$$

when $i = 1$. Substituting the expression for α_1' in terms of α_1 into Eqn. (16) gives:

$$Z = 1 + (\alpha_1/RT)\, P \tag{19}$$

Equation (19) is has slope α_1/RT; thus given CH_4 data we can estimate α_1 by computing the slope of P versus Z for at different temperatures.

Data driven equations of state for solids and liquids.

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 $v(T, P)$:

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP \tag{20}$$

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

$$\int_{v_o}^{v} \frac{dv}{v} = \int_{T_o}^{T} \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P dT + \int_{P_o}^{P} \frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T dP \tag{21}$$

gives (after some algebraic rearrangement):

$$v = v_o \exp\left(\beta \Delta T - \kappa \Delta P\right) \tag{22}$$

where

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad \kappa \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{23}$$

are the volume expansivity and the isothermal compressibility, respectively and $\Delta P = P - P_o$ and $\Delta T = T - T_o$. Equation (22) forms an approximate equation of state, for materials in any phase provided β and κ can be measured in the neighborhood of the operating point (T_o, P_o). Of course, because this approximate equation of state is only the linear terms of the Taylor series, its performance will degrade the further away we get from the operating point.

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

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

For acetone estimate:

(a) The value of $\left(\partial P/\partial T\right)_v$

(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

Solution

(a) The approximate equation of state reduces to:

$$\beta dT - \kappa dP = 0 \tag{24}$$

at constant volume. Rearranging the constant volume equation of state gives:

$$\left(\frac{dP}{dT}\right)_v = \frac{\beta}{\kappa} = 24 \text{ bar } {}^\circ\text{C}^{-1} \tag{25}$$

(b) Lets assume that β and κ are constant across the 10°C temperature difference. At constant volume, we can solve for dP:

$$dP = \left(\frac{\beta}{\kappa}\right) dT \tag{26}$$

Integrating the pressure expression:

$$\int_{P_0}^{P_1} dP = \int_{T_0}^{T_1} \left(\frac{\beta}{\kappa}\right) dT \tag{27}$$

gives:

$$P_1 = P_0 + \left(\frac{\beta}{\kappa}\right) \Delta T \tag{28}$$

Substituting in the values for ΔT, β and κ gives:

$$P_1 = 240 + (24)(10) = 241 \text{ bar} \tag{29}$$

(c) Direct substitution of the change in pressure, temperature, β and κ to calculate the new volume:

$$v \simeq (1.287) \exp\left((1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9)\right) = 1.26 \text{ cm}^3 \text{ g}^{-1} \tag{30}$$

where gives $\Delta v = (1.26 - 1.3) = -0.039 \text{ cm}^3 \text{ g}^{-1}$.

Generalized correlation models

Generalized correlation models for the compressibility factor Z and the second Virial coefficient α_1 find widespread industrial use. The most popular of these correlations was developed by Pitzer and coworkers [5]. The correlation for the compressibility factor is given by:

$$Z = Z^0 + \omega Z^1 \tag{31}$$

where Z^0 and Z^1 are functions of the *reduced temperature* $\text{T}_r = \text{TT}_{cr}^{-1}$ and *reduced pressure* $\text{P}_r = \text{PP}_{cr}^{-1}$, and ω denotes the *acentric factor*. The acentric factor, introduced by Pitzer in 1955, is a tool to characterize the phase of single components; at a molecular level the acentric factor is a measure of the non-sphericity (centricity) of molecules. A similar model can be developed for the second Virial coefficient. See the study of Pitzer and coworkers [5] and Section 4.4 of MDK for details.

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