

---

## Equations of State (EoS)

### Equations of State

- From molecular considerations, identify which intermolecular interactions are significant (including estimating relative strengths of dipole moments, polarizability, etc.)
- Apply simple rules for calculating  $P$ ,  $v$ , or  $T$ 
  - Calculate  $P$ ,  $v$ , or  $T$  from non-ideal equations of state (cubic equations, the virial equation, compressibility charts, and ThermoSolver)
  - Apply the Rackett equation, the thermal expansion coefficient, and the isothermal compressibility to find  $v$  for liquids and solids
- State the molecular components that contribute to internal energy
- Relate macroscopic thermodynamic properties/behaviors with their molecular origins, including point charges, dipoles, induced dipoles, dispersion interactions, repulsive forces, and chemical effects
- Define van der Waals forces and relate it to the dipole moment and polarizability of a molecule
- Define a potential function
- Write equations for ideal gas, hard sphere, Sutherland, and Lennard-Jones potentials and relate them to intermolecular interactions
- Explain the origin of an use "complex" equations of state
  - State the molecular assumptions of the ideal gas law
  - Explain how the terms in the van der Waals equation relax these assumptions
  - Describe how cubic equations of state account for attractive and repulsive interactions
  - State and use the principle of corresponding states to develop expressions for the critical property data of a species
  - Describe the purpose of the acentric factor and its role in the construction of compressibility charts
- Adapt our approach to mixtures
  - Write the van der Waals mixing rules and explain their functionality in terms of molecular interactions
  - Write the mixing rules for the virial coefficients and for pseudo-critical properties using Kay's rule
  - Using mixing rules to solve for  $P$ ,  $v$ , and  $T$  of mixtures
- Write the exact differential of one property in terms of two other properties
- Use departure functions to calculate property data for real fluids (and use them to solve engineering problems)
  - Calculate departure functions from Lee-Kesler charts
  - Use equations of state to calculate departure functions

## Ideal Gas Law DEFINITION

An **equation of state** relates the molar density (or specific molar volume) of a fluid (i.e., a vapor or a liquid) to the temperature and pressure of the fluid.

The state postulate claims that any two intensive variables can fix the state of a system, therefore, we can tabulate all state variables with respect to any two (measurable) properties (see the steam tables), or (more conveniently) we can write an explicit mathematical expression of one property in terms of any two others:

$$P = f(T, v)$$

The most common and simplest equation of state is the ideal gas law:

$$P = \frac{nRT}{V} = \frac{RT}{v}$$

## DEFINITION

A generic expression for an equation of state is to define a property, **the compressibility factor**, as the ratio of  $Pv$  to  $RT$ :

$$z \equiv \frac{Pv}{RT}$$

Obviously,  $z=1$  for an ideal gas. Real gases often show  $z < 1$  at modest pressures and  $z > 1$  at very high  $P$

## NOTE

Interestingly, the ideal gas law can be derived from our molecular understanding of the properties  $T$  ( $E_{k_{\text{molecular}}} = (1/2)m\bar{V}^2 = (3/2)kT$ ) and  $P$  ( $(1/A)\sum\left[\frac{d(m\bar{V})}{dt}\right]$ ). This requires the following assumptions:

- Ideal gases involve molecules that occupy no volume
- Ideal gases involve molecules that exert no intermolecular forces

## IMPORTANT

The ideal gas law is an approximation (!) that has only limited applicability. It is usually used for diatomic gas when  $(RT/P) > 5$  L/mol and for other gases when  $(RT/P) > 20$  L/mol (i.e., at high specific volumes!).

## OUTCOME:

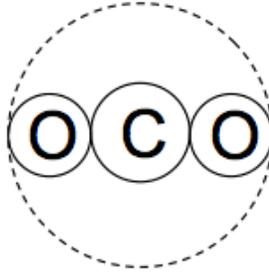
State the molecular assumptions of the ideal gas law

## TEST YOURSELF:

44 g  $\text{CO}_2$  are placed in a 0.23 liter container at 26C. The pressure is recorded to be 6 MPa. Evaluate whether ideal gas conditions are well-approximated.

## Excluded Volume

Real gases occupy volume because the atoms/molecules have an effective radius:



The volume occupied per mole is given by:

$$v_{\text{molecules}} = \frac{4}{3}\pi R^3 x N_{\text{Avo}}$$

### TEST YOURSELF:

*If our CO<sub>2</sub> from the previous example has effective radii given as Carbon : 0.07 nm ; Oxygen : 0.062 nm; molecule : approx 0.19 nm, determine what the fractional volume occupied is.*

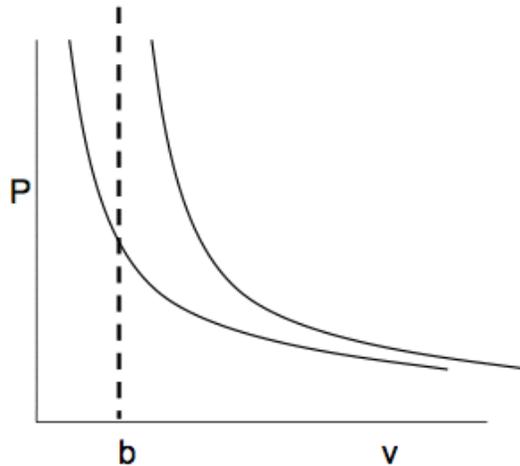
How to account for this effect?

### DEFINITION

*The **excluded volume**, is the volume that is occupied by atoms/molecules and is therefore "unavailable" for molecular motion. Many EoS simply directly correct for this effect by subtracting the excluded volume,  $b$ .*

$$P = \frac{RT}{v-b}$$

This is one of the most common (and simplest) modifications of the ideal gas law.



## Intermolecular Forces

Molecules are made of positively charged nuclei and negatively charged electrons, therefore, it is useful to think of many of the interactions between molecules as electronic in nature. The electric field intensity is given by:

$$\vec{E} = \frac{\vec{F}}{Q} = \frac{-\vec{\nabla}\Gamma}{Q}$$

where  $\vec{\nabla}$  denotes a spatial derivative, and  $\Gamma$  is the molecular potential energy. The electrostatic intermolecular interactions that we will consider are:

- Point charges: between ions, or in plasmas
- Permanent Dipoles
- Induced Dipoles
- Dispersion Forces

### DEFINITION

*Interactions between **point charges** are the simplest kind of electrostatic interactions. Here we assume that all of the charge of a molecule is concentrated at a point.*

The interaction force/potential between point charges is given as:

$$F_{12} \propto \frac{Q_1 Q_2}{r^2}$$

$$\Gamma_{12} \propto \frac{Q_1 Q_2}{r}$$

### NOTE:

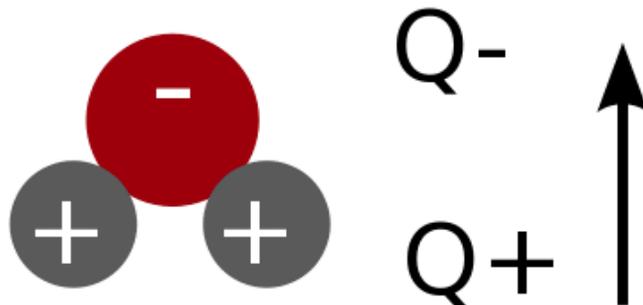
*If the charges are the same, then the force is positive (repulsive).*

---

EoS: Permanent Dipoles

### Permanent Dipoles

Some molecules, while not having a net charge, have an asymmetrical distribution of charges (Ex: water, ammonia, acetone).



## DEFINITION

The **dipole moment**,  $\mu$ , of a molecule is the charge times the distance separating the charge(s) and has units of Debye (D) (which is  $3.336 \times 10^{-30} \text{ Cm}$ ).

$$\mu = Ql$$

$$F_{12} \propto -\frac{\mu_1^2 \mu_2^2}{r^7}$$

$$\Gamma_{12} \propto -\frac{\mu_1^2 \mu_2^2}{r^6}$$

## NOTE

The potential energy of a dipole drops off dramatically faster with  $r$  than the energy between point charges. (Also, because it is an even power, there is a negative in both expressions.)

---

Eos: Induced Dipoles and Dispersion Forces

### Induced Dipoles and Dispersion Forces

Symmetric molecules have no net charge and a symmetrical distribution of charges, so there is no dipole interaction between them (Ex:  $\text{CO}_2$ ,  $\text{CH}_4$ ).

Nevertheless, proximity to permanent dipoles can *induce* a temporary dipole in these symmetric molecules.

## DEFINITION

An **induced dipole** is caused when a molecule that would not by itself have a dipole moment is brought close to a molecule with a dipole moment. (That is, the dipole "pushes" the electron cloud of the symmetric molecule.)

## DEFINITION

The **polarizability**,  $\alpha$ , of a molecule characterizes the ease to which that molecule's electrons are "pushed". What do you think influences this value?

$$F_{12} \propto -\frac{\mu_1^2 \alpha_2}{r^7}$$

$$\Gamma_{12} \propto -\frac{\mu_1^2 \alpha_2}{r^6}$$

Even if two symmetric molecules (with no net charge) come into proximity, fluctuations in the electron cloud density can induce dipole-like behavior.

## DEFINITION

**Dispersion (London) Forces** arise when two non-polar (i.e., do not have a dipole) molecules are brought close together so that their time-varying electron clouds "push" each other.

$$F_{12} \propto -\frac{\alpha_1 \alpha_2}{r^7}$$

$$\Gamma_{12} \propto -\frac{\alpha_1 \alpha_2}{r^6}$$

## DEFINITION

Dipole-dipole, dipole-induced-dipole, and dispersion forces are all attractive and all decay as  $r^{-7}$  (potential decays as  $r^{-6}$ ). All are lumped together as **van der Waals forces**.

## OUTCOME

Define van der Waals forces and relate it to the dipole moment and polarizability of a molecule.

EoS: Intermolecular Potentials

### Intermolecular forces and potentials

So far, we have discussed attractive portion of potentials. The simplest way to include the idea of excluded volume is to assume a "hard sphere" repulsion when the molecules approach too closely. That is, we assume an impenetrable molecule radius,  $\sigma$ .

$$\Gamma = 0 \text{ for } r > \sigma$$

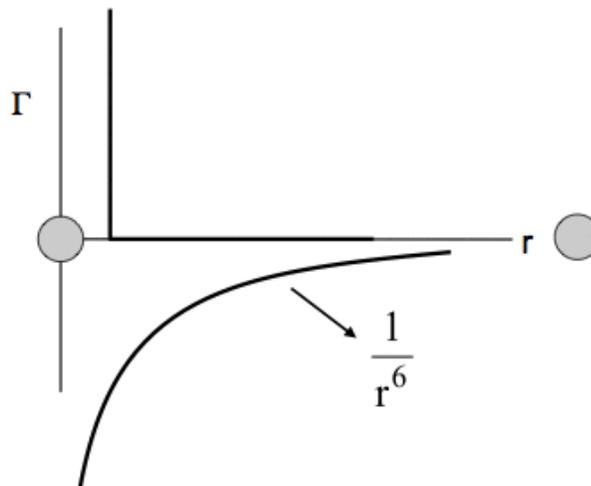
$$\Gamma = \infty \text{ for } r \leq \sigma$$

## DEFINITION

The simplest total model of intermolecular potential available is the **Sutherland Potential** which simply adds van der Waals potential(s) to the hard sphere potential.

$$\Gamma = \frac{-C_6}{r^6} \text{ for } r > \sigma$$

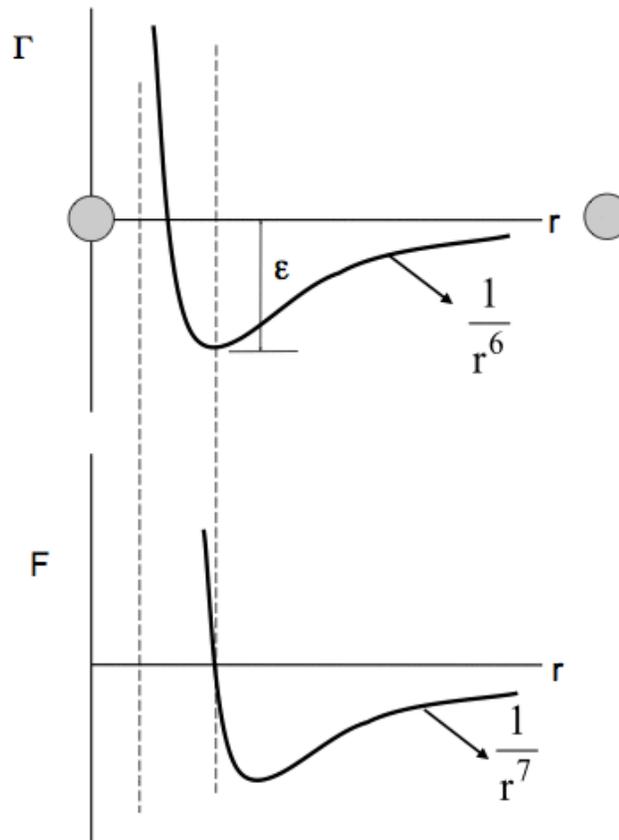
$$\Gamma = \infty \text{ for } r \leq \sigma$$



## DEFINITION

A more "realistic" model of intermolecular potential is the **Lennard-Jones Potential** which includes van der Waals-like attraction and a strong (but not hard sphere) repulsion.

$$\Gamma = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$



### OUTCOME

*Define a potential function*

### OUTCOME

*Write equations for ideal gas, hard sphere, Sutherland, and Lennard-Jones potentials and relate them to intermolecular interactions*

EoS: The principle of corresponding states

### The principle of corresponding states

Since the Lennard-Jones potential can be used somewhat generically to describe the interactions between molecules and it depends on only two parameters --  $\sigma$  and  $\varepsilon$  -- it is intriguing to postulate the following.

#### DEFINITION

*The **principle of corresponding states** suggests that (for normalized choices of  $\varepsilon$  and  $\sigma$ ) the dimensionless potential energy is the same for all species.*

In other words, rather than having

$$\Gamma_{ii} = 4\varepsilon_i \left[ \left( \frac{\sigma_i}{r} \right)^{12} - \left( \frac{\sigma_i}{r} \right)^6 \right]$$

apply solely to interactions between  $i$  molecules (i.e., having a new version of this equation for every molecule), we can instead define a function:

$$f\left(\frac{\Gamma_{ii}}{\varepsilon_i}, \frac{r}{\sigma_i}\right) = 0$$

that works for everything.

Adapting this statement to macroscopic quantities, van der Waals suggested that we could instead normalize using the critical properties of a fluid so that

### DEFINITION

*The **principle of corresponding states (take 2)** states that all fluids at the same "reduced temperature" ( $\frac{T}{T_c}$ ) and "reduced pressure" ( $\frac{P}{P_c}$ ) have the same compressibility factor.*

Mathematically, this means that we can define a function:

$$f\left(\frac{T}{T_c}, \frac{P}{P_c}, \frac{v}{v_c}\right) = 0$$

or

$$z = \frac{Pv}{RT} = f'\left(\frac{T}{T_c}, \frac{P}{P_c}\right)$$

### NOTE

*This expression actually works quite well for non-polar fluids. That is, it works for fluids that exhibit only induced dipoles, rather than permanent ones.*

In order to extend this idea to asymmetrical (polar) molecules, we define:

### DEFINITION

*The **Pitzer acentric factor**,  $\omega$ , quantifies the degree of polarity of a molecule (that is, how asymmetrical it is).*

$$\omega \equiv -1 - \log_{10} [P^{sat}(T_r = 0.7) / P_c]$$

Finally, we can mathematically write this generic idea as:

$$f\left(\frac{T}{T_c}, \frac{P}{P_c}, \frac{v}{v_c}, \omega\right) = 0$$

or

$$z = \frac{Pv}{RT} = f'_o\left(\frac{T}{T_c}, \frac{P}{P_c}\right) + \omega f'_1\left(\frac{T}{T_c}, \frac{P}{P_c}\right) = z_o + \omega z_1$$

### NOTE

*The **generalized compressibility charts** plot  $z_o$  and  $z_1$  as a function of  $T_r$  and  $P_r$ .*

### OUTCOME

*State and use the principle of corresponding states to develop expressions for the critical property data of a species*

### OUTCOME

*Describe the purpose of the acentric factor and its role in the construction of compressibility charts*

### TEST YOURSELF

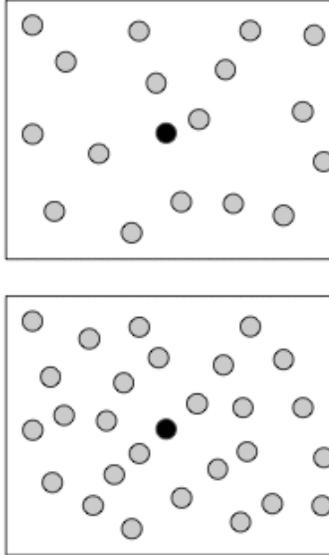
*Let's revisit our friend and calculate the container size when 44 g  $CO_2$  is at  $P=6\text{MPa}$  and  $26\text{C}$  (i.e., do we get 0.23 liters?)*

## Intermolecular Potentials and Equations of State

We are now ready to build EoS based on our understanding on intermolecular interactions.

### NOTE

*Intermolecular interactions are at least pairwise, therefore, as  $v$  decreases binary interactions are the first ones to become important*



The number of pairwise interactions scales with the number of molecules as follows:

# of pairwise interactions **per** molecule =  $(N - 1)$

total # of pairwise interactions = # of pairwise interactions **per** molecule X # of molecules

total # of pairwise interactions =  $(N - 1) \times N \approx N^2$

### NOTE

*Since the number of pairwise interactions increases with decreasing*

*$v$  -- total # of pairwise interactions  $\propto \frac{1}{v^2}$*

Revisiting our friend the van der Waals equation, we can then write:

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

### QUESTION?

*Why do we "correct"  $P$ ? Why is that "correction" negative?*

We could also write this as:

$$v^3 - \left(\frac{RT+Pb}{P}\right)v^2 + \left(\frac{a}{P}\right)v - \frac{ab}{P} = 0$$

### OUTCOME

*Explain how the terms in the van der Waals equation relax these assumptions*

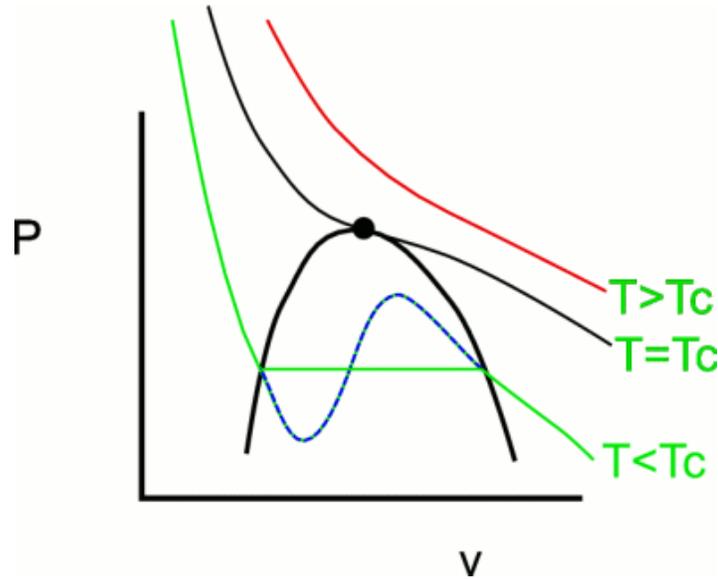
### OUTCOME

*Describe how cubic equations of state account for attractive and repulsive interactions*

---

### Cubic Equations of State

The general form of correcting the  $v$  for "excluded volume" and subtracting a term proportional to  $v^{-2}$  (top correct the pressure to account for attractive forces) leads to a class of equations of state called cubic equations of state, that have the interesting property of being able to capture both the liquid and vapor conditions:



In order to use the van der Waals equation of state, we need to determine the material-dependent constants,  $a$  and  $b$ .

Using the principle of corresponding states, we can argue that the constants for all materials may be obtained by recognizing that, at the critical point:

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0$$

We can then use three equations (the vdW EOS and these two derivatives) at the critical point to write  $a$  and  $b$  in terms of  $P_c$  and  $T_c$ :

$$P_c = \frac{RT_c}{v_c b} - \frac{a}{v_c^2}$$

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 = -\frac{RT_c}{(v_c b)^2} + \frac{2a}{v_c^3}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 = \frac{2RT_c}{(v_c b)^3} - \frac{6a}{v_c^4}$$

this approach leads to (i.e., solving the two equations -- above -- for the two unknowns --  $a$  and  $b$ ):

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}$$

$$b = \frac{RT_c}{8P_c}$$

doing a bit more algebra, we can write an expression for  $z_c$ :

$$z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$$

which is higher than is typically observed experimentally.

Following the same procedure for a few of the more common other cubic equations:

Name	Attractive term	$a$	$b$
------	-----------------	-----	-----

van der Waals	$\frac{a}{v^2}$	$\frac{27}{64} \frac{(RT_c)^2}{P_c}$	$\frac{RT_c}{8P_c}$
Redlich-Kwong	$\frac{a}{\sqrt{T} v(v+b)}$	$\frac{0.42748R^2T_c^{2.5}}{P_c}$	$\frac{0.08664RT_c}{P_c}$
Soave-Redlich-Kwong	$\frac{a\alpha(T)}{v(v+b)}$	$\frac{0.42748R^2T_c^2}{P_c}$	$\frac{0.08664RT_c}{P_c}$
Peng-Robinson	$\frac{a\alpha(T)}{v(v+b)+b(v-b)}$	$\frac{0.45724R^2T_c^2}{P_c}$	$\frac{0.0778RT_c}{P_c}$

### NOTE:

*The critical compressibility factor for the Redlich-Kwong is improved, at 1/3, and is even more in line with experimental observations for SRK and PR (closer to 0.3)*

In the SRK and PR equations,  $\alpha(T)$  is a function that replaces the  $\sqrt{T}$  from the RK equation. Both functions are similar, and given by:

$$\alpha_{SRK}(T) = \left[ 1 + (0.48508 + 1.55171\omega - 0.17613\omega^2)(1 - \sqrt{T_r}) \right]^2$$

$$\alpha_{PR}(T) = \left[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r}) \right]^2$$

### OUTCOME

*Describe how cubic equations of state account for attractive and repulsive interactions*

### OUTCOME

*Calculate  $P$ ,  $v$ , or  $T$  from non-ideal equations of state (cubic equations, the virial equation, compressibility charts, and ThermoSolver)*

### TEST YOURSELF

*Use the vdW EoS to calculate the pressure of 44 g  $CO_2$  in a 0.23 liter container at 26C (i.e., do we get  $P=6$  Mpa?)*

EoS: Virial Equation of State

### Virial Equations of State

The virial equations of state are power series expansions for the compressibility factor in either specific volume:

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

or pressure:

$$z = \frac{Pv}{RT} = 1 + B' P + C' P^2 + D' P^3 + \dots$$

An interesting consequence of this form for an equation of state is that the coefficients can be directly related to a first principles (statistical mechanics and/or physical chemistry) analysis of intermolecular potentials.

- $B$  is related to "two body" interactions
- $C$  is related to "three body" interactions
- ...

## NOTE:

*As pressure increases, multi-body interactions become more important and more terms in the virial equation should be used. Conversely, as pressure decreases, even two-body interactions become negligible and the ideal gas law is recovered.*

While these coefficients can be derived from first principles, there are a number of correlations that are in common use. One example includes the following (for the virial equation truncated at two-body interaction):

$$B = \frac{RT_c}{P_c} (B_0 + \omega B_1)$$

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

## OUTCOME

*Calculate  $P$ ,  $v$ , or  $T$  from non-ideal equations of state (cubic equations, the virial equation, compressibility charts, and ThermoSolver)*

### EoS: Equations of State for Mixtures

#### Equations of State for Mixtures

When dealing with mixtures the material-dependent constants require **mixing rules** due to the fact that the potential number of combinations is infinite.

#### Virial Equation for Mixtures

The most straight-forward, and theoretically sound, mixing rules apply to the virial equation.

- $B$  depends on two-body interactions
  - two-body interactions ( $i-j$ ) depend on  $y_i$  and  $y_j$ 
    - $B_{mix} = \sum_i \sum_j y_i y_j B_{ij}$
- $C$  depends on three body interactions
  - three-body interactions ( $i-j-k$ ) depend on  $y_i$ ,  $y_j$ , and  $y_k$ 
    - $C_{mix} = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk}$

#### Cubic EOS for Mixtures

While not as theoretically sound the terms in the cubic equations of state have the following rough meanings:

- $b$  relates to the excluded volume due to molecule size
- $a$  relates to intermolecular interactions (assumed to be two-body interactions, for simplicity)

therefore:

$$a_{mix} = \sum_i \sum_j y_i y_j a_{ij}$$

or

$$a_{mix} = \sum_i \sum_j y_i y_j [a\alpha(T)]_{ij}$$

where

$$a_{ij} = \sqrt{a_i a_j}$$

or (for some EOS)

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{12})$$

The excluded volume is simpler (and more "correct"), given by:

$$b_{mix} = \sum_i y_i b_i$$

### Corresponding States for Mixtures

There is no theoretically sound way to adapt the concept of corresponding states. The most commonly used is **Kay's Rules**, which defines "pseudo-critical" properties:

$$T_{r,mix} = \frac{T}{T_{pc}}, \text{ for example, where}$$

$$T_{pc} = \sum_i y_i T_{c,i}$$

$$P_{pc} = \sum_i y_i P_{c,i}$$

$$\omega_p = \sum_i y_i \omega_i$$

### OUTCOME

*Write the van der Waals mixing rules and explain their functionality in terms of molecular interactions*

### OUTCOME

*Write the mixing rules for the virial coefficients and for pseudo-critical properties using Kay's rule*

### OUTCOME

*Using mixing rules to solve for P, v, and T of mixtures*

### TEST YOURSELF

*A gas mixture contains 20.0 mole % CH<sub>4</sub>, 30.0% C<sub>2</sub>H<sub>6</sub>, and the balance C<sub>2</sub>H<sub>4</sub>. Ten kilograms of this gas is compressed to 200 bar at 90C. What is the volume?*

EoS: Equations of State for Liquids and Solids

### Liquids and Solids

The specific volume (or density) of liquids and solids are essentially constant (except for the liquid near the critical point), therefore they are often called "incompressible".

Nevertheless, there is, in fact, a small dependence of the specific volume on temperature and pressure:

### DEFINITION:

*The **coefficient of thermal expansion** is a measure of the dependence of a liquid/solid's specific volume on temperature and is given as*

$$\beta \equiv \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p$$

## DEFINITION:

The **isothermal compressibility** is a measure of the dependence of a liquid/solid's specific volume on pressure and is given as

$$\kappa \equiv -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T$$

These quantities can be used in a simple equation of state in the following way:

$$v = v_d [1 + \beta(T - T_o) - \kappa(P - P_o)]$$

## DEFINITION:

Alternatively, the liquid specific volume at saturation conditions is given by the **Rackett Equation**:

$$v^{l,sat} = \frac{RT_c}{P_c} (0.29056 - 0.08775\omega)^{[1+(1-T_r)^{2.7}]}$$

## OUTCOME

Apply the Rackett equation, the thermal expansion coefficient, and the isothermal compressibility to find  $v$  for liquids and solids

## EOS: Fundamental Property Relations

### Fundamental Property Relations and the Maxwell Equations

All of thermodynamics is built on the two premises of the first and second law, which can mathematically be written as

$$du = w_{rev} + q_{rev}$$

$$ds = \frac{q_{rev}}{T}$$

Combining these and using the definition of the (reversible) work, we get

$$du = Tds - Pd v$$

In addition to these two fundamental properties ( $u, s$ ), we have also defined several "derived properties":

$$h \equiv u + Pv$$

$$a \equiv u - Ts$$

$$g \equiv h - Ts$$

The way that much of the rest of thermodynamics is constructed is to use these definitions/relations and mathematically manipulate them. To do so, we need to recall the following two mathematical truths (note that the subscripts on the  $()$ 's refer to variables held constant during the differentiation):

## NOTE:

For a function  $Y$  that depends on two variables  $x$  and  $z$ , we can write

$$dY = \left( \frac{\partial Y}{\partial x} \right)_z dx + \left( \frac{\partial Y}{\partial z} \right)_x dz$$

## NOTE:

The **order** of differentiation does not matter, so :

$$\left[ \frac{\partial}{\partial z} \left( \frac{\partial Y}{\partial x} \right)_z \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial Y}{\partial z} \right)_x \right]_z$$

Taking the first of these facts and using it to write an expression for  $u$  as a function of  $s$  and  $v$ , leads to:

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$$

Equating the terms in front of the  $ds$  and  $dv$  to their counterparts in the earlier expression for  $du$  (above) leads to:

$$T = \left(\frac{\partial u}{\partial s}\right)_v$$

$$-P = \left(\frac{\partial u}{\partial v}\right)_s$$

By following the same procedure for  $h$  by writing it as a function of  $s$  and  $p$ , leads to:

$$T = \left(\frac{\partial h}{\partial s}\right)_p$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s$$

Finally, doing the same for  $g$  and  $a$ , gives:

$$-s = \left(\frac{\partial a}{\partial T}\right)_v$$

$$-P = \left(\frac{\partial a}{\partial v}\right)_T$$

$$-s = \left(\frac{\partial g}{\partial T}\right)_p$$

$$v = \left(\frac{\partial g}{\partial p}\right)_T$$

## EOS: Maxwell Relations

### Fundamental Property Relations and the Maxwell Equations (cont.)

Further manipulating these relations by using our second mathematical fact yields the Maxwell relations as follows:

Take our equations that originated from the  $du$  analysis:

$$T = \left(\frac{\partial u}{\partial s}\right)_v$$

$$-P = \left(\frac{\partial u}{\partial v}\right)_s$$

and take the partial derivative with respect to  $v$  for the top and with respect to  $s$  for the bottom yields:

$$\left(\frac{\partial T}{\partial v}\right)_s = \left[\frac{\partial}{\partial v} \left(\frac{\partial u}{\partial s}\right)_v\right]_s$$

$$-\left(\frac{\partial P}{\partial s}\right)_v = \left[\frac{\partial}{\partial s} \left(\frac{\partial u}{\partial v}\right)_s\right]_v$$

Our second mathematical fact tells us that the right-hand side of both of these expressions is equivalent, so that we can write:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

Performing the same analysis on the expressions that originated from the  $dh$ ,  $da$ , and  $dg$  expressions gives the other three Maxwell relations:

$$\left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$-\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial s}{\partial p}\right)_T$$

### NOTE:

*The "beauty" of the Maxwell equations, as well as the fundamental property relations derived early, is that they can be used to relate **measurable** quantities (like  $T$ ,  $P$ , and  $v$ ) to fundamental and derived*

quantities. Also, in many cases, we can substitute equations of state into these expressions to aid in calculating quantities of interest.

EoS: Departure Functions

### Departure Functions

In this section, we learned how to handle  $PvT$  data for non-ideal-gas materials; however, the only way that we have handled non-measurable properties for such materials was to use the steam tables (which, obviously, only works for water).

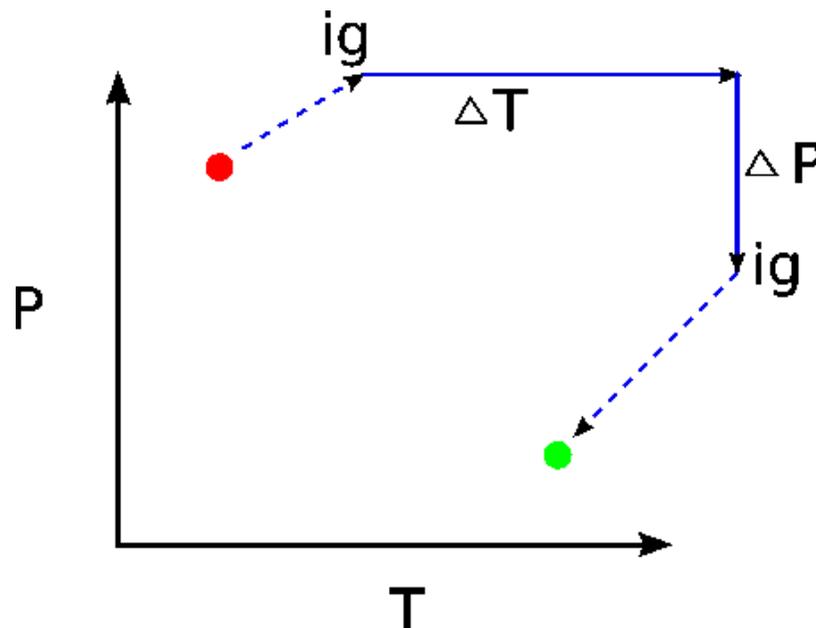
One conceptually satisfying way to alleviate that shortcoming is to exploit the fact that we need to choose a reference state when calculating fundamental or derived properties. In this approach, we choose as our reference state, the material of interest in its "ideal gas state".

In this way, if we could calculate the difference between the material in its "ideal gas state" versus in its "real state", we could make use of the ideal-gas relations that we have thus far used.

#### DEFINITION:

**Departure functions** (here denoted as  $M^{dep}$  for a generic property,  $M$ ) are defined as the difference between the property of interest in its real state (designated here as  $M$ ) and its ideal gas state (designated here  $M^{ig}$ ):

$$M^{dep} = M - M^{ig}$$



In this way, we can write the *actual* value of a property as:

$$M = M^{ig} + M^{dep}$$

Using this approach, we can then express our differences in any state function (for example entropy) between states 1 and 2 as:

$$s_2 - s_1 = (s_2^{ig} + s_2^{dep}) - (s_1^{ig} + s_1^{dep})$$

$$s_2 - s_1 = (s_2^{dep} - s_1^{dep}) + (s_2^{ig} - s_1^{ig}) = (s_2^{dep} - s_1^{dep}) + \Delta s_{1 \rightarrow 2}^{ig}$$

We have already discussed  $\Delta s^{ig}$ , so we can replace that to get:

**IMPORTANT:**

$$s_2 - s_1 = (s_2^{dep} - s_1^{dep}) + \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{P_2}{P_1}$$

**NOTE:**

*The way that we "convert" a real fluid to an ideal gas is to drop the pressure from  $P$  down to  $P=0$ . So that (as can be seen in our schematic), we can get the departure function at  $T_i$  and  $P_i$  by going from  $(T_i, P_i)$  to  $(T_i, P=0$  -- ideal gas) to  $(T_i, P=P_i$  -- ideal gas). Doing this for both  $T_1$  and  $T_2$  allows us to calculate  $s_2^{dep} - s_1^{dep}$ .*

We note that our analysis of the fundamental property relations told us the exact differential for  $s$  at constant  $T$ :

$$(ds)_T = -\left(\frac{\partial v}{\partial T}\right)_P dP$$

So that our steps for calculating  $s^{dep}$  yield:

$$s_i^{dep} = \int_0^{P_i} -\left(\frac{\partial v}{\partial T}\right)_P dP - \left[ \int_0^{P_i} -\left(\frac{\partial v}{\partial T}\right)_P dP \right]^{ig}$$

$$s_i^{dep} = \int_0^{P_i} -\left(\frac{\partial v}{\partial T}\right)_P dP + \int_0^{P_i} \frac{R dP}{P}$$

A similar analysis for  $h$  gives:

**IMPORTANT:**

$$h_2 - h_1 = (h_2^{dep} - h_1^{dep}) + \int_{T_1}^{T_2} c_p dT$$

where  $h_i^{dep}$  can be calculated from (noting that  $h^{ig}$  is independent of  $P$ ):

$$h_i^{dep} = \int_0^{P_i} \left[ -T \left(\frac{\partial v}{\partial T}\right)_P + v \right] dP$$

**NOTE:**

*The easiest way to calculate  $s_i^{dep}$  or  $h_i^{dep}$  is to look them up on Lee-Kesler tables in the same way that we did for  $z$  values!*

**OUTCOME:**

*Use equations of state to calculate departure functions*

**OUTCOME:**

*Calculate departure functions from Lee-Kesler charts*