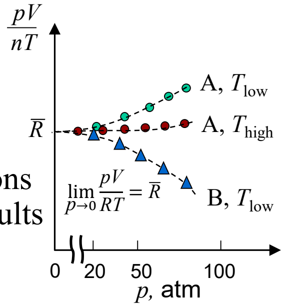
Imperfect (Real) Gases

- Ideal (tpg) gas law limited to “low” density (or pressure), “high” temperature conditions
  - later will see this is related to minimal (short range, repulsive) intermolecular interactions
- Other **p-v-T EoS** (Eqn. of State)
  - to account for molecular interactions in **real** gases ⇒ more accurate results
  - can evaluate in terms of
    - compressibility factor, Z



$$\boxed{Z \equiv \frac{p\hat{v}}{\bar{R}T}}$$

Z≠1 represents non-ideal behavior

- fugacity, f

f defined in terms of μ

Using Real Gas EoS

- Once we have our real gas *p*-*v*-*T* equation of state, can use it to find other relations
- Examples
  - compressibilities
  - caloric state relations

$$\alpha \equiv \frac{1}{V}\boxed{\left.\frac{\partial V}{\partial T}\right|_p} \qquad \kappa \equiv \frac{-1}{V}\boxed{\left.\frac{\partial V}{\partial p}\right|_T}$$

from p-v-T EoS

$$dU = C_v dT + \left[T\boxed{\left(\frac{\partial p}{\partial T}\right)_V} - p\right]dV$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

from reciprocity

$$dH = C_p dT + \left[1 - \alpha T\right]V dp$$

Van der Waals EoS

- One of earliest corrections to ideal gas law was by Van der Waals (1873)
  - originally motivated by kinetic theory

$$\boxed{\left(p+\boxed{\frac{a}{\hat{v}^2}}\right)\left(\hat{v}\boxed{-b}\right)=\bar{R}T}$$

corrects for intermolecular attractive forces which reduce pressure from that predicted by ideal EoS

corrects for volume occupied by molecules, and thus repulsive forces

  - which gives a compressibility factor

$$Z=1-\left(\frac{a}{\hat{v}}-\frac{ab}{\hat{v}^2}-pb\right)\Big/\bar{R}T$$

    - so $Z\to 1$ at high v, low p, high T

Examples Using Van der Waals EoS

- p-v-T derivatives/compressibilities for Van der Waals gas are

$$\left(p+\frac{a}{\hat{v}^2}\right)\left(\hat{v}-b\right)=\bar{R}T$$

$$p=\frac{\bar{R}T}{\hat{v}-b}-\frac{a}{\hat{v}^2}\quad\Rightarrow\kappa=\frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T=\frac{-1}{\hat{v}\left(\partial p/\partial\hat{v}\right)_T}=\frac{1}{v\left(\dfrac{\bar{R}T}{\left(\hat{v}-b\right)^2}-\dfrac{2a}{\hat{v}^3}\right)}$$

$$\Rightarrow\left(\frac{\partial p}{\partial T}\right)_V=\frac{\bar{R}}{\hat{v}-b}$$

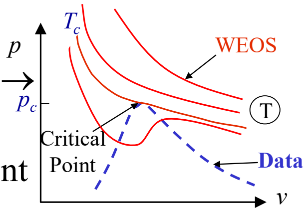
$$\Rightarrow\alpha=\kappa\left(\frac{\partial p}{\partial T}\right)_V=\frac{\bar{R}/\left(\hat{v}-b\right)}{\hat{v}\left(\dfrac{\bar{R}T}{\left(\hat{v}-b\right)^2}-\dfrac{2a}{\hat{v}^3}\right)}$$

  - and internal energy

function of v only

$$dU=C_v dT+\left[T\left(\frac{\partial p}{\partial T}\right)_V-p\right]dV=C_v dT+\left[\frac{\bar{R}T}{\hat{v}-b}-p\right]dV=C_v dT+\overbrace{\frac{a}{\hat{v}^2}}^{=(\partial U/\partial V)_T}dV$$

Comparison to Critical State



- Van der Waals EoS (WEOS) is cubic in v; produces isotherms like→
- Positive slopes unphysical for gas, but one isotherm has inflection point
  - 1^{st} and 2^{nd} deriv. of $p(v)$ are zero
- Match inflection point to critical point
  - can show $a = \frac{27}{64}\frac{(\bar{R}T_c)^2}{p_c}$ $\quad b = \frac{\bar{R}T_c}{8p_c}$
  - insert these into WEOS and define **reduced *T*, *p*** $\Rightarrow \boxed{\left(Z + \frac{1}{Z}\frac{27}{64}\frac{p_r}{T_r^2}\right)\left(1 - \frac{1}{8Z}\frac{p_r}{T_r}\right) = 1}$

$$T_r \equiv \frac{T}{T_c};\, p_r \equiv \frac{p}{p_c}$$

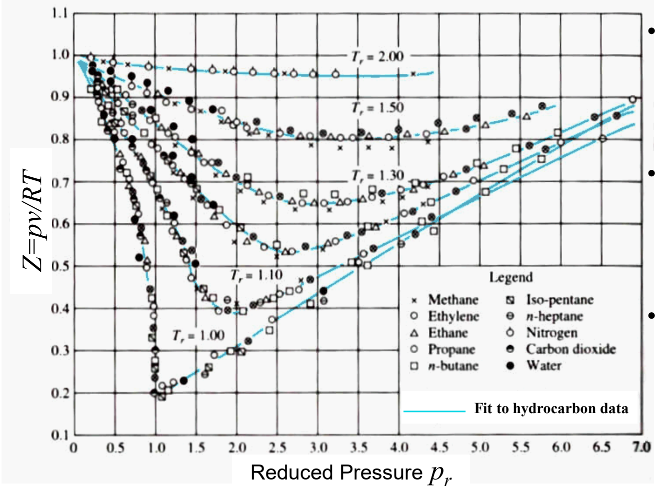
max T and p where liquid and gas coexist as unique phases

can also write as
$Z^3 - AZ^2 + BZ - (AB+1) = 0$

so $Z=Z(p_r, T_r)$ for WEOS gases
is there universal relationship for gases?

also gives Z_c=0.375

Generalized Compressibility Chart



- Empirically shown that Z is nearly the same function of (p_r, T_r) for *many* gases (not WEOS relation)
- This relationship known as the **Principle of Corresponding States**
- Useful for estimating properties if more precise EoS data not available

from Gour-Jen Su, Ind. Eng. Chem. **38**, 803 (1946)

Critical Properties

note Z_c<0.375 ($Z_{c,\text{WEOS}}$)

Gas	T_c (K)	p_c (atm)	$\hat{v}_c$ (cm^3/mol)	Z_c
Air	132.41	37.25	92.4	
Ar	150.72	47.99	75	0.291
*He	5.19	2.26	58	0.308
CO	132.91	34.53	93	0.294
*H_2	33.24	12.80	65	0.304
N_2	126.2	33.54	90	0.291
O_2	154.78	50.14	74	0.292
CO_2	304.20	72.90	94	0.275
H_2O	647.27	218.17	56	0.230
C_2H_2 (acetylene)	309.5	61.6	113	0.274
C_2H_6 (ethane)	305.48	48.20	148	0.285
C_2H_4 (ethylene)	283.06	50.50	124	0.270
CH_4 (methane)	190.17	45.8	99	0.290
C_3H_8 (propane)	370.01	42.1	200	0.277

*unusual low T behavior

Obert, Concepts of Thermodynamics, McGraw-Hill (1960)

Higher Order EoS

- Van der Waal equation is a “two-constant” equation
  - better accuracy ⇒ more terms and more complex terms
- Virial EoS $\dfrac{p\hat{v}}{\overline{R}T}=1+\dfrac{c_1(T)}{\hat{v}}+\dfrac{c_2(T)}{\hat{v}^2}+\dfrac{c_3(T)}{\hat{v}^3}+\ldots$
- Beattie-Bridgeman (1928)
  - 5 constants $\dfrac{p\hat{v}}{\overline{R}T}=\dfrac{1}{\hat{v}}\left(1-\dfrac{c}{\hat{v}T^3}\right)\left[\hat{v}+B_o\left(1-\dfrac{b}{\hat{v}}\right)\right]-\dfrac{A_o\left(1-\dfrac{a}{\hat{v}}\right)}{\overline{R}T\hat{v}}$
- Benedict-Webb-Rubin (1940)

not isobaric compressibility

$$\frac{p\hat{v}}{\overline{R}T}=1+\frac{1}{\hat{v}}\left(B_o-\frac{A_o}{\overline{R}T}-\frac{C_o}{\overline{R}T^3}\right)+\frac{1}{\hat{v}^2}\left(b-\frac{a}{\overline{R}T}\right)+\frac{1}{\hat{v}^5}\frac{a\alpha}{\overline{R}T}+\frac{c}{\hat{v}^2\overline{R}T^3}\left(1+\frac{\gamma}{\hat{v}^2}\right)e^{-\gamma/\hat{v}^2}$$

  - 8 constants, usually applied for $\rho/\rho_{\text{crit}} < 2.5$
  - especially good for hydrocarbons

can also handle liquid and liquid gas mixtures

Cubic EoS

- Cubic EoS (cubic in $\hat{v}$) often used
  - computationally less expensive, analytically tractable

$$p = \frac{\bar{R}T}{\hat{v}-b} - \frac{\Theta}{\hat{v}^2 + \delta\hat{v} + \varepsilon}$$

- Already noted Van der Waals was a cubic EoS

$$p = \frac{\bar{R}T}{\hat{v}-b} - \frac{a}{\hat{v}^2}$$

- Other examples
  - Redlich-Kwong (1949)

$$p = \frac{\bar{R}T}{\hat{v}-b} - \frac{a/\sqrt{T}}{\hat{v}\left(\hat{v}+b\right)}$$

  - Peng-Robinson (1975)

$$p = \frac{\bar{R}T}{\hat{v}-b} - \frac{a\alpha}{\underbrace{\hat{v}\left(\hat{v}+b\right)+b\left(\hat{v}-b\right)}_{=\hat{v}^2+2b\hat{v}-b^2}}$$

  - like WEOS, R-K and P-R EoS use a,b = functions of ($\bar{R}$, T_c, p_c)
    - also $\alpha = \alpha(T_r)$

can also handle liquid and liquid-gas mixtures

Fugacity

- Instead of relying on expressions for Z, can also define gas properties of real (imperfect) gas using similar approach used for perfect gases
  - based on chemical potential
- For **single (pure)** gas

$$\mu \equiv \mu^o + \bar{R}T \ln\left(f/f^o\right)$$

  - $\mu^o = \mu^o(T)$
  - f is **fugacity** (units of pressure)
  - f^o is fugacity at standard state ($\mu = \mu^o$ at $f = f^o$)
  - for $f = p$ get TPG relation
  - for all gases, $f/p \rightarrow 1$ as $p \rightarrow 0$

Measuring Fugacity

- We showed earlier $\hat{v} = \left.\frac{\partial \mu}{\partial p}\right|_T$ $\mu \equiv \mu^o + \bar{R}T\ln\left(f/f^o\right)$
  - for f^o=1 $\hat{v} = \left.\frac{\partial\left(\bar{R}T\ln f\right)}{\partial p}\right|_T \Rightarrow \left.\frac{\partial(\ln f)}{\partial p}\right|_T = \frac{\hat{v}}{\bar{R}T}$
- Consider constant T process

$$d(\ln f) = \frac{\hat{v}}{\bar{R}T}dp$$

  - subtract $d(\ln p)$

$$d\ln f - d\ln p = \frac{\hat{v}}{\bar{R}T}dp - d\ln p$$

$$d\ln\left(\frac{f}{p}\right) = \left(\frac{\hat{v}}{\bar{R}T} - \frac{1}{p}\right)dp$$

Measuring Fugacity

$$d\ln\left(\frac{f'}{p'}\right) = \left(\frac{\hat{v}}{\bar{R}T} - \frac{1}{p'}\right)dp'$$

- Integrate from p'=0→p (f'/p'=1→f/p)

$$\int_1^{f/p} d\ln\frac{f'}{p'} = \int_0^p\left(\frac{\hat{v}}{\bar{R}T} - \frac{1}{p'}\right)dp'$$

$$\ln\frac{f}{p} - \ln 1 = \boxed{\ln\frac{f}{p} = \int_0^p\left(\frac{\hat{v}}{\bar{R}T} - \frac{1}{p'}\right)dp'} = \int_0^p (Z-1)\frac{dp'}{p'}$$

Integral represents nonideal behavior

  - $f/p = 1 \Rightarrow$ TPG
  - get fugacity from integrating RHS w/ experimental data

Real Gas Mixtures

- Fugacity is more commonly employed for mixtures of real (imperfect) gases
- Define **partial fugacity** f_i by

$$\boxed{\mu_i \equiv \mu_i^o + \bar{R}T\ln f_i}$$

  - similar to pure gas, $f_i/p_i \to 1$ as $p_i \to 0$ and $p \to 0$
  - similar to TPG $\mu_i^o = \mu^o(T)$ for pure i
  - BUT $f_i = f_i(p, T, \chi_j)$
    - partial fugacity can depend on composition

Determining Partial Fucacity

- Similar to pure gas approach, we have

$$\left.\frac{\partial \mu_i}{\partial p}\right|_{T,x_{j\neq i}} = \bar{v}_i = \bar{R}T\left.\frac{\partial \ln f_i}{\partial p}\right|_{T,x_{j\neq i}}$$

  - and for constant T and χ_j

$$d\mu_i = \bar{R}Td\ln f_i = \bar{v}_i dp$$

$$d\ln f_i - d\ln p_i = \frac{\bar{v}_i}{\bar{R}T}dp - d\ln p_i$$

$p_i = p\chi_i$

$$d\ln\frac{f_i}{p_i} = \frac{\bar{v}_i}{\bar{R}T}dp - d\ln p - \cancelto{0}{d\ln\chi_i}$$

$$\ln\frac{f_i}{p_i} = \int_0^p \left(\frac{\bar{v}_i}{\bar{R}T} - \frac{1}{p'}\right)dp'$$

Determining Partial Fugacity

$$\boxed{\ln\frac{f_i}{p_i}=\int_0^p\left(\frac{\bar{v}_i}{\bar{R}T}-\frac{1}{p'}\right)dp'}$$

- Analogous relation to single imperfect gas
  - but must now measure partial molar volume for many compositions at each (T,p)
- If interactions between components are not too strong (e.g., ρ not too high), can assume ideal solution result

Lewis-Randall Rule $f_i=\chi_i f^i \leftarrow$ fugacity of pure i at p,T