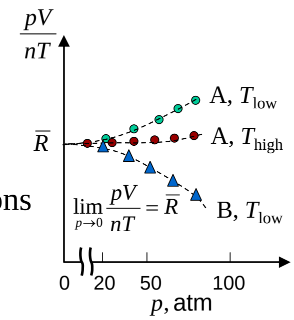
Imperfect Gases

- Perfect gas law limited to “low” density, “high” temperature conditions
  - later will see this is related to minimal (short range, repulsive) intermolecular interactions
- Other **virial** equations of state
  - include other molecular interactions
  - can present in terms of
    - compressibility factor, Z



$$Z \equiv \frac{pv}{RT}$$

$Z \neq 1$ represents nonideal behavior

- fugacity, f

Using Virial State Equations

- Once we have virial equation of state, can use it to find other relations
- Example, caloric state relations

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

from virial state eqn.

$$dH = C_p dT + \left[1 - \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right] V dp$$

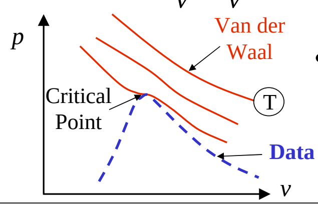
Van der Waal State Equation

- One of earliest corrections to ideal gas law by Van der Waal (1873)

$$\left(p+\frac{A}{v^2}\right)(v-B)=RT$$

  – based on kinetic theory

  – $Z=1-\frac{A}{v}+\frac{AB}{v^2}+pB$ $\quad Z\to 1$ at high v (low p)



- Match theory to experiment at critical point
  – isotherm has inflection point (1st and 2nd deriv. of $p(v)$ are zero)

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Higher Order Virial Equations

- Van der Waal equation is a "two-constant" equation
- More accuracy with higher number of terms $\quad \frac{pv}{RT}=1+\frac{c_1}{v}+\frac{c_2}{v^2}+\frac{c_3}{v^3}+\ldots$
- Beattie-Bridgeman (1928)

  – 5 constants $\quad \frac{pv}{RT}=\frac{1}{v}\left(1-\frac{c}{vT^3}\right)\left[v+B_o\left(1-\frac{b}{v}\right)\right]-\frac{A_o\left(1-\frac{b}{v}\right)}{RTv}$

- Benedict-Webb-Rubin (1940)

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

  – 8 constants, usually applied for $\rho/\rho_{crit}< 2.5$

  – especially good for hydrocarbons

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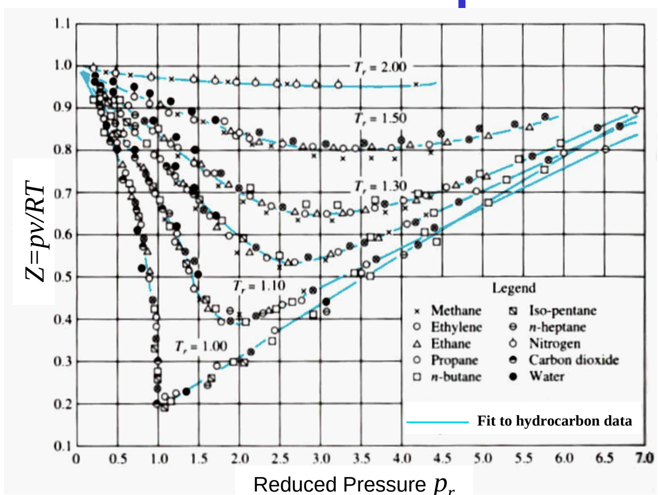
Generalized Compressibility Chart



- Preferable to get constants for specific gas
  - however can find general behavior
  - characterized by **reduced *T* and *p***
  - $T_r = T/T_{crit}$
  - $p_r = p/p_{crit}$

Principle of Corresponding States

critical point is max T and p where l and g coexist as unique phases

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

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Critical Properties

Gas	T_c (K)	p_c (atm)	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)

Fugacity

- Can define imperfect gas properties using similar approach used for perfect gases
  - based on chemical potential
- Single imperfect 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 PG relation
  - for all gases, $f/p \to 1$ for $p \to 0$

Measuring Fugacity

- We showed earlier $\hat{v} = \left.\dfrac{\partial \mu}{\partial p}\right|_T$ $\qquad \mu \equiv \mu^o + \bar{R}T \ln\left(f / f^o\right)$
  - for $f^o = 1$ $\quad \hat{v} = \left.\dfrac{\partial\left(\bar{R}T \ln f\right)}{\partial p}\right|_T \Rightarrow \left.\dfrac{\partial(\ln f)}{\partial p}\right|_T = \dfrac{\hat{v}}{\bar{R}T}$
- 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 $p'=0\rightarrow p$ ($f'/p'=1\rightarrow f/p$)

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

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

Integral represents nonideal behavior

  - $f/p = 1 \Rightarrow$ P.G.
  - get fugacity from integrating RHS w/ exper. data

Mixtures of Imperfect Gases

- Define partial fugacity f_i by

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

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

Mixtures of Imperfect Gases

- Similar to pure gas approach

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

  - and for constant T and χ_j

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

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

$p_i = p\chi_i$

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

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

Mixtures of Imperfect Gases

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

- 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 $f_i = \chi_i f^{\,i}$ ← fugacity of pure i at p,T