

# Thermodynamics: Phenomenology

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- Work and other forms of energy
  - Transfer and dissipation
    - 1. & 2. Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
  - Technological applications, cyclic engines
- Real gases equation of state
  - Technological applications
- Phase equilibria
- Free energy in chemical reactions

## Reading Assignments

Weeks 13&14

LN V-VI:

Kondepudi Ch. 6 & 7  
Additional Material

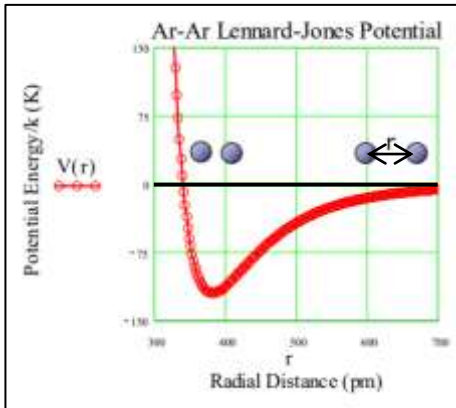
McQuarrie & Simon  
Ch. 7 & 8

# Critical TD Parameters for Real Gases

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Acetic Acid	CH3-CO-OH	841	58	612	322	1.15
Acetone	CH3-CO-CH3	691	47.6	455	235	-
Acetylene	C2H2	911	62.9	97	36	1.26
Air	O2+N2	547	37.8	-222	-141	1.4
Ammonia	NH3	1638	113	270	132	1.33
Argon	A	705	48.6	-188	-122	1.67
Benzene	C6H6	701	48.4	552	289	1.12
Butane	C4H10	529	36.5	307	153	1.09
Carbon Dioxide	CO2	1072	74	88	31	1.3
Carbon Monoxide	CO	514	35.5	-218	-139	1.4
Carbon Tetrachloride	CCl4	661	45.6	541	283	-
Chlorine	Cl2	1118	77	291	144	1.26
Ethane	C2H6	717	49.5	90		
Ethyl Alcohol	C2H5OH	927	64	469		
Ethylene	CH2=CH2	742	51.2	50		
Ethyl Ether	C2H5-O-C2H5	522	36	383		
Fluorine	F2	367	25.3	-247		
Helium	He	33.2	2.29	-450		
Heptane	C7H16	394	27.2	513		
Hydrogen	H2	188	13	-400		
Hydrogen Chloride	HCl	1199	82.6	124		

Material	Formula	psia	bar (abs)	°F	°c	k = Cp/Cv
Isobutane	(CH3)CH-CH3	544	37.5	273	134	1.1
Isopropyl Alcohol	CH3-CHOH-CH3	779	53.7	455	235	-
Methane	CH4	673	46.4	-117	-83	1.31
Methyl Alcohol	H-CH2OH	1156	79.6	464	240	1.2
Nitrogen	N2	492	34	-233	-147	1.4
Nitrous Oxide	N2O	1054	72.7	99	37	1.3
Octane	CH3-(CH2)6-CH3	362	25	565	296	1.05
Oxygen	O2	730	50.4	-182	-119	1.4
Pentane	C5H12	485	33.5	387	197	1.07
Phenol	C6H5OH	889	61.3	786	419	-
Phosgene	COCl2	823	56.7	360	182	-
Propane	C3H8	617	42.6	207	97	1.13
Propylene	CH2=CH-CH3	661	45.6	198	92	1.15
Refrigerant 12	CCl2F2	582	40.1	234	112	1.14
Refrigerant 22	CHClF2	713	49.2	207	97	1.18
Sulfur Dioxide	SO2	1142	78.8	315	157	1.29
Water	H2O	3206	221	705	374	1.32

# Internal Energy of Real Gases



Effect of interaction on internal energy  $U_{RG}(n, V, T)$ .

Use knowledge  $U(n, V, T) \xrightarrow{V \rightarrow \infty} U_{IG}(n, V, T)$

van der Waals EoS (**linear** function of **T**)

$$p = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2} \rightarrow T^2 \left( \frac{\partial p}{\partial V} \frac{\partial p}{\partial T} \right)_V = a \cdot \left( \frac{n}{V} \right)^2$$

$$U(n, V, T) = U_{IG}(n, V, T) - a \cdot \left( \frac{n}{V} \right)^2 \cdot V < \underline{U_{IG}(n, V, T)}$$

Heat Capacity

$$C_V = C_{V,IG} - \frac{\partial}{\partial T} \int_V^\infty T^2 \left( \frac{\partial p}{\partial V} \frac{\partial p}{\partial T} \right)_V dV$$

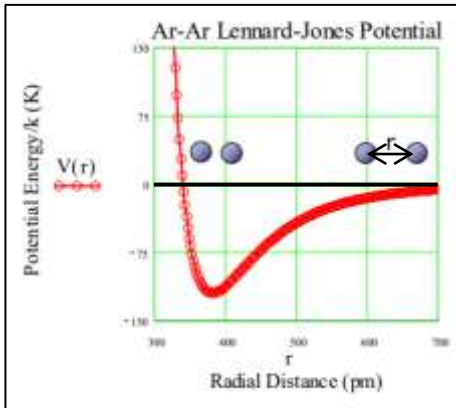
$$C_V = C_{V,IG} - \int_V^\infty T \left( \frac{\partial^2 p}{\partial T^2} \right)_V dV$$

➔ **vdW EoS**:  $\partial^2 p / \partial T^2 = 0 \rightarrow$

$$C_V^{vdW} = C_{V,IG}$$

$$vdW \text{ EoS} \rightarrow C_p - C_V = \left( \alpha^2 / \kappa_T \right) \cdot V \cdot T$$

# Free Energy of Real Gases: V and p Dependence



Use asymptotic equivalence of real and ideal gases, e.g.,

$$A(n, V, T) \xrightarrow{V \rightarrow \infty} A_{IG}(n, V, T)$$

$$\text{and } \left( \frac{\partial A}{\partial V} \right)_T = -p$$

Generic real-gas EoS

$$A(n, V, T) = A_{IG}(n, V, T) + \int_V^{\infty} (p - p_{IG}) dV \xrightarrow{V \rightarrow \infty} A_{IG}(n, V, T)$$

$$G(n, p, T) = G_{IG}(n, p, T) + \int_0^p (V - V_{IG}) dp \xrightarrow{p \rightarrow 0} G_{IG}(n, p, T)$$

Helmholtz free energy

$$A(n, V, T) = U - T \cdot S$$

Gibbs free energy

$$G(n, p, T) = H - T \cdot S$$

Insert van der Waals Eos:  $p_{vdW} = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2}$

$$p_{vdW} - p_{IG} = n \cdot R \cdot T \left( \frac{(n \cdot b)}{V(V - n \cdot b)} \right) - \frac{n^2 \cdot a}{V^2}$$

*n moles/  
particles*

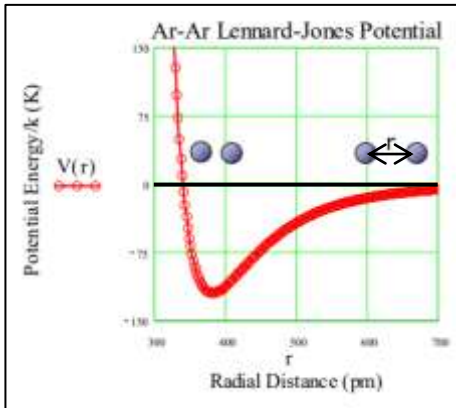
van der Waals EoS

$$A_{vdW}(n, V, T) = A_{IG}(n, V, T) - a \left( \frac{n}{V} \right)^2 - n \cdot R \cdot T \cdot \ln \left( 1 - \frac{n \cdot b}{V} \right)$$

solve **A** for **S**

$$S_{vdW} = \frac{1}{T} \cdot (A_{vdW} - U_{vdW}) = n \cdot \left[ s_0 + C_V \cdot \ln T + R \cdot \ln \left( \frac{(V - n \cdot b)}{n} \right) \right]$$

# Chemical Potential of Real Gases: $p$ Dependence



Use asymptotic equivalence of real and ideal gases,  
 $G(p, T) \rightarrow$

$$\mu(p, T) = \mu_{IG}(p, T) + \int_0^p (V - V_{IG}) dp'$$

One mol:  $V = Z \cdot R \cdot T \cdot p^{-1} \rightarrow \mu(p, T) = \mu_{IG}(p, T) + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p'} dp'$

$$\mu(p, T) = \left[ \mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p'} dp' \quad \leftarrow = f(n, a, b)$$

Chemical potential

$$\mu(p, T) = \left( \frac{\partial G(p, T)}{\partial n} \right)_{p, T}$$

Pressure equivalent "Fugacity"  $f$ :  $\ln\left(\frac{f}{p}\right) := \int_0^p \frac{(Z-1)}{p'} dp'$ ;  $\lim_{p \rightarrow 0} (f/p) = 1$   
 "Activity"  $a := f/p$

$$\ln\left(\frac{f}{p}\right) \approx B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 + \dots \rightarrow \text{Virial expansion of real-gas EoS}$$

Virial coefficients  $B'$  and  $C'$  from fit of  $Z$  to EoS.  
 Found in tables or can be calculated from EoS parameters.

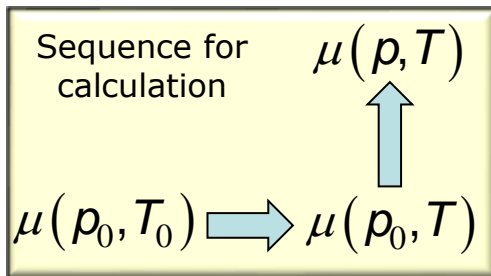
$$\mu(p, T) \approx \mu_{IG}(p_0, T) + R \cdot T \cdot \left[ B'(T) \cdot p + \frac{1}{2} C'(T) \cdot p^2 \right]$$

# Chemical Potential of Real Gases: $T$ Dependence

Calculate chemical potential of real gases from relations to ideal gases @  $p_0, T_0$

$$\mu(p, T) = \left[ \mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p} dp$$

→ Tabulations are normally as Gibbs energies of formation  $\Delta G_f^0 = \mu(p_0, T_0)$   
 @  $p_0 = 1\text{bar}, T_0 = 298.15\text{K}$  → need to scale up. Since  $\mu \rightarrow \mathbf{G(p, T)}$ :



Per mol  $G(p, T) = H - T \cdot S = H + T \cdot \left(\frac{\partial G}{\partial T}\right)_p$

$$\rightarrow -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p = -\frac{H}{T^2}$$

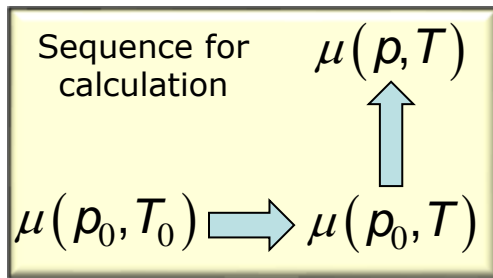
**Gibbs-Helmholtz Equation**

$$\frac{\partial}{\partial T} \left(\frac{G}{T}\right) = -\frac{H}{T^2}$$

# Parameterizing the Chemical Potential

Calculate chemical potential of real gases from relations to ideal gases @  $p_0$

$$\mu(p, T) = \left[ \mu_{IG}(p_0, T) + R \cdot T \cdot \ln\left(\frac{p_{IG}}{p_0}\right) \right] + R \cdot T \cdot \int_0^p \frac{(Z-1)}{p} dp \quad \frac{\partial}{\partial T} \left( \frac{G}{T} \right) = -\frac{H}{T^2}$$



$$\mu(p_0, T) = \frac{T}{T_0} \mu(p_0, T_0) - T \cdot \int_{T_0}^T \frac{H(p_0, T')}{T'^2} dT'$$

$$\mu(p, T) = \mu(p_0, T) + \int_{p_0}^p V(p', T) dp'$$

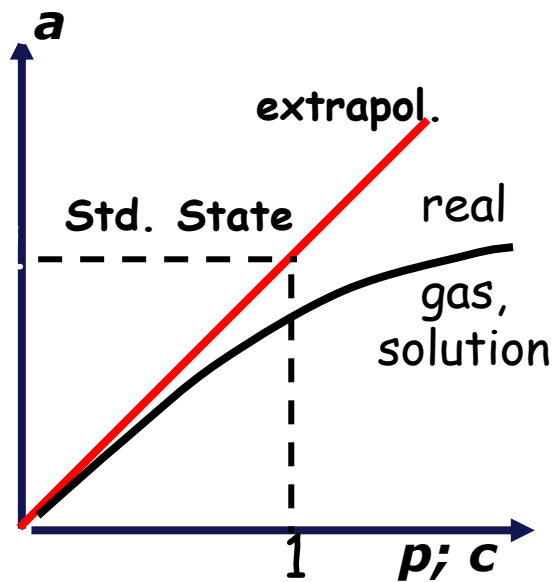
$$H(p, T) = \int_0^T C_p(T') dT'$$

Molar heat capacity  $C_p(T) = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^{-2}$

Gas	A (J mol <sup>-1</sup> K <sup>-1</sup> )	B (10 <sup>-3</sup> J mol <sup>-1</sup> K <sup>-2</sup> )	C (10 <sup>-6</sup> J mol <sup>-1</sup> K <sup>-3</sup> )	D (10 <sup>-9</sup> J mol <sup>-1</sup> K <sup>-4</sup> )	E (10 <sup>6</sup> J mol <sup>-1</sup> K <sup>-5</sup> )
O <sub>2</sub> (g)	29.66	6.137	-1.186	0.0958	-0.2197
N <sub>2</sub> (g)	29.09	8.218	-1.976	0.1592	0.0444
CO <sub>2</sub> (g)	24.99	55.19	-33.69	7.948	-0.1366

NIST  
Data Base

# Effective Pressures of Liquids and Solids



Non-ideal behavior of gases (at high pressures) and of solutions.

Effective quantities simulating pressure of an ideal gas and all the associated laws.

$$\text{Activity } a: G(a) = G^\circ + nRT \cdot \ln(a)$$

$$G^\circ = G(\text{standard state}) \quad 1M$$

$$\text{ideal gas } a = p / 1\text{atm}$$

$$\text{real gas } a = \gamma \cdot p \quad \gamma = \text{activity coefficient}$$

$$\text{pure solids or liquids } a = 1$$

$$\text{solutions } a = \gamma \cdot c \quad c = \text{concentration (mol / L)}$$

$$\text{standard state: } \gamma = 1 \text{ like dilute solutions}$$

$$\text{solvent: } a = \gamma \cdot x \quad x = \text{mole fraction}$$

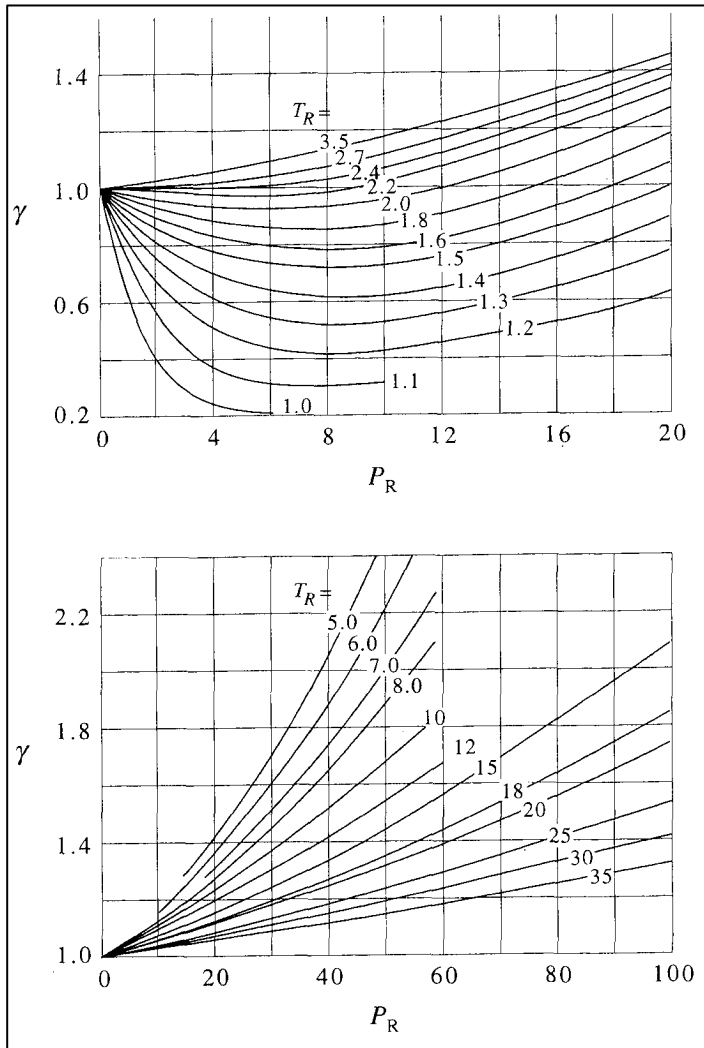
$$\text{Real gas } a = \frac{f}{p} \rightarrow \text{"Fugacity" } f: \quad \ln\left(\frac{f}{p}\right) = \int_0^p \frac{(Z-1)}{p} dp;$$

$$\text{Pure solids and liquids: } a_k \approx 1$$

$$\text{Solutions with mole fraction } x_k \text{ and activity coefficient } \gamma_k: \quad a_k \approx \gamma_k \cdot x_k$$



# Fugacity of Gases vs Reduced Pressure



Activity  $a$ :  $G(a) = G^o + nRT \cdot \ln(a)$

$G^o = G(\text{standard state}) \quad 1M$

ideal gas  $a = p / 1\text{atm}$

real gas  $a = \gamma \cdot p \quad \gamma = \text{activity coefficient}$

pure solids or liquids  $a = 1$

solutions  $a = \gamma \cdot c \quad c = \text{concentration (mol / L)}$

standard state:  $\gamma = 1$  like dilute solutions

solvent:  $a = \gamma \cdot x \quad x = \text{mole fraction}$

Real gas / liquid  $a = \frac{f}{p} \rightarrow$  "Fugacity"  $f$ :

$$\ln\left(\frac{f}{p}\right) = \int_0^p \frac{(Z-1)}{p} dp;$$

Pure solids and liquids:  $a_k \approx 1$

Solutions with mole fraction  $x_k$

and activity coefficient  $\gamma_k$ :  $a_k \approx \gamma_k \cdot x_k$