PROCESSES FOR IDEAL GAS (CON'T)

LAST TIME WE CONSIDERED

CONSTANT VOLUME
CONSTANT PRESSURE
CONSTANT TEMPERATURE

NOW - ADIABATIC (NO HEAT TRANSFER TO SURROUNDINGS)

$$dU = dQ + dW \qquad dQ = 0$$

$$c_v dT = -p\,dV$$

$$p = \frac{RT}{V}$$

$$c_v dT = -\frac{RT}{V} dV$$

$$c_v \frac{dT}{T} = -R\frac{dV}{V}$$

$$c_v \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1}$$

$$\left(\frac{T_2}{T_1}\right)^{c_v} = \left(\frac{V_1}{V_2}\right)^{R}$$

DEFINE $\gamma \equiv \frac{c_p}{c_v}$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{c_v}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}$$

LAST LECTURE

PHASE DIAGRAMS

- PHASE TRANSITIONS
- SINGLE PHASE REGIONS
  - EQUATION OF STATE, EOS $f(P,V,T)=0$
  - PARTICULAR EOS - IDEAL GAS

VARIETY OF PROCESSES FOR IDEAL GAS

- MANY TYPES OF RESTRICTIONS
  - REVERSIBLE, ADIABATIC
  - CONSTANT C_p or C_v, etc.

GENERAL EQUATIONS

$$\Delta U^t = Q + W$$

$$W = -\int P dV$$

$$\Delta U \equiv \int C_v dT$$

$$\Delta H \equiv \int C_p dT$$

REAL GASES

IDEAL GAS SATISFACTORY FOR REAL GAS AT HIGH ENOUGH T, LOW ENOUGH P

WE WILL LOOK AT P, V, T BEHAVIOR
LATER WILL CONSIDER H, S, U

REAL GASES HAVE INTERMOLECULAR INTERACTIONS

- ATTRACTIONS
  - DIPOLE - DIPOLE
  - HYDROGEN BOND
- REPULSIONS
  - ELECTRONIC
  - PHYSICAL SIZE

COMPRESSIBILITY - Z

$$Z = \frac{PV}{RT}$$ P, V, T ARE MEASURED

$$V = \frac{ZRT}{P} = Z V^{ig}$$

Z = 1 IDEAL GAS   Z = ANYTHING, REAL GAS

VIRIAL EQUATIONS

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \cdots$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots$$

B, B'   2nd VIRIAL COEFFICIENTS
PAIRWISE INTERACTION

C, C'   3RD VIRIAL COEFFICIENTS
THREE-WAY AND OTHER
INTERACTIONS

VAN DER WAALS (1873)

SPECIFIC CASE OF CUBIC
EQUATION OF STATE

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

b – MOLECULAR SIZE

a – ATTRACTION / REPULSION

GENERAL CUBIC EOS

$$Z = \frac{V}{V-b} - \frac{a}{RTV}$$

$$V^3 + \alpha V^2 + \beta V + \gamma = 0 \qquad \alpha, \beta = f(T \,\&\, P)$$

$$P = \frac{RT}{V-b} - \frac{\alpha'(T)}{V^2 + \beta' V + \gamma'}$$

CAPTURES MOLECULE SPECIFIC INTERACTIONS AND SIZE

SOLUTIONS TO CUBIC EOS

<u>CUBIC</u>

1 REAL, 2 IMAGINARY

2 REAL, 1 IMAGINARY

3 REAL

<u>IDEAL</u>

1 REAL

AT $T = T_c$, $P = P_c$

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0, \quad (V - V_c)^3 = 0$$

UNFORTUNATELY,

$$Z_c = \frac{P_c V_c}{R T_c} = 3/8 \quad \text{ALL GASES}$$

CUBIC EOS IS BETTER THAN IDEAL GAS EOS BUT NOT GOOD ENOUGH

NEXT LECTURES

FURTHER DISCUSSION OF CUBIC EQUATIONS OF STATE

REDUCED PARAMETERS T_R, P_R, V_R

$Z = f(T_R, P_R)$

$Z = Z^0 + \omega Z'$

HEAT EFFECTS (SENSIBLE, LATENT, REACTION)

Figures not included in this .pdf file are (from Smith, Van Ness, and Abbott:
Fig. 3.1, Fig. 3.2, Fig. 3.10, Fig. 3.12