Thermodynamic Properties

- **Property Table --** **from direct measurement**
- **Equation of State --** **any equation that relates P,v, and T of a substance**

jump

Exercise 3-12

A bucket containing 2 liters of R-12 is left outside in the atmosphere (0.1 MPa)

a) What is the R-12 temperature assuming it is in the saturated state.

b) the surrounding transfer heat at the rate of 1KW to the liquid. How long will take for all R-12 vaporize?

See R-12 (diclorindifluormethane) on Table A-2

Solution - page 1

Part a)

From table A-2, at the saturation pressure of 0.1 MPa one finds:

- **Tsaturation = - 30^{o}C**
- **v_{liq} = 0.000672 m^3/kg**
- **v_{vap} = 0.159375 m^3/kg**
- **h_{lv} = 165KJ/kg (vaporization heat)**

Solution - page 2

Part b)

The mass of R-12 is m = Volume/v_L,
m = 0.002/0.000672 = ***2.98 kg***

The vaporization energy:

Evap = vap energy * mass = 165*2.98 =
492 KJ

Time = Heat/Power = ***492 sec or 8.2 min***

GAS PROPERTIES

Ideal -Gas Equation of State

$$PV = nR_uT; \quad n = \frac{M}{mol}$$

Universal gas constant is given on

R_u = 8.31434 kJ/kmol-K

= 8.31434 kPa-m^3/kmol-k

= 0.0831434 bar-m^3/kmol-K

= 82.05 L-atm/kmol-K

= 1.9858 Btu/lbmol-R

= 1545.35 ft-lbf/lbmol-R

= 10.73 psia-ft^3/lbmol-R

Example

Determine the particular gas constant for air (28.97 kg/kmol) and hydrogen (2.016 kg/kmol).

$$\mathbf{R_{air} = \frac{R_u}{M} = \frac{8.1417 \dfrac{kJ}{kmol - K}}{28.97 \dfrac{kg}{kmol}} = 0.287 \frac{kJ}{kg - K}}$$

$$\mathbf{R_{hydrogen} = \frac{8.1417 \dfrac{kJ}{kmol - K}}{2.016 \dfrac{kg}{kmol}} = 4.124 \frac{kJ}{kg - K}}$$

Ideal Gas "Law" is a simple Equation of State

$$PV = MRT$$

$$Pv = RT$$

$$PV = NR_uT$$

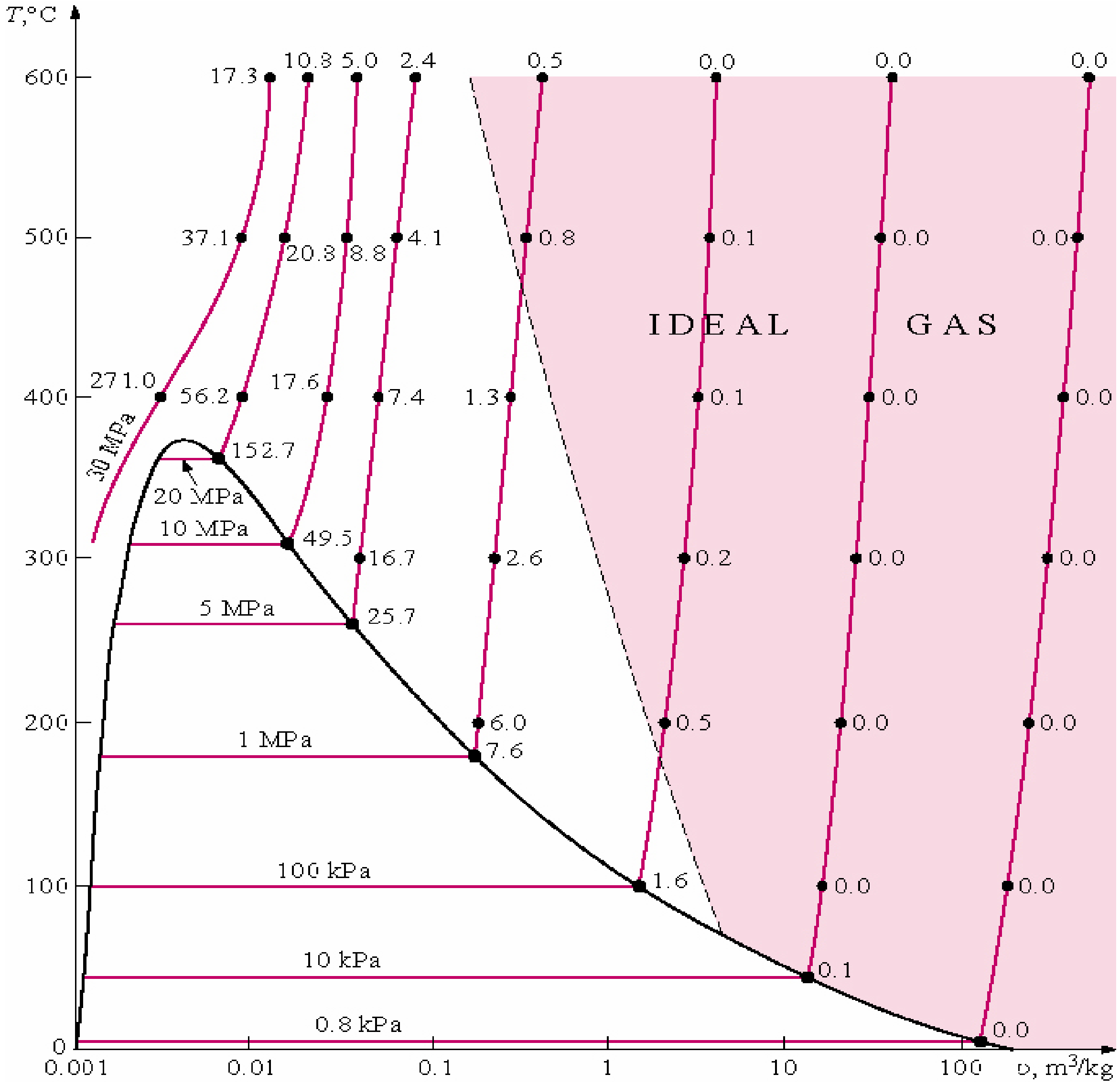
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Question ……

Under what conditions is it appropriate to apply the ideal gas equation of state?

- **Good approximation for P-v-T behaviors of real gases at low densities (low pressure and high temperature).**
- **Air, nitrogen, oxygen, hydrogen, helium, argon, neon, carbon dioxide, …. (< 1% error).**

Percent error for applying ideal gas equation of state to steam



Compressibility Factor

- **It accounts mainly for two things**
  - Molecular structure
  - Intermolecular attractive forces

Ideal Gas

$Z=1$

Real Gases

$Z > 1$ **or**

$Z < 1$

- **What is it <u>really</u> doing?**

Compressibility Factor

- **The deviation from ideal-gas behavior can be properly accounted for by using the *compressibility factor Z*, defined as**

$$Z = \frac{Pv}{RT} \quad \text{or} \quad Z = \frac{v_{actual}}{v_{ideal}}$$

•Z represents the volume ratio or compressibility,

•Ideal Gas: Z =1;

•Real Gases: Z>1 or Z<1.

jump

Principle of corresponding states

- The compressibility factor Z is approximately the same for all gases at the same *reduced temperature* and *reduced pressure.*

$$\boxed{Z = Z(P_R, T_R) \text{ for all gases}}$$

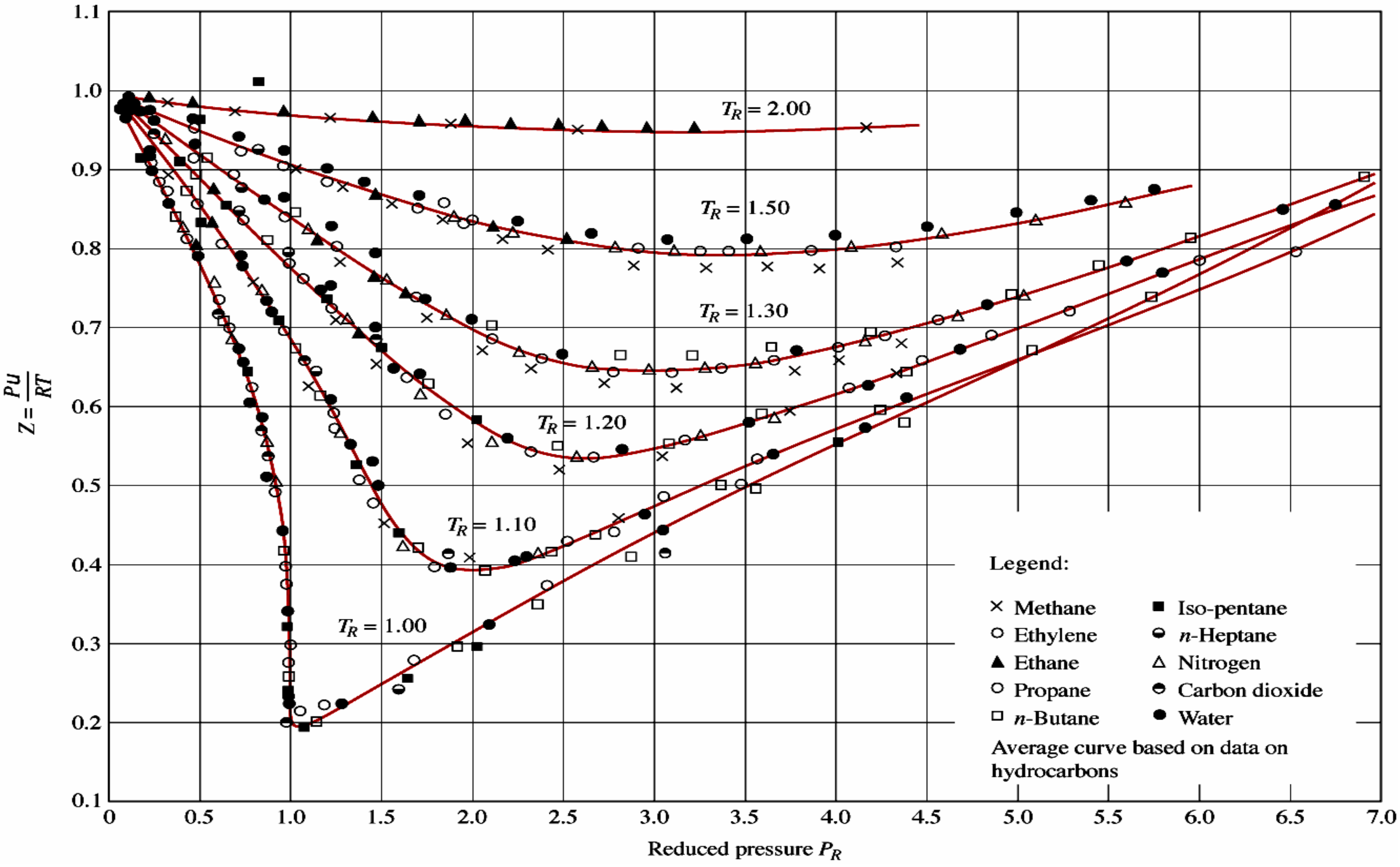
Reduced Pressure and Temperature

$$P_R \equiv \frac{P}{P_{cr}}; \quad T_R \equiv \frac{T}{T_{cr}}$$

where:

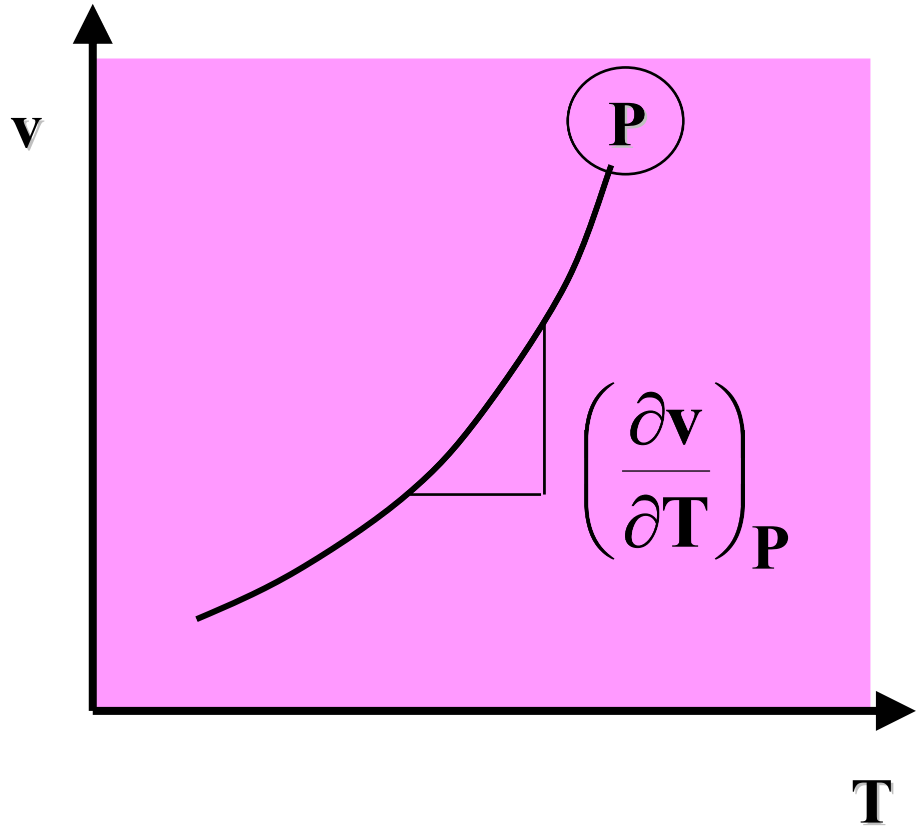
P_R and T_R are <u>reduced</u> values.
P_{cr} and T_{cr} are <u>critical</u> properties.

Compressibility factor for ten substances (applicable for all gases Table A-3)



OTHER THERMODYNAMIC PROPERTIES

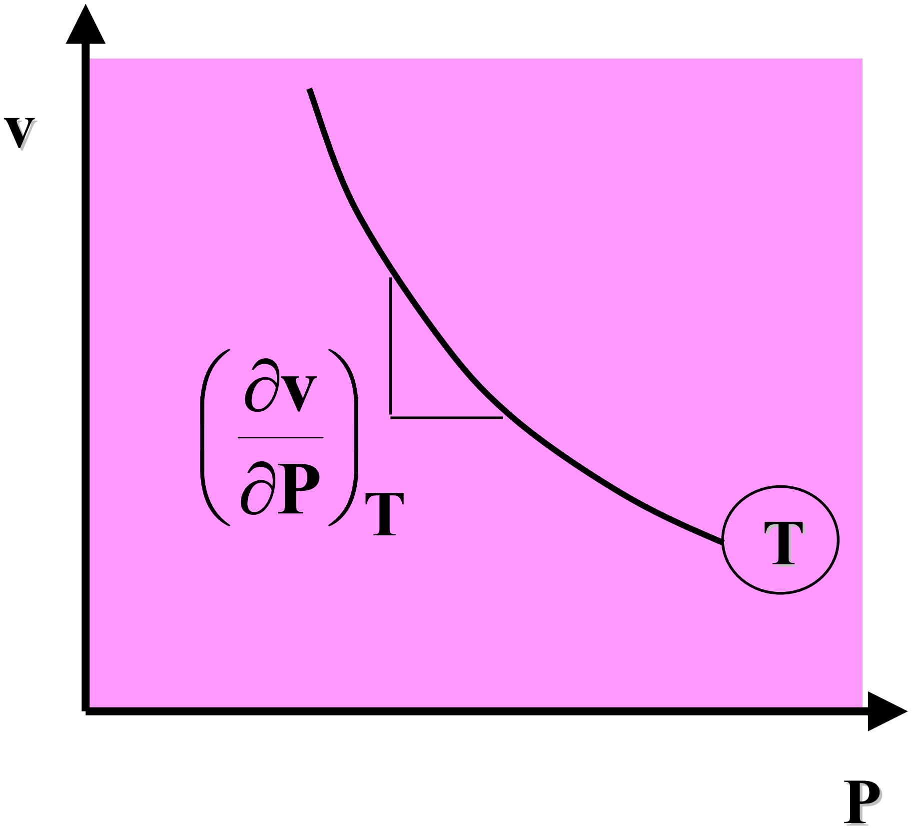
Other Thermodynamic Properties: Isobaric (c. pressure) Coefficient



$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P > 0$$

For ideal gas,
$\beta = 1/T$

Other Thermodynamic Properties: *Isothermal (c. temp) Coefficient*



$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T > 0$$

For ideal gas,
$\kappa = 1/P$

Other Thermodynamic Properties:

We can think of the volume as being a function of pressure and temperature, v = v(P,T). Hence infinitesimal differences in volume are expressed as infinitesimal differences in P and T, using κ and β coefficients

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP \equiv \beta v dT - \kappa v dP$$

For ideal gas: dv/v = dT/T- dP/P →VP/T = const!
For substances other than ideal gas, it can be approximated by:

$$Ln\left(\frac{v}{v_0}\right) = \beta(T - T_0) - \kappa(P - P_0)$$

<u>If κ and β are nearly constant,</u>

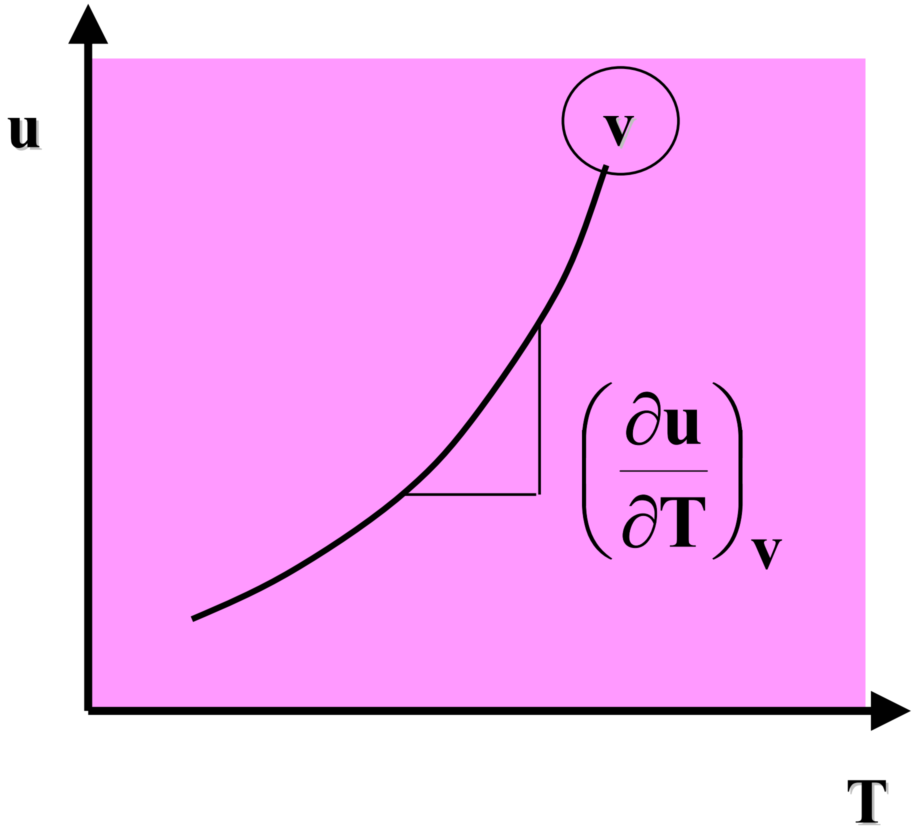
Other Thermodynamic Properties:

$u = u(T, v)$ **- Internal Energy**

$h = h(T, P) \equiv u + Pv$ **- Enthalpy**

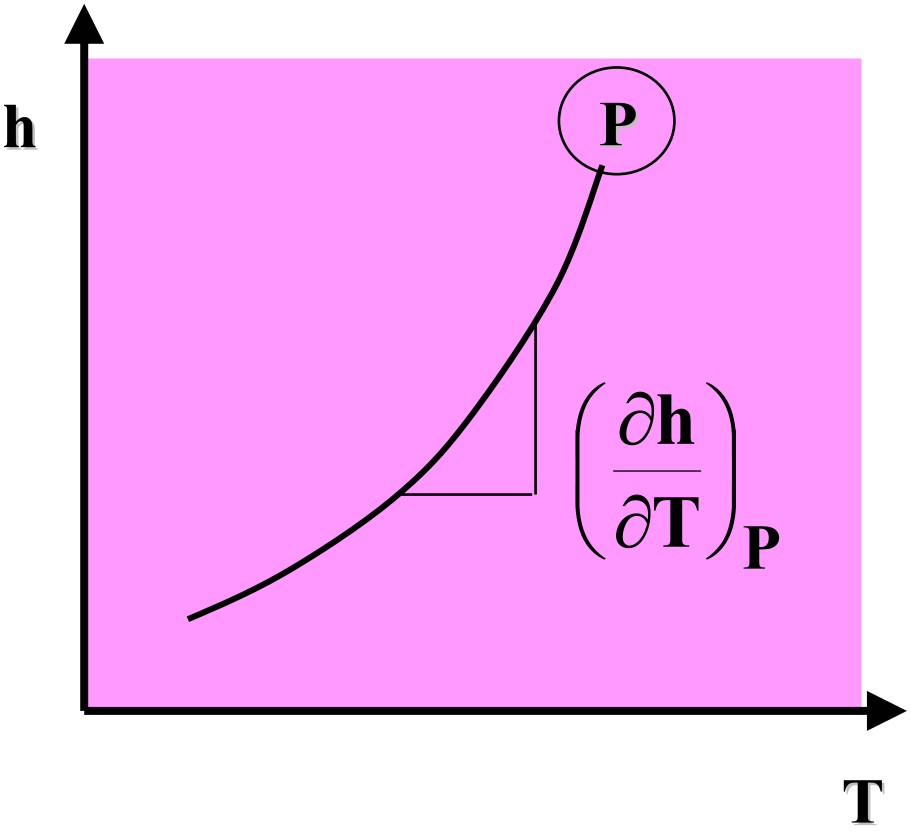
$s = s(u, v)$ **- Entropy**

Other Thermodynamic Properties: *<u>Specific Heat at Const. Volume</u>*



$$C_v = \left(\frac{\partial u}{\partial T}\right)_v > 0$$

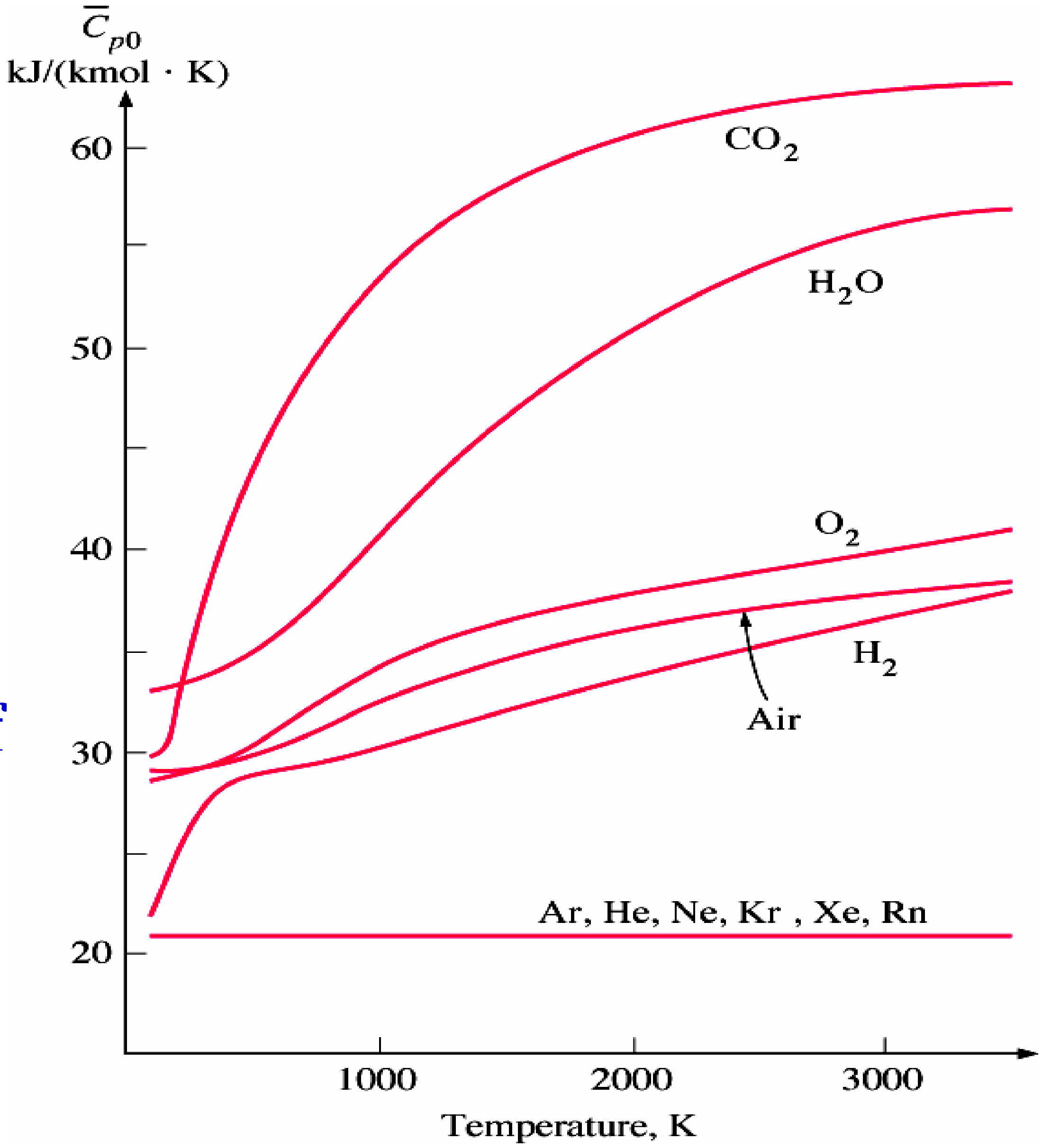
Other Thermodynamic Properties:
Specific Heat at Const. Pressure



$$C_P = \left(\frac{\partial h}{\partial T}\right)_P > 0$$

Specific Heats for Some Gases

- $C_p = C_p(T)$ a function of temperature



Ideal Gases: u = u(T)

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \cancelto{0}{\left(\frac{\partial u}{\partial v}\right)_T} dv$$

Therefore,

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT = C_v(T)dT$$

The internal energy change is:

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} C_v(T)\, dT$$

As C_v changes with temperature it cannot be pulled out from the integral *(for general cases).*

Enthalpy for an Ideal Gas

- $h = u + Pv$ where Pv can be replaced by RT because $Pv = RT$.
- Therefore, $h = u + RT$ => since u is only a function of T, R is a constant, then h is also only a function of T!
- so $h = h(T)$

Similarly, for a change in enthalpy for ideal gases:

$$\boxed{C_p = C_p(T) \quad \& \quad \left(\frac{\partial h}{\partial P}\right) \equiv 0}$$

$$dh = C_p dT, \quad and$$

$$\Delta h = h_2 - h_1 = \int_{T_1}^{T_2} C_p(T) dT$$

Summary: Ideal Gases

- For ideal gases u, h, C_v, and C_p are functions of temperature alone.
- For ideal gases, C_v and C_p are written in terms of ordinary differentials as

$$C_v = \left(\frac{du}{dT}\right)_{ideal\ gas} \quad ; \quad C_p = \left(\frac{dh}{dT}\right)_{ideal\ gas}$$

Three Ways to Calculate Δu and Δh

- $\Delta u = u_2 - u_1$ (table)
- $\Delta u = \int_1^2 C_v(T)\, dT$
- $\Delta u = C_{v,av} \Delta T$

- $\Delta h = h_2 - h_1$ (table)
- $\Delta h = \int_1^2 C_p(T)\, dT$
- $\Delta h = C_{p,av} \Delta T$

Problem 3.31 – N_2 is heated from 373K to 1773K at constant pressure. Evaluate the specific entalpy change (KJ per kg).

- $\Delta h \approx C_{p,300k} \Delta T =$ *(tab. A-7)*

$1,0416x(1773-373) = 1457kJ/kg$

- $\Delta h = \int_1^2 C_p(T)\, dT$ *tab A-5*, $\theta = t(K)/100$

$Cp = 39,060 - 512,79\theta^{-1.5}+1072,7\theta^{-2}-820,40\theta^{-3}$

$\Delta h =1635.98\ kJ/kg$

There is an error of 11% for using Cp constant when the temperature span is of 1400K!

Cp x Cv Relationship for an Ideal Gas,

- $h = u + Pv = u + RT$

$$\frac{dh}{dT} = \frac{du}{dT} + R$$

$$C_p = C_v + R$$

$$\left[\frac{kJ}{kg \cdot K}\right]$$

Ratio of Specific Heats γ

$$\gamma \equiv \frac{C_p}{C_v} = \frac{C_p(T)}{C_v(T)} = \gamma(T)$$

For most gases γ is almost constant with temperature and equals to 1.4

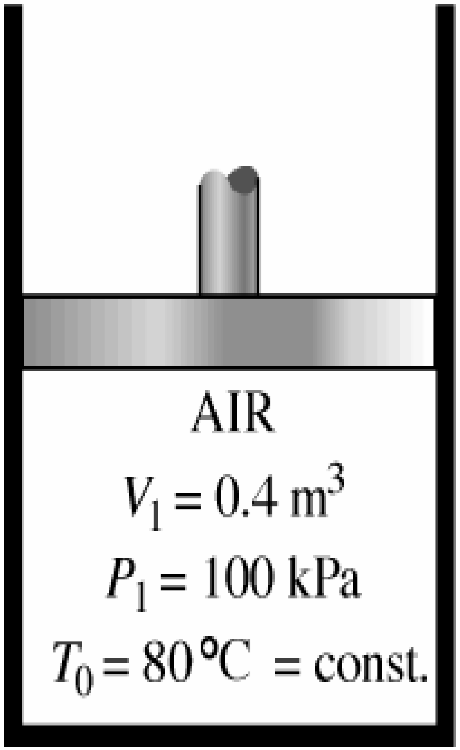
$$\frac{C_p}{C_v} = 1 + \frac{R}{C_v} = \gamma > 1$$

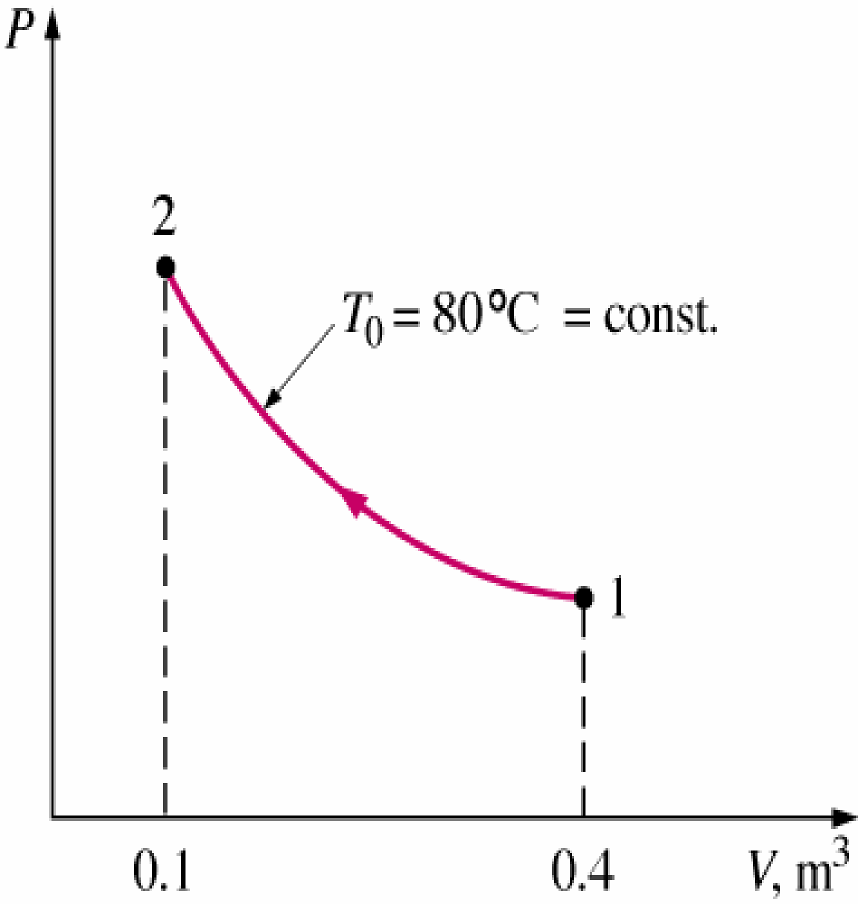
$$C_v = \frac{R}{\gamma\text{-}1} \quad \text{and} \quad C_p = \frac{\gamma R}{\gamma\text{-}1}$$

ISOTHERMAL, POLITROPIC AND ADIABATIC PROCESSES FOR AN IDEAL GAS

Isothermal Process

- Ideal gas: $PV = mRT = constant$





For ideal gas, PV = mRT
We substitute into the integral

$$W_b = \int_1^2 P\,dV = \int_1^2 \frac{mRT}{V}\,dV$$

Collecting terms and integrating yields:

$$W_b = mRT\int_1^2 \frac{dV}{V} = mRT\,\ell n\left(\frac{V_2}{V_1}\right)$$

Polytropic Process: $PV^n = C$; $1 \leq n \leq \gamma$

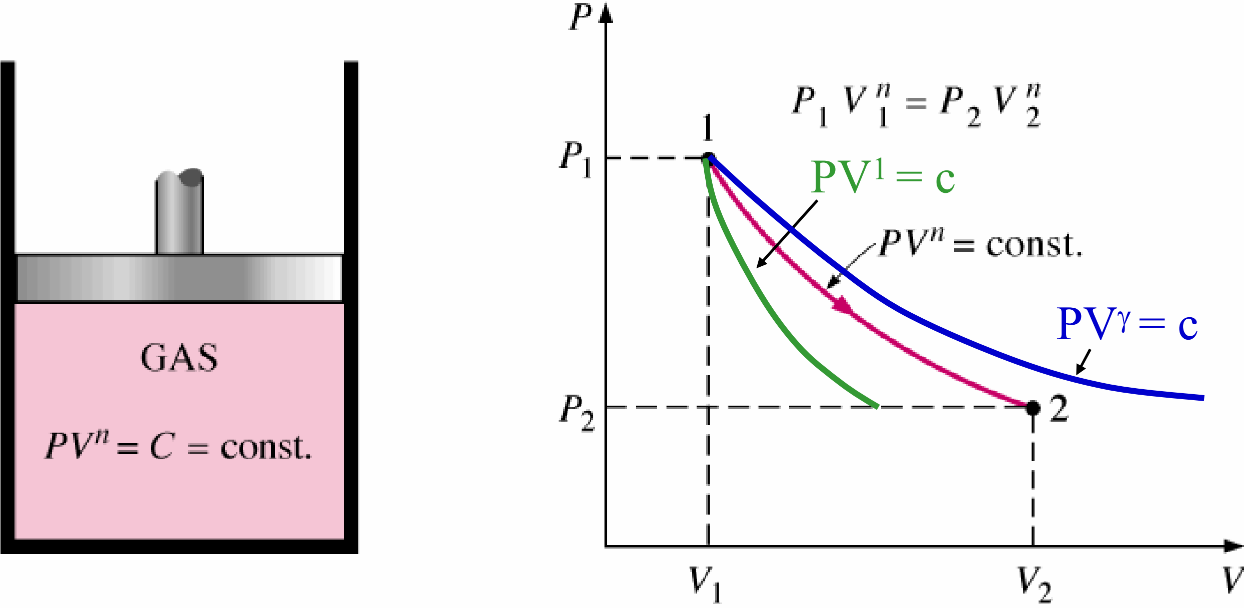
Isothermal .... $n = 1$

Adiabatic (Q=0).......... $n = \gamma = Cp/Cv$

Others:

Constant pressure..........$n = 0$

Co



The politropic lines are always to the right of the isothermal lines.

P, v and T Relationship in a Polytropic Process, 1≤n ≤1

- The path is described by: $Pv^n = C$
- The ideal gas state equation is: $Pv = RT$
- Combining these two expressions is possible to relate the initial to the final states

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{v_1}{v_2}\right)^{n} \qquad \left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{n-1}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$$

jump

Boundary work for a gas which obeys the polytropic equation

$$W_b = \int_1^2 P\,dV = c\int_1^2 \frac{dV}{V^n}$$

$$= c\left[\frac{V^{1-n}}{1-n}\right]_{V_1}^{V_2} = c\left[\frac{V_2^{1-n} - V_1^{1-n}}{1-n}\right] \quad \text{para } (n \neq 1)$$

Where C stands for the constant $Pv^n = C$

We can further simplify

The constant c = $P_1V_1^n = P_2V_2^n$

$$W_b = \frac{P_2V_2^n(V_2^{1-n}) - P_1V_1^n\left(V_1^{1-n}\right)}{1\text{-}n}$$

$$= \frac{P_2V_2 - P_1V_1}{1-n}, \qquad n \neq 1$$

Summary for Polytropic Process

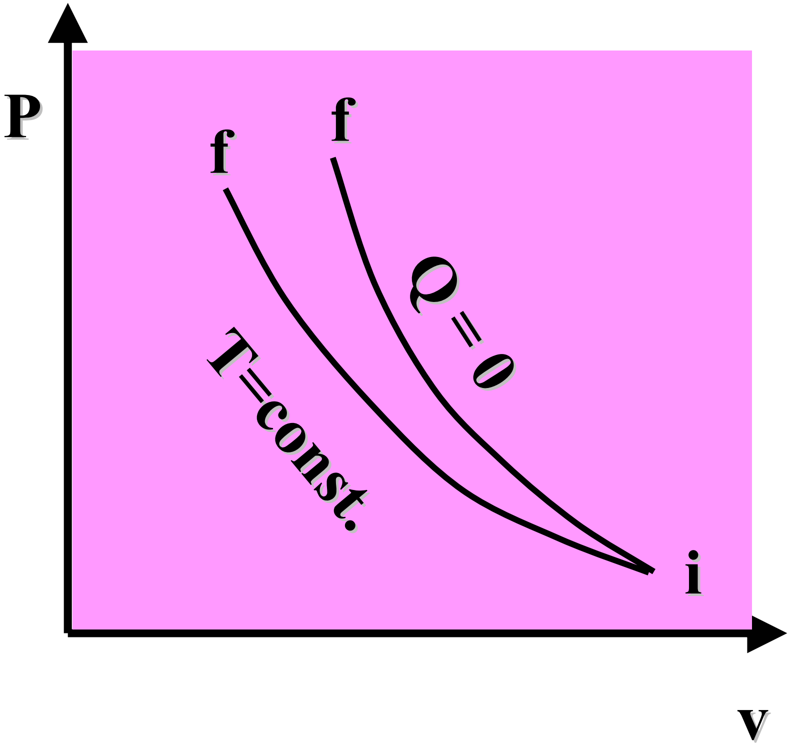
$$W_b = \int_1^2 P\,dV = \int_1^2 \frac{c}{V^n}\,dV$$

$$= \frac{P_2V_2 - P_1V_1}{1-n}\,, \quad n \neq 1$$

$$= PV\ell n\left(\frac{V_2}{V_1}\right), \quad n = 1$$

Ideal Gas Adiabatic Process and Reversible Work

- **Why $Pv^{\gamma} = C$ represents a process where the volume is expanding or contracting without heat flux, Q = 0?**



Ideal Gas Adiabatic Process and Reversible Work (cont)

First Law:

$$\underbrace{dQ}_{=0} - \underbrace{dW}_{PdV} = \underbrace{dU}_{MC_V dT}$$

Substituting
P = MRT/V

$$\left(\frac{dV}{V}\right) = -\frac{C_V}{\underbrace{R}_{(1-\gamma)^{-1}}}\left(\frac{dT}{T}\right)$$

Integrating from
(1) to (2)

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_1}\right)^{(1-\gamma)} \Rightarrow \left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

Which are the polytropic relations seen before!

Exercise 3-30

Air is compressed reversibly and adiabatically from a pressure of 0.1 MPa and a temperature of 20^{o}C to a pressure of 1.0 MPa.

a) Find the air temperature after the compression
b) What is the density ratio (after to before compression)
c) How much work is done in compressing 2 kg of air?
d) How much power is required to compress 2kg per second of air?

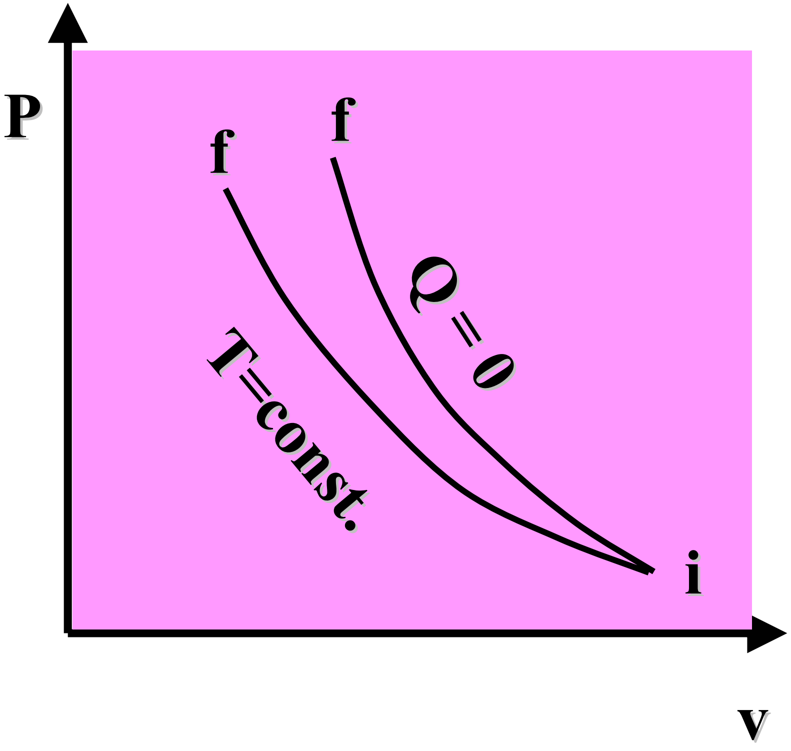
Solution - page 1

- **In a reversible and adiabatic process P, T and v follows:**

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

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$



Solution - page 2

Part a)

The temperature after compression is

$$T_2 = T_1 \cdot \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} \rightarrow T_2 = 293 \cdot \left(\frac{1}{0.1}\right)^{0.4/1.4} = 566\text{K} \quad (293\text{oC})$$

Part b)

The density ratio is

$$\left(\frac{V_2}{V_1}\right) \equiv \left(\frac{\rho_1}{\rho_2}\right) = \left(\frac{P_2}{P_1}\right)^{-1/\gamma} \rightarrow \left(\frac{\rho_2}{\rho_1}\right) = \left(\frac{1}{0.1}\right)^{1/1.4} = 5.179$$

Solution - page 3

Part c)

The reversible work:

$$W_{REV} = -\frac{\lfloor (PV)_2 - (PV)_1 \rfloor}{(\gamma - 1)} \equiv \frac{M \cdot R(T_2 - T_1)}{(\gamma - 1)} =$$

$$= \frac{2 \cdot 287 \cdot (566 - 293)}{0.4} = 391KJ$$

Part d)

The power is:

$$P = \frac{dW}{dt} = -\frac{\dot{M}R(T_2 - T_1)}{(\gamma - 1)} = 391KW$$

Exercícios – Capítulo 3 Propriedades das Substâncias Puras

Exercícios Propostos: 3.6 / 3.9 / 3.12 / 3.16 / 3.21 / 3.22 / 3.26 / 3.30 / 3.32 / 3.34

Team Play: 3.1 / 3.2 / 3.4