MME 2009 Metallurgical Thermodynamics

Pressure – Volume – Temperature Relationship of Pure Fluids

Volumetric data of substances are needed to calculate the thermodynamic properties such as internal energy and enthalpy, from which the heat and work requirements of processes are obtained

Understanding the P-V-T behavior of pure substances allows the engineer to make accurate estimations to the changes in properties accompanying their state changes

Pressure, volume and temperature are experimentally controllable properties that are connected by equation of state

$$V(P, T)$$

$$V = RT/P \qquad \text{For ideal gas}$$

A pure substance can have as many as 3 phases coexisting at the same conditions: gas, liquid, solid

P-V-T behavior of any substance can be experimentally obtained and represented in the form of phase diagrams

The word *fluid* covers both gases and liquids, any gas and any liquid is a fluid

A phase is considered a *liquid* if it can be vaporized by reduction in pressure at constant temperature

A phase is considered a *gas* if it can be condensed by reduction of temperature at constant pressure

Vapor is the preferred term for gas when the gaseous phase is in equilibrium with the corresponding liquid or solid, although there is no significant physical or chemical difference between a vapor and a gas

Vaporization curve in a P-T diagram of a pure substance seperates vapor and liquid phases upto a critical temperature and pressure where the curve ends

Above the critical temperature and/or critical pressure, *fluid* is the preferred term, because there is no meaningful distinction between liquid/vapor/gas
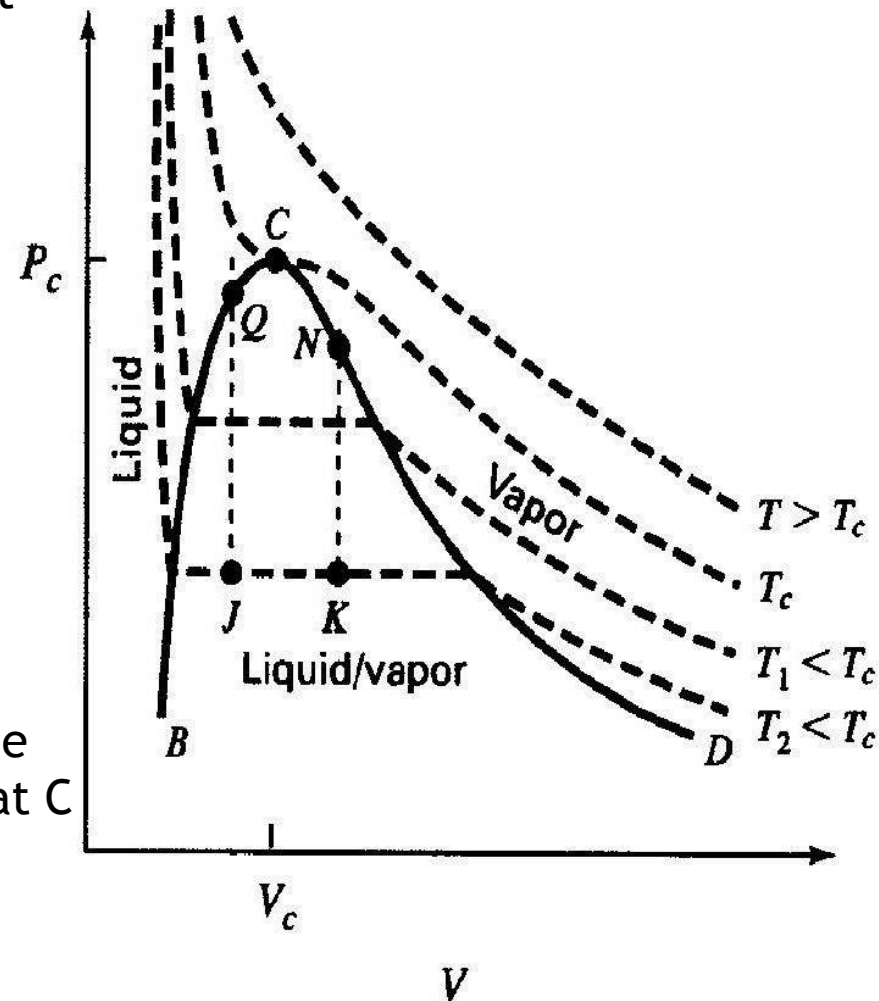
Pressure – Temperature diagram of water
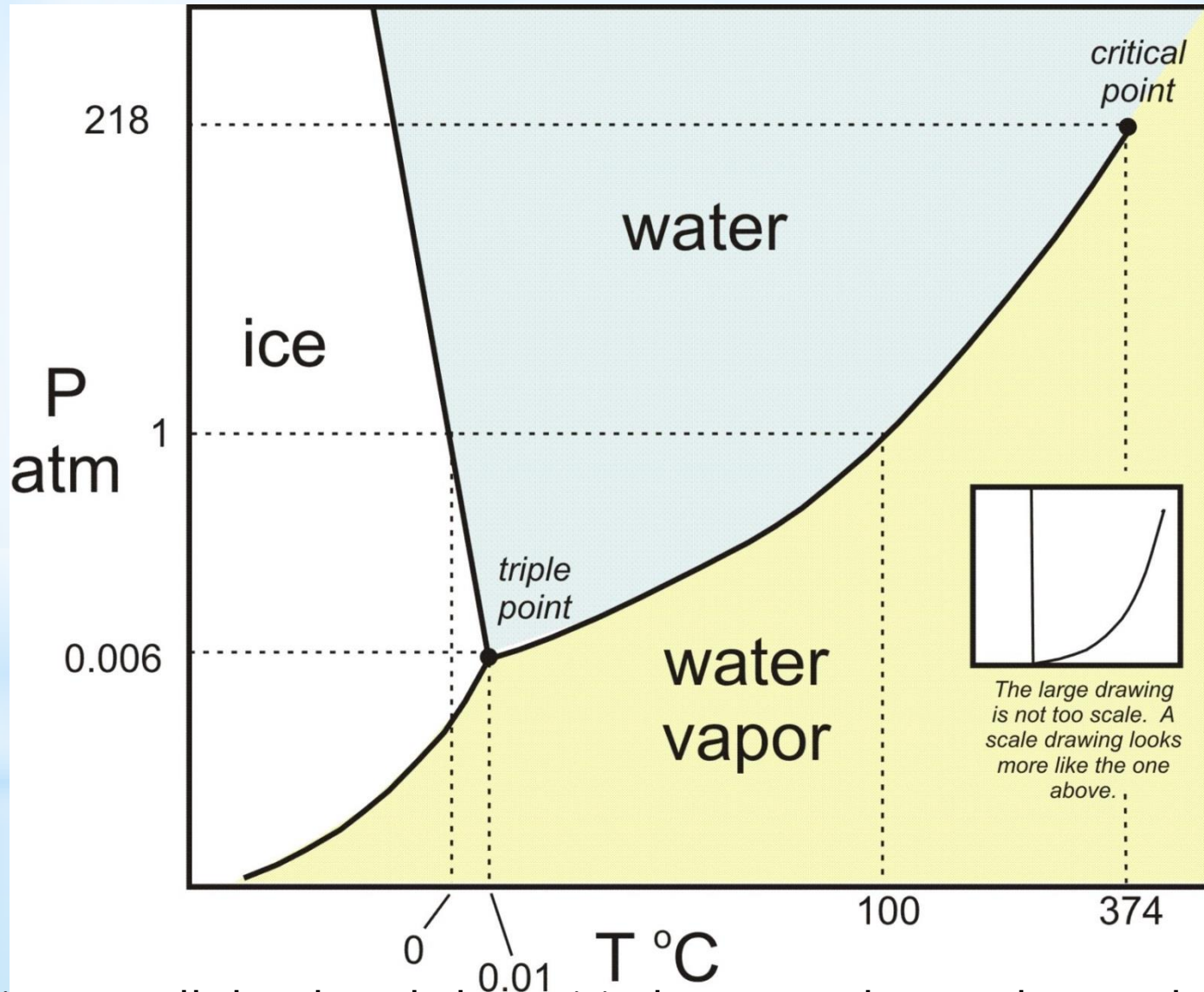
It is convinient to call the phase below critical pressure the gas phase and the gas phase below critical temperature the vapor phase which can be condensed to liquid vapor

Pressure – Volume diagram of a pure fluid

Isotherms greater than the critical temperature do not cause phase changes and therefore are smooth

Isotherms lower than the critical temperature consist of three distinct regions: vapor, liquid-vapor, liquid

- At the horizontal sections which represent the phase change between vapor and liquid, the constant pressure is the vapor pressure
- Ratio of liquid and vapor phases can be obtained by the lever rule
- The curve B-C represents saturated liquid
- The curve C-D represents saturated vapor
- Isotherms in the liquid region are steep because liquid volumes change little with large changes in pressure
- The horizontal sections of the isotherms get gradually shorter with increasing T, approaching point C
- The liquid and vapor phases have the same properties at the horizontal inflection point at C

Temperature - Volume diagram of a pure fluid
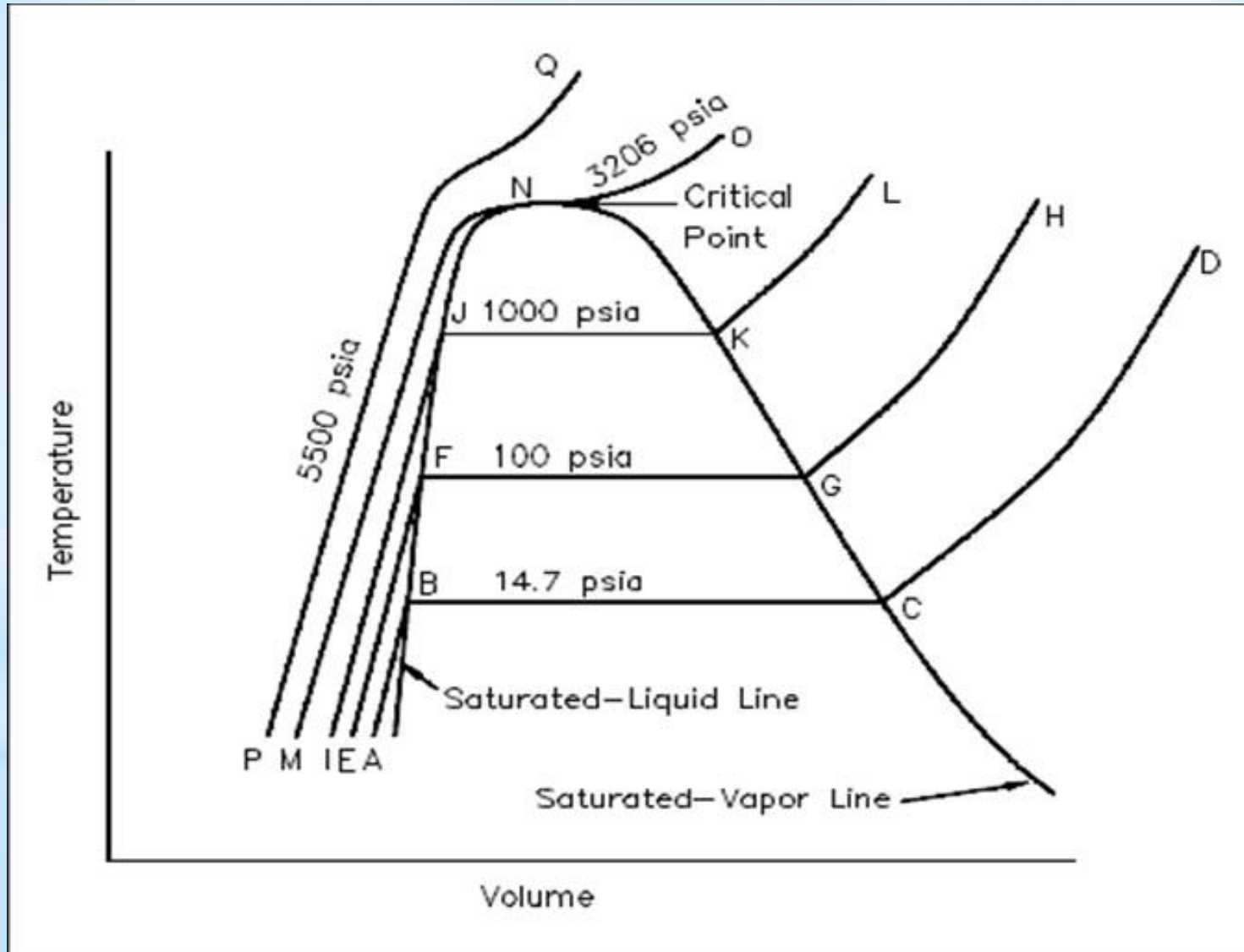
Temperature increase is proportional to volume except the phase change region

A relation connecting pressure, volume and temperature exists for the regions of the diagrams where single phase exists:

$$f(P,V,T) = 0$$

or

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

The partial derivatives in this equation have definite physical meanings and measurable quantities for fluids

The volume expansion coefficient

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The isothermal compression coefficient

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

Combining provides the general equation relating P, V and T for fluids:

$$\frac{dV}{V} = \beta dT - \kappa dP$$

$$\mathrm{d}V = V\beta dT - V\kappa dP$$

The isotherms for the liquid phase on the left side of the P-V and T-V diagrams are steep and closely spaced which means both volume expansion and isothermal compression coefficients of liquids are small

A useful idealization known as *incompressible fluid* is employed in fluid mechanics for a sufficiently realistic model of liquid behavior

The volume expansion and isothermal compression coefficient of the incompressible fluid are zero so it cannot be described by an equation of state relating V to T and P

β and κ are weak functions of temperature and pressure for real liquids Thus error introduced by taking them constant is low for small changes in T and P

$$\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

Example – The volume expansion and isothermal compression coefficients of water at room temperature and 1 atm pressure are given as:

β = 0.257 x 10^{-3} $°C^{-1}$

κ = 4.6 x 10^{-5} atm^{-1}

and V = 1.00296 cm³ for 1 gram

- Calculate the pressure generated when water is heated at constant volume from 25°C and 1 atm to 40°C

V, β and κ are assumed constant in the small temperature interval

$$\ln \frac{V_2}{V_1} = 0 = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

$$\Delta P = \frac{\beta}{\kappa} \Delta T = 5.587 * (15) = 83.8 \text{ atm}$$

$$P_2 = P_1 + \Delta P = 1 + 83.8 = 84.8 \text{ atm}$$

- Obtain the value of $\left(\frac{\partial P}{\partial T}\right)_V$

$$\frac{dV}{V} = 0 = \beta dT - \kappa dP$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{0.257 * 10^{-3}}{4.6 * 10^{-5}} = 5.587 \frac{\text{atm}}{°\text{C}}$$

- Calculate the volume change when the state of water is changed from 25°C and 1 atm to 0°C and 10 atm

β and κ are assumed constant in the small temperature and pressure interval

$$\ln\frac{V_2}{V_1} = 0.257 * 10^{-3}(-25) - 4.6 * 10^{-5}(9)$$

$$= -0.006839$$

$$\frac{V_2}{V_1} = 0.9932$$

$$V_2 = 0.9961 \text{ cm}^3 \text{ for 1 gram}$$
$$\Delta V = -0.00682 \text{ cm}^3 \text{ for 1 gram}$$

The P-V-T relationship of fluids is hard to formulate

However relatively simple equations can describe
the P-V-T behavior of gas regions

For gases P decreases proportionally to
the increase in V
Thus $P \propto 1/V$, $PV \approx constant$

PV along an isotherm is represented by a power
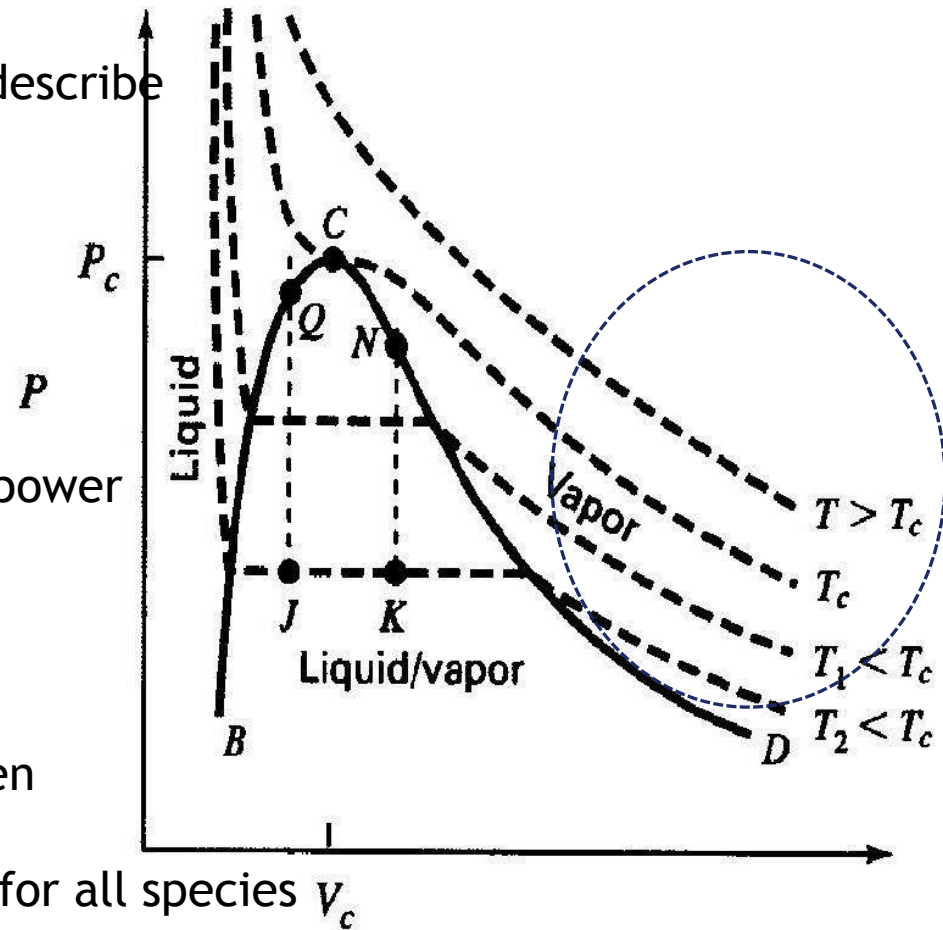series expansion

$$PV = a + bP + cP^2 + \cdots$$

$$PV = a(1 + BP + CP^2 + \cdots)$$

where a, B, C, etc are constants for a given
temperature and chemical species

Parameter a is a function of temperature for all species

The relationship is truncated for simplicity
In general, the greater the pressure range the larger the number of terms required

Data taken for various gases at a specific constant temperature show that P-V plots have the same limiting value of PV/T as P→0

$$\lim_{P=0}(PV) \equiv (PV)_o = a = f(T)$$

a is the same for all gases!

$$PV = a(1 + BP + CP^2 + \cdots)$$

This remarkable property of gases helped scientists establish a temperature scale that is independent of the gas used as thermometric fluid:

$\dfrac{PV}{nT} \Big/ \mathrm{J\,K^{-1}\,mol^{-1}}$

T=273.16 K

8.3200

8.314510

8.3100

8.3000

H_2

He
ideal-gas

N_2

O_2

0.5   1.0
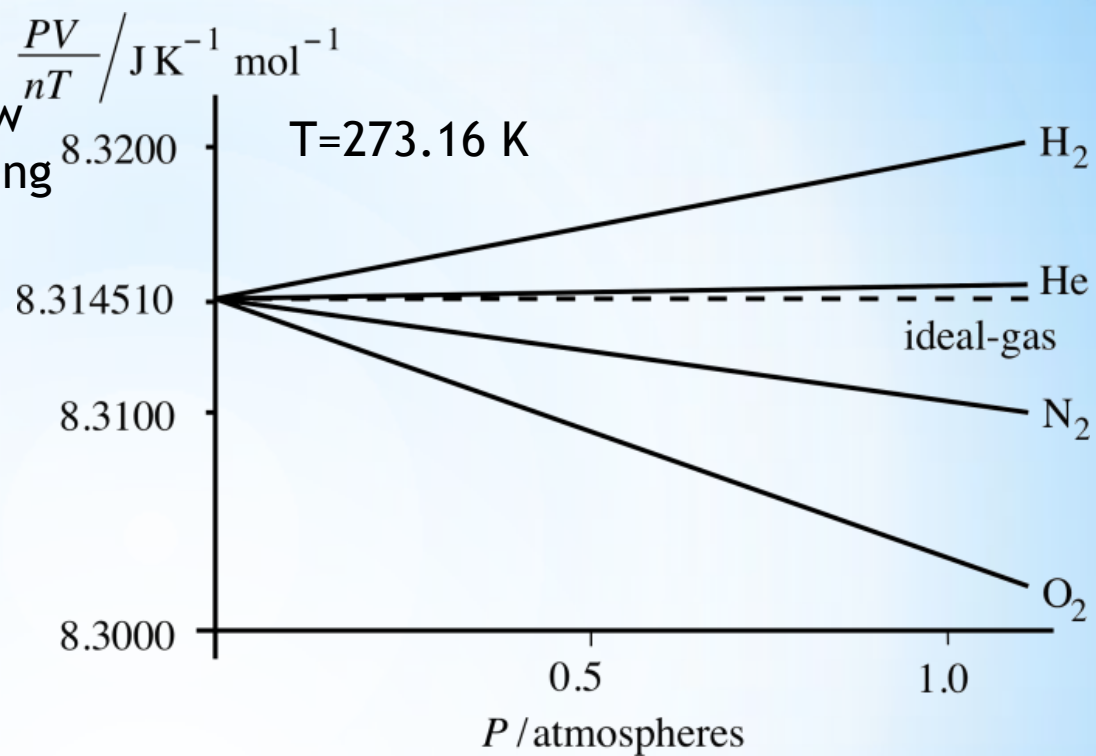
$P/\mathrm{atmospheres}$

$$(PV)_o = a = RT$$ where R denotes the universal gas constant

$$(PV)_o{}^t = R * 273.16 \text{ K}$$ where the t denotes the value of the triple point of water

$$\boxed{T \text{ K} = 273.16 \, \frac{(PV)_o}{(PV)_o{}^t}}$$

Thus Kelvin or ideal gas temperature scale established throughout the temperature range for which limiting values of PV as P→0 are experimentally accessible

Constant *a* is replaced by RT with the establishment of ideal gas temperature scale

$$PV = a(1 + BP + CP^2 + DP^3 + \cdots)$$

$$Z = \frac{PV}{RT} = 1 + BP + CP^2 + DP^3 + \cdots$$

where the ratio *PV/RT, Z* is called the *compressibility factor*
An alternative representation of Z:

$$Z = 1 + \frac{B'}{V} + \frac{C'}{V^2} + \frac{D'}{V^3} + \cdots$$

B, C, D, etc called virial coefficients represent the interaction between pairs of molecules, three-body interactions, four-body interactions respectively

Contributions to Z of the higher-ordered terms fall off rapidly
As the pressure of a real gas is reduced at constant temperature, its volume increases and the contributions of the terms B'/V, C'/V² decrease

As pressure of the gas approaches zero, molecular distance become infinite, molecular attractions become negligible and Z approaches unity

$$PV = RT$$ for 1 mole of ideal gas

so

The use of the compressibility factor and the associated equation expansion is practical when no more than two or three terms are required
This requirement is satisfied for gases at low to moderate pressures

The plots of compressibility factors of gases as a function of pressure at various temperatures show that Z=1 at P=0 and the isotherms are nearly straight at low to moderate pressures

The tangent to an isotherm at P=0 is a good approximation of the isotherm for a finite pressure range

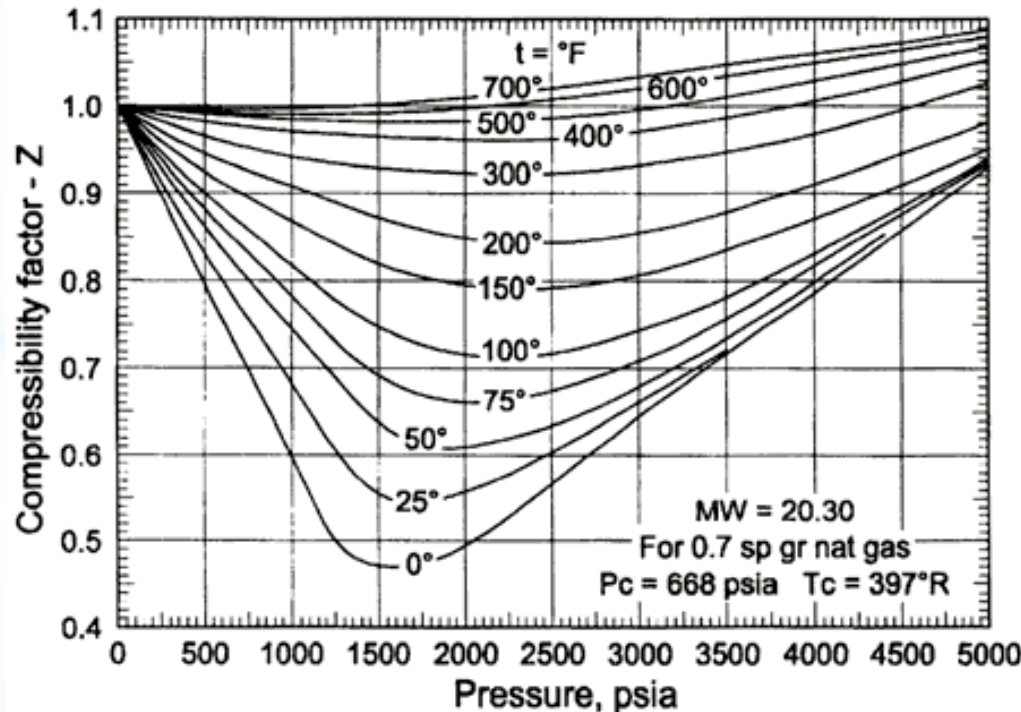$$Z = 1 + BP + CP^2 + DP^3 + \cdots$$

$$\frac{dZ}{dP} = B + 2CP + 3DP^2 + \cdots$$

$$\left(\frac{dZ}{dP}\right)_{P=0} = B$$

$$Z = 1 + BP$$

or

$$Z = 1 + \frac{B'}{V}$$

$$Z = 1 + \frac{B}{V}$$

$$B = B'/RT$$

$$Z = 1 + \frac{B'P}{RT}$$

Represent the PVT behavior of most gases up to a P of 15bar

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

Applicable to gases below pressures of 50 bar

The equation is cubic in volume so solution for V is usually done by an iterative way

Example – Calculate the volume and compressibility factor of isopropanol vapor at 200 °C and 10 bar. The virial coefficients of isopropanol at 200 °C is given as
B'= -388 cm^3 mol^{-1}, C'= -26000 cm^6 mol^{-2}
Calculate by
• The ideal gas equation
• $Z = 1 + \frac{B'P}{RT}$
• $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$

The compressibility factor accurately describes the PVT behavior of gases at low to medium pressures

A cubic equation of higher complexity is applied to define the PVT behavior of liquids as well as gases

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

The equation also known as Redlich/Kwong equation has three roots at most of the low pressure range

The smallest root is liquid volume, the highest vapor volume and the middle is of no significance

Thus volumes of saturated liquid and saturated vapor are given by the smallest and largest roots when P is the saturation or vapor pressure

The equation is solved by iteration

See text book for iteration steps and calculation of the constants a and b

Ideal gas equation of state is a model equation applicable to all gases to understand their P-V-T behavior and the energy requirements of processes within small margins of error
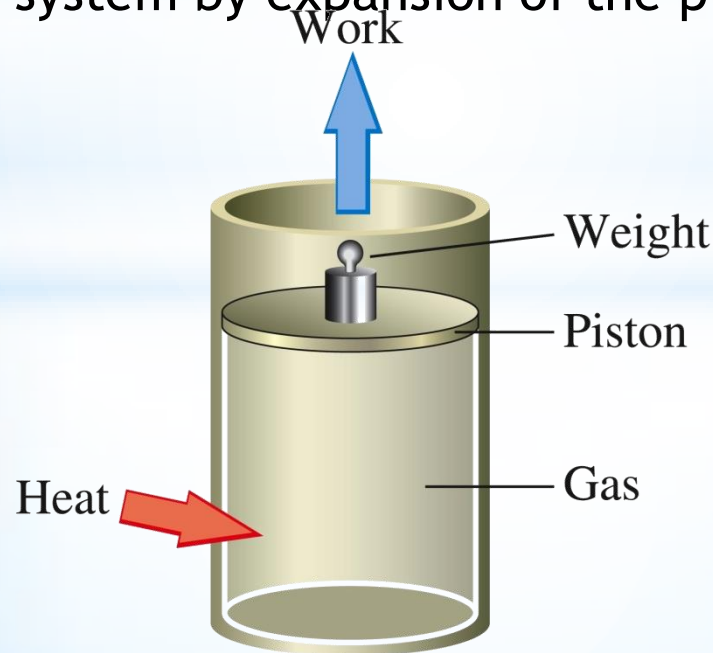
Consider an engine piston full of ideal gas

Total energy of the ideal gas can only be changed through transfer of energy across its boundary and work done on or by the system

Heat is admitted to the system by conduction through metal block
Work is done on the system by compressing the piston
Work is done by the system by expansion of the piston

Let U be a thermodynamic state function of the system called the *internal energy*
ΔU is the change in internal energy of the system for any process

Q is the quantity of *heat* that flows into the system during process
W is defined as the *mechanical work* done on the system by the external pressure
W' is defined as *all other kinds of work* done on the system during the process

Thus $$\Delta U = Q + W + W'$$ Mathematical formulation of the First law of thermodynamics

U is a state function and is independent of the path
Q,W, and W' are process variables that depend on the path

Mechanical work is the only work done in practical applications and W' is omitted

The signs of Q and W depend on the direction of the energy transfer
They are positive when heat is transferred <u>into</u> the system and work is done <u>by</u> it through expansion
They are negative when heat flows <u>out of </u>the system and work is done <u>on</u> it by compression

$$\Delta U = Q - W$$

Specific Heat:
It is the amount of heat required to raise the temperature of a 1 kg mass 1°C or 1°K

$$C = \frac{dQ}{dt}$$

$$dQ = CdT$$

by integration

$$Q = C\,(T_2 - T_1)\ \frac{KJ}{kg}$$

Considering the mass m,

$$Q = mC\,(T_2 - T_1)\ KJ$$

Example – A batch of 20 tons of liquid copper is to be cooled from 1200 °C to 1150 °C by adding solid copper at 25 C. 40000 kJ are lost during the time it takes to make the addition and the temperature to stabilize. What quantity of solid is used?
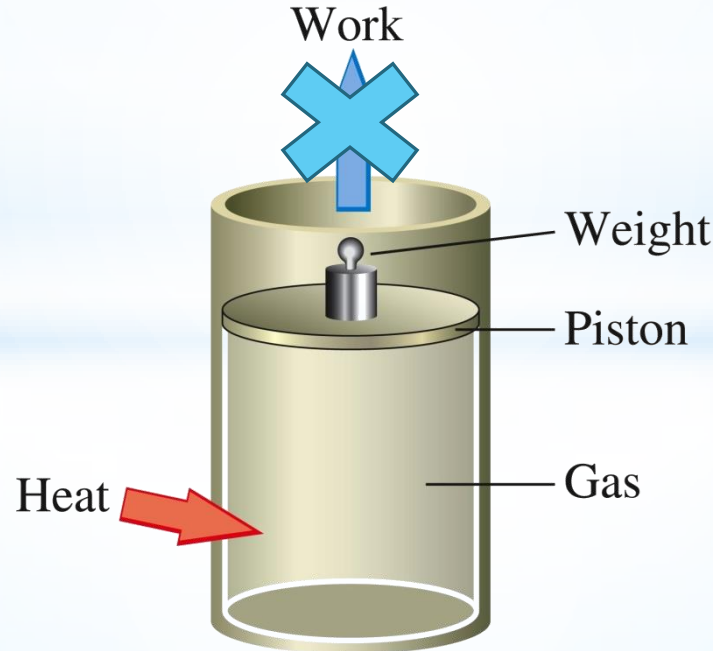
The Constant Volume Process

Internal energy of the ideal gas only changes by heat flow when the piston is not allowed to expand or compress

$$\Delta U = Q - W$$

$$dU = dQ = C_V dT$$

where C_V is the molar constant-volume heat capacity of the gas

ΔU and C_V of ideal gases are functions of only temperature so ΔU for an ideal gas can always be calculated by $\int C_V dT$, regardless of the process

Work

Weight

Piston

Heat

Gas

The Constant Pressure Process
The first law of thermodynamics simplifies accordingly for the special case of constant P:

$$\Delta U = Q - W$$

$$\Delta U = Q - P\Delta V$$

$$Q = \Delta U + P\Delta V \text{ state function}$$

Enthalpy change $\Delta H = Q$ for a constant P process

$$C = \frac{\delta Q}{dT}$$
$$dH = \delta Q = C_p dT$$
$$H = U + PV = U + RT$$

Both enthalpy and C_p of ideal gases also depend only on temperature

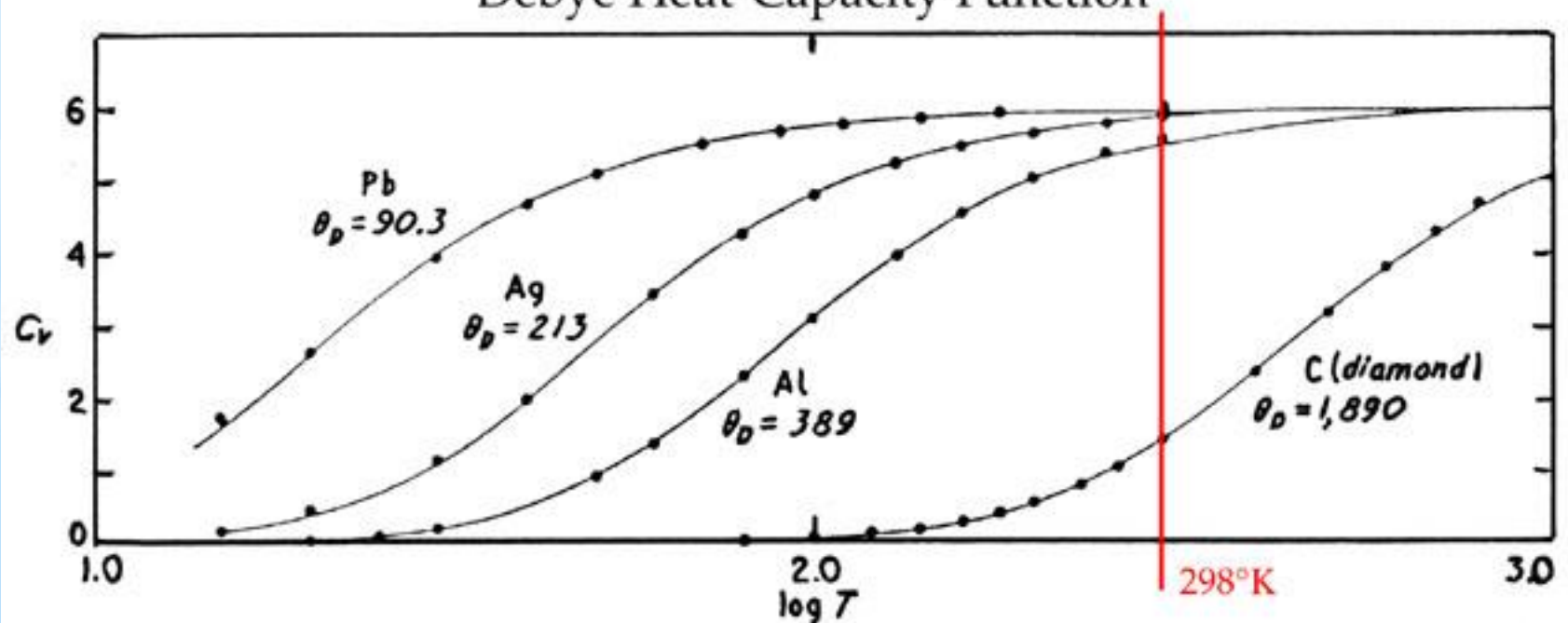$$dH = C_p dT \text{ for all process of ideal gas just as } dU = C_V dT$$

$$dH = dU + PdV$$

$$dH = dU + RdT$$

$$C_p dT = C_V dT + RdT$$

$C_p - C_V = R$ for ideal gas

Debye Heat-Capacity Function

Pb
$\theta_D = 90.3$

Ag
$\theta_D = 213$

Al
$\theta_D = 389$

C (diamond)
$\theta_D = 1,890$

C_V

298°K

log T

Lewis & Randall, *Thermodynamics*, Revised by Pitzer & Brewer, 2nd Edition, McGraw-Hill, 1961, p. 56.

The Constant Temperature Process
Internal energy of ideal gas stays constant in an isothermal process
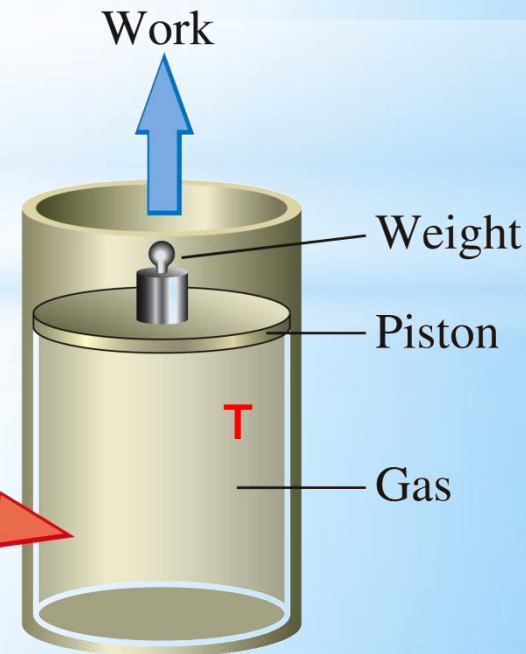
$$dU = dQ - dW = 0$$

$$Q = W$$

For a mechanically reversible process work is done by expansion

$$W = \int P dV = \int RT \frac{dV}{V}$$

$$Q = W = RT \ln \frac{V_2}{V_1}$$

Since $P_1/P_2 = V_2/V_1$ for constant temperature,

$$Q = W = RT \ln \frac{P_1}{P_2}$$

Work

Weight

Piston

T

Heat

Gas

The Adiabatic Process
There is no heat flow into or out of the system in adiabatic processes

$$dU = -dW = PdV$$

Since internal energy change of ideal gas for any process is $dU = C_V dT$,

$$C_V dT = -PdV = -\frac{RT}{V}dV$$
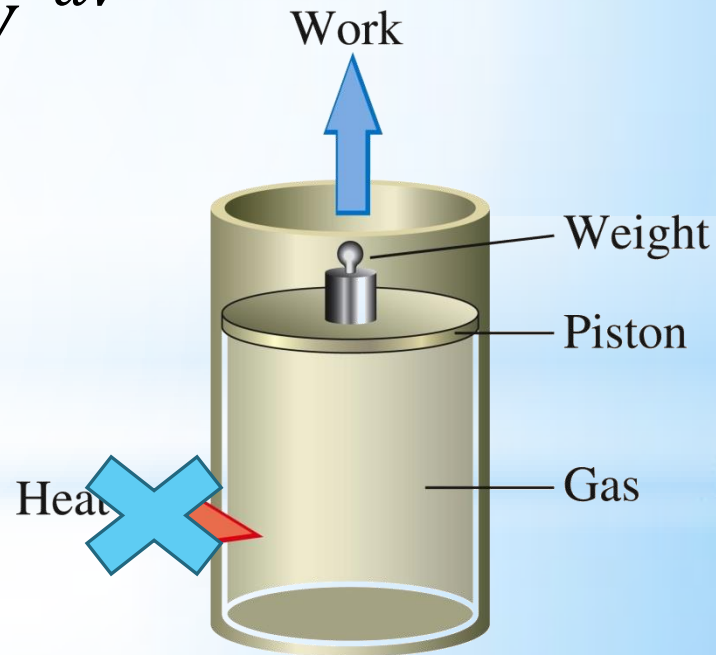
$$\frac{dT}{T} = \frac{-R}{C_V}\frac{dV}{V}$$

Work

Weight

integrating,

$$C_v\ln\left(\frac{T_2}{T_1}\right) = R\ln\left(\frac{V_1}{V_2}\right)$$

Piston

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

Heat

Gas

$$R/_{C_v} = \frac{C_p}{C_v} - 1 \qquad \text{since} \qquad C_p - C_v = R \quad \text{for ideal gases}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2 V_2}{P_1 V_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v}-1} \implies \left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v}} \implies P_1 V_1^{\frac{C_p}{C_v}} = P_2 V_2^{\frac{C_p}{C_v}} = constant$$

Remember the reversible isothermal expansion of an ideal gas

$$Q = W = PdV = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right)$$

so $P_1V_1 = P_2V_2 = constant$

The work done by an reversible isothermal process exceeds that of the reversible adiabatic because the internal energy of the adiabatically contained system decreases while performing work

Isothermal paths are utilized in heat engines to perform higher work
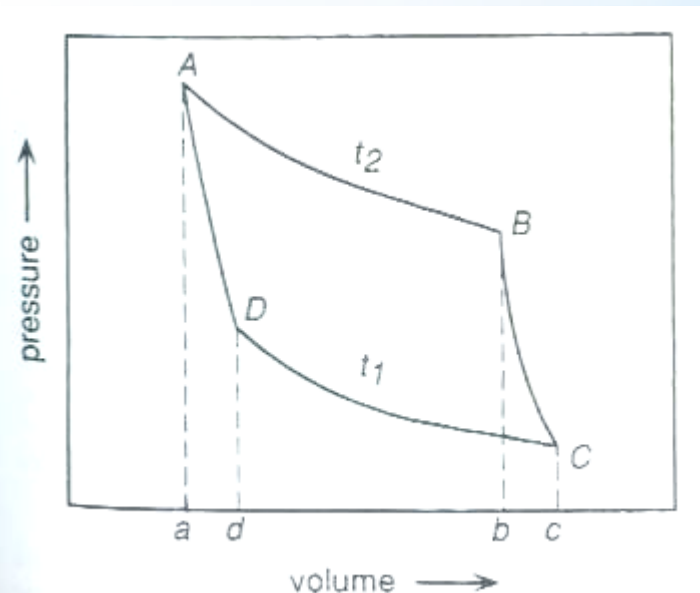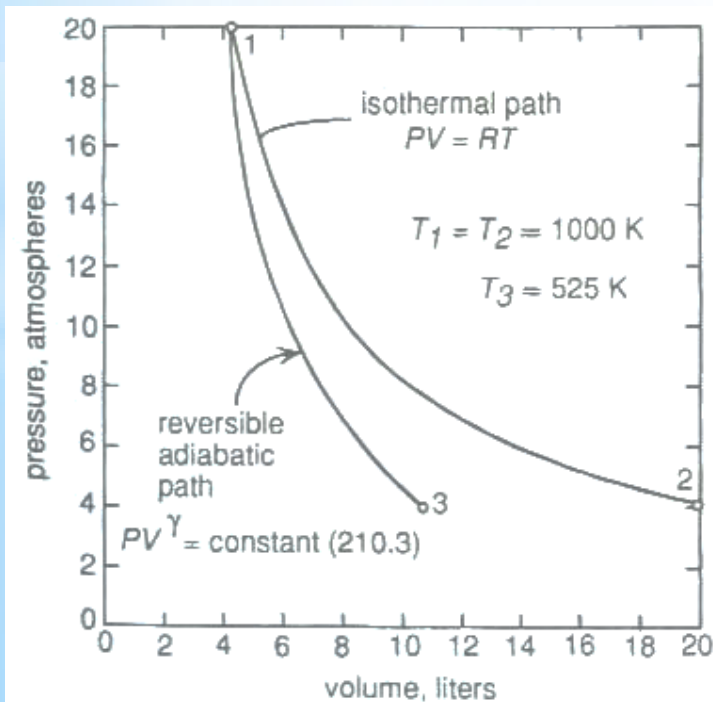
The General Process

When no specific conditions other than mechanical reversibility are present, the following general equations apply to ideal gas:

$$dU = dQ - dW \qquad\qquad \Delta U = \Delta Q - \Delta W$$

$$dW = PdV \qquad\qquad \Delta W = \int PdV$$

$$dU = C_V dT \qquad\qquad \Delta U = \int C_V dT$$

$$dH = C_P dT \qquad\qquad \Delta H = \int C_P dT$$

Values for Q cannot be determined directly and is obtained from the first law:

$$dQ = C_V dT + PdV$$

$$Q = \int C_V dT + \int PdV$$

Example – A closed system undergoes a process, during which 1000 J of heat is removed from it and 2500 J of work is done by it. The system is then restored to its initial state. If1500 J of heat addition is required for the second process, what is the amount of work done by or to the system in the second process?

$$\Delta U = \Delta Q - \Delta W$$

Example – Most real gases obey the following equation of state:

$$PV = nRT + bP$$

Find an expression for work when the gas undergoes a reversible isothermal volume expansion

$$dW = PdV \qquad\qquad \Delta W = \int PdV$$

Example – The general relationship between P-V-T of a solid is
$$V = V_0[1 + \beta \Delta T - \kappa \Delta P]$$
where subscript 0 represents a reference state. β for copper is $5*10^{-5}$ K^{-1} and κ is $7*10^{-7}$ bar^{-1}. For reference state $P_0=1$ bar, T_0 is 300 K and the density of copper is 0.94 g/cm³. 40 kJ of heat is added to a 5 kg block of copper starting at this state, at <u>constant pressure</u>. The resulting increase in temperature is 200 C. Determine the amount of work done and the change in internal energy.

Example – What pressure increase is needed to make a block of magnesium metal retain its initial volume while it is being heated from 0 to 50 $^\circ$C? The metal block is cubic in shape

β for magnesium is 2.5×10^{-7} K^{-1} and κ is 2.95×10^{-1} bar^{-1}.

$$V = V_0[1 + \beta \Delta T - \kappa \Delta P]$$