THERMAL & STATISTICAL PHYSICS
SSP3133

MECHANICAL & DIFFUSIVE INTERACTION

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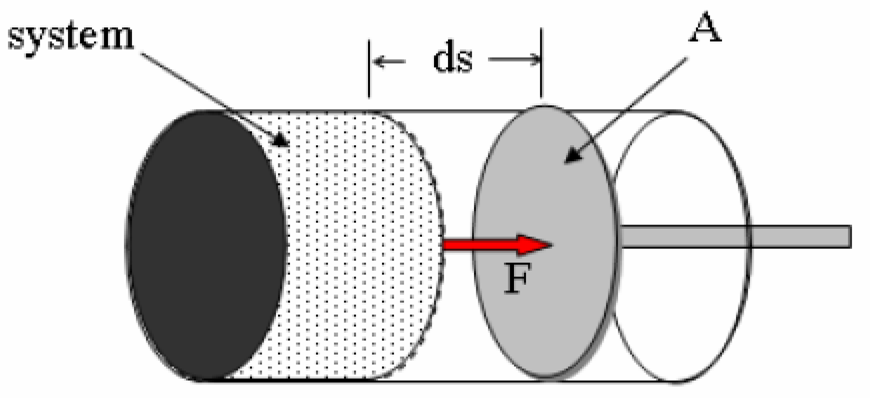


The system exerts force F against the piston of area A, and the piston moves distance ds,

The work done by the system,

$$\delta W = F.\, ds = P\,(A\, ds) = PdV$$

Note: δW is inexact, can be changed into exact diff. dV

$\delta W.\,(1/P)$ ….. exact

And $\delta Q\,.(1/T)$ ….. exact , dS ,entropy

(*)

1^{st} Law (exact differential form)

$$dU = TdS - PdV + \mu dN$$

Where $U = U(T,S,P)$

$\mu = \mu(P,V,N)$

$T = T(P,\mu,N)$ ……..etc..

From (*)

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

change in entropy,

$$\boxed{dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN}$$

from (*)

if $S = S(U, V, N)$

$$\boxed{dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{S,N} dV + \left(\frac{\partial S}{\partial N}\right)_{S,V} dN}$$

Comparing the above 2 equations:

$$\text{and } \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} ,\text{...........thermal interaction}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} ,\quad \text{........mechanical (work) int.}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} \quad \text{..........diffusive (particles) int.}$$

mechanical interaction.

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \qquad S = k \ln \Omega$$

$$P = kT\left(\frac{\partial \ln \Omega}{\partial V}\right)_{U,N} = kT\left(\frac{\Delta \ln \Omega}{\Delta V}\right)_{U,N}$$

or

$$\frac{P\Delta V}{kT} = \Delta \ln \Omega = \ln \Omega_2 - \ln \Omega_1 = \ln \frac{\Omega_2}{\Omega_1}$$

or

$$\boxed{\frac{\Omega_2}{\Omega_1} = e^{P\Delta V / kT}}$$

1st Law: $\Delta U = \Delta Q - p\Delta V + \mu \Delta N$

but $\Delta U = \Delta N = 0$, then $\Delta Q = P\Delta V$

$$\frac{\Omega_2}{\Omega_1} = e^{\Delta Q / kT}$$

Expansion

When heated – materials tend to expand

Gases: increase the force & frequency of collisions with the container wall, --- pushing outward.

Solid & liquid: oscillate with greater amplitudes, increase the intermolecular spacing ---expand !!

Coefficient of volume expansion, γ ---- a measure of the relative increase in volume per unit increase in temperature.

$$\gamma \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Note: generally $\gamma = \gamma(T,P)$ but most expansions are at atmospheric pressure, --- const. pressure.

For small change in temperature, $V = V(T)$

$$\Delta V = \left(\frac{\partial V}{\partial T}\right)_P \Delta T = V\gamma\,\Delta T$$

α, coefficient of linear expansion

a measure of relative increase in length (X)

$\alpha = \alpha(T, P)$

$$\Delta X = \left(\frac{\partial X}{\partial T}\right)_P \Delta T = X\alpha\,\Delta T$$

relation : α and γ

$$V' = V + \Delta V = V(1 + \gamma\,\Delta T) \qquad (*)$$

$$V' = V + \Delta V = V\,(1 + \gamma\,\Delta T) \qquad (*)$$

But $V' = X'Y'Z' = X(1+\alpha\Delta T)\,Y(1+\alpha\Delta T)\,Z(1+\alpha\Delta T)$

$$= XYZ\,(1+\alpha\Delta T)^3$$

$$= V(1+\alpha\Delta T)^3$$

$$= V(1 + 3\alpha\Delta T + \ldots\ ) \qquad (**)$$

for small ΔT, … $\Delta T^2 \cong 0$

therefore , from (*) & (**),

$$\gamma = 3\alpha$$

Isothermal compressibility (symbol: κ)

-a measure of relative change in volume per unit increase in pressure (temperature: constant)

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

κ = κ (T, P) and V = V(P, T)

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

$$\boxed{\text{bulk modulus}: \frac{1}{\kappa} = -V\left(\frac{\partial P}{\partial V}\right)_T}$$

The Diffusive interaction

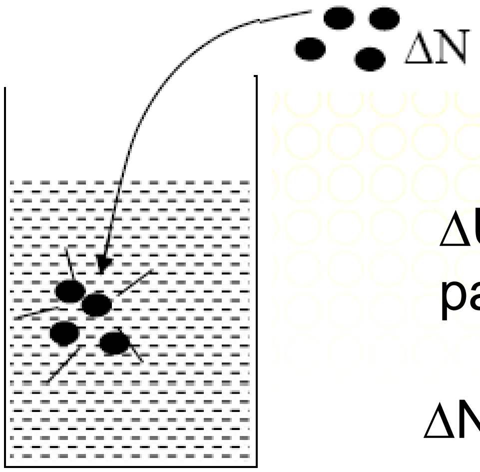
Chemical Potential (symbol: μ)

(in many cases, Free Energy is used instead of chemical potential)

The **chemical potential** : the change in the energy of the sytem when an additional constituent particle is introduced, with the entropy and volume held fixed.

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{s,v}$$

- It express how eager system is for particles.
- In equilibrium, it is equal in two systems placed in diffusive contact.
- Particles move form a region of high chemical potential to a region of low chemical potential.
- It can be found by differentiating themodynamic potentials with respect to N.



ΔU is released when ΔN energyless particles are added

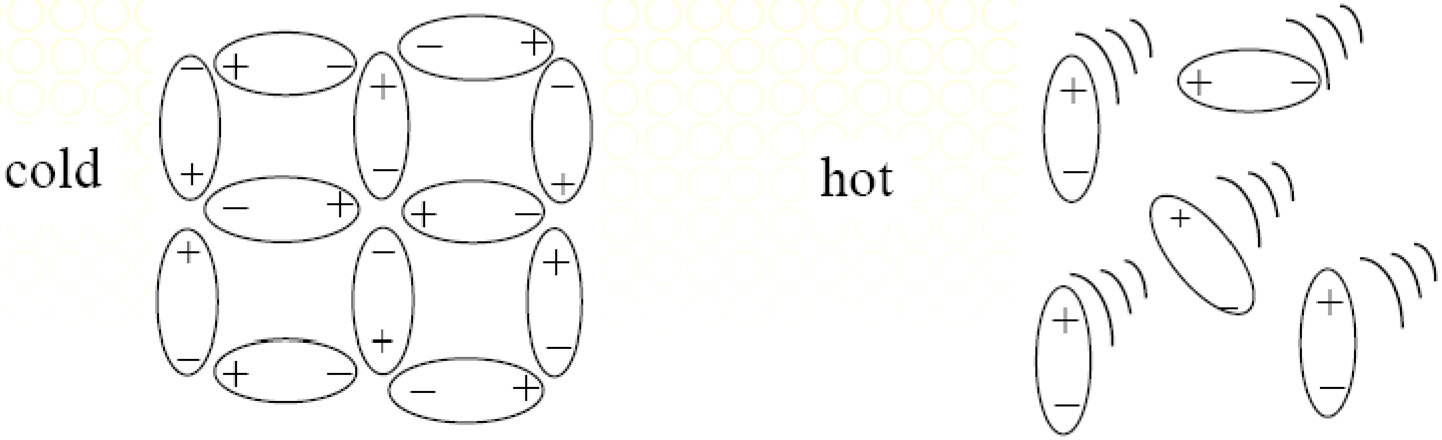
ΔN : a known number of particles are added into the system.

The gain in thermal energy is ΔU.

$$\mu \, \Delta N = - \Delta U$$

note: - ΔU : inside the potential $\mu = -\frac{\Delta U}{\Delta N}$

μ and temperature



μ and pressure

at higher P, particles are closer , increase the strength of interactions :attractive (reduce μ) or repulsive (increase μ)

μ and particles concentration

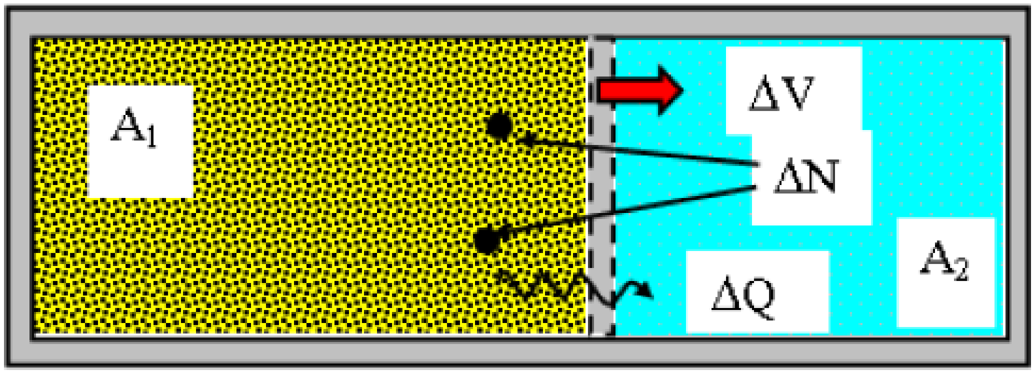
will increase or decrease --- depending on the nature of the interaction.

the chemical potential increases as

- the internal energy, U, of the phase increases,
- the entropy, S, of the phase decreases at a given temperature, T.
- the volume, V increases for a given pressure, P.

components that possess HIGHER U are *de*stabilized relative to those with LOWER U
components with LOWER S are *de*stabilized relative to those with HIGHER S.

Equilibrium Conditions



Let A_1 and A_2 : interacting – thermally,mechanically and diffusively

1st Law $$\Delta U = T\Delta S - P\Delta V + \mu\Delta N$$

or $$\Delta S = \frac{1}{T}\Delta U + \frac{P}{T}\Delta V - \frac{\mu}{T}\Delta N$$

law of conservation

$$\Delta U_2 = -\Delta U_1$$

$$\Delta V_2 = -\Delta V_1$$

$$\Delta N_2 = -\Delta N_1$$

the change in entropy due to redistribution of energy, volume, or number of particles,

$$\Delta S_0 = \Delta S_1 + \Delta S_2$$

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1 \ldots(*)$$

at equilibrium, entropy is maximum

$$\Delta S_0 = 0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta N_1$$

therefore

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \qquad \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0$$

$$\frac{\mu_1}{T} - \frac{\mu_2}{T} = 0$$

and

$T_1 = T_2$ $P_1 = P_2$ $\mu_1 = \mu_2$

For 2 systems interacting thermally, mechanically and diffusively are in equilibrium.

Approach to equilibrium (not yet in equilibrium)

$$\Delta S_0 > 0$$

Let A_1 and A_2 : interacting – thermally,mechanically and diffusively

1st Law: $\Delta U_1 = \Delta Q_1 - P_1 \Delta V_1 + \mu_1 \Delta N_1$

using (*)

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) (\Delta Q_1 - P_1 \Delta V_1 + \mu_1 \Delta N_1) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \Delta N_1$$

$$\Delta S_0 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta Q_1 + \frac{1}{T_2}(P_1 - P_2) \Delta V_1 - \frac{1}{T_2}(\mu_1 - \mu_2) \Delta N_1 \quad \rangle 0$$

therefore $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta Q_1 \rangle\ 0$, $\frac{1}{T_2}(P_1 - P_2)\Delta V_1 \rangle\ 0$

$\frac{1}{T_2}(\mu_1 - \mu_2)\Delta N_1 \quad \rangle\ 0$

from the three equations;

1. if $T_1 > T_2$, $\Delta Q_1 < 0$, and if $T_2 > T_1$, $\Delta Q_1 > 0$
   interacting thermally: heat flow from hotter towards the cooler, NOT vice versa
2. if $P_1 > P_2$, $\Delta V_1 > 0$, and if $P_2 > P_1$, $\Delta V_1 < 0$
   int. Mechanically: volume is gained by the system having higher pressure at the expense of the other, and NOT vice versa.
3. if $\mu_1 > \mu_2$, $\Delta N_1 < 0$, and if $\mu_2 > \mu_1$, $\Delta N_1 > 0$
   int. diffusively: particles flow from the system with higher μ toward the one with lower μ, and NOT vice versa.

μ and Ω

Let A_1 and A_2 : interacting – thermally,mechanically and diffusively

$$dU = TdS - PdV + \mu dN$$

and

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

1st Law

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

if U and V constants

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} \quad \text{or} \quad -\mu = T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

but $S = k \ln \Omega$

$$-\mu = kT\left(\frac{\partial \ln \Omega}{\partial N}\right)_{U,V} \qquad \ldots\ldots\ldots\ldots\ldots(\$)$$

Ω, accessible states – increasing function of number of particles.

μ neg. or dS/dN pos. – attract particles

μ pos. or dS/dN neg. – release particles

let ΔN – energyless particles added to a system at constant volume. From ($)

$$\Delta \ln \Omega = -\frac{\mu}{kT}\Delta N$$

$\Delta \ln \Omega = \ln \Omega_2 - \ln \Omega_1 = \ln \dfrac{\Omega_2}{\Omega_1}$ but $\boxed{\dfrac{\Omega_2}{\Omega_1} = e^{-(\mu \Delta N / kT)}}$

Ideal Gas
a hypothetical gas with molecules of negligible size that exert no intermolecular forces

their energies are entirely kinetic
for 1 molecule, mass m and momentum p

$$\varepsilon = \frac{p^2}{2m} = \frac{1}{2m}p_X^2 + \frac{1}{2m}p_Y^2 + \frac{1}{2m}p_Z^2$$

each molecule : 3 degrees of freedom
for N molecules : 3N degrees of freedom

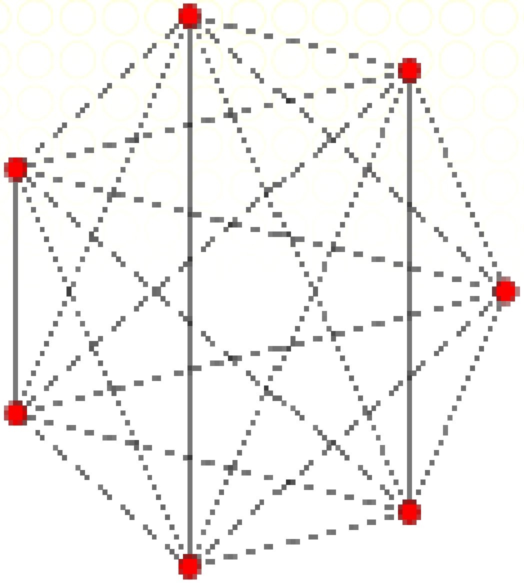
number of quantum states available (6 dim.)

Six-dimensional space

Six-dimensional space is any space that has six dimensions, that is, six degrees of freedom, and that needs six pieces of data, or coordinates, to specify a location in this space. There are an infinite number of these, but those of most interest are simpler ones that model some aspect of the environment. Of particular interest is six-dimensional Euclidean space, in which 6-polytopes and the 5-sphere are constructed.

Uniform polytopes in six dimensions

6-simplex



In geometry, a 6-simplex is a self-dual regular 6-polytope. It has 7 vertices, 21 edges, 35 triangle faces, 35 tetrahedral cells, 21 5-cell 4-faces, and 7 5-simplex 5-faces. Its dihedral angle is $\cos^{-1}(1/6)$, or approximately 80.41°.

$$\Omega_{1\,particles} = \frac{\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z}{h^3}$$

$$= (\mathrm{const})\ \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$$

for N particles

$$\Omega_{N\,particles} = \prod_{i=1}^{N} \Omega_i = \prod_{i=1}^{N} \left(\frac{1}{h^3} \right) dx_i dy_i dz_i dp_{ix} dp_{iy} dp_{iz}$$

limit: volume V

and let U = total energy of the gas

$$\Omega_{N\,particles} = \left(\frac{1}{h^3} \right) V^N \int \prod_{i=1}^{N} dp_{ix} dp_{iy} dp_{iz} \quad ......(*)$$

since $P_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + \ldots + p_{Nz}^2 = 2mU$

-integral in (*) is equivalent to over the surface of a 3N dimension sphere of radius $(2mU)^{1/2}$

-surface area of 3N-dim. Sphere $\propto$ (radius)$^{(3N-1)}$ or

$\propto$ (radius)^{3N}

$$\Omega_{N\ particles} \propto V^N (\sqrt{2mU})^{3N}$$

$$\Omega_{N\ particles} = (const)(2m)^{3N/2} V^N U^{3N/2}$$

$$\Omega_{N\ particles} = (const) V^N U^{3N/2}$$

$$\boxed{S_{ideal\ gas} = k \ln \Omega_{ideal\ gas} = (const) + Nk \ln V + \frac{3}{2} Nk \ln U}$$

using

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

Thermal interaction

Mechanical interaction

V:constant

$$\left(\frac{\partial S}{\partial U}\right)_V = 0 + 0 + \frac{\frac{3}{2}Nk}{U} = \frac{1}{T}$$

$$\boxed{U = \frac{3}{2} NkT}$$

U:constant

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_U = 0 + \frac{Nk}{V} + 0 = \frac{P}{T}}$$

$$\boxed{PV = NkT}$$

...........ideal gas law

.... gas model

Real gas

- degrees of freedom may be larger than 3

$$U = \frac{\upsilon}{2} NkT$$

where υ is degrees of freedom (we will use R for gas constant)

- mutual interactions and sizes cannot be ignored

le v : molar volume

$R = N_A k$: gas constant

$$Pv = RT$$

Compress gas, will become liquid, and cannot compress anymore

b = molar volume of liquid phase – limit on the molar volume

$$v \rightarrow v-b$$

mutual interaction – reduce the velocity of molecules hitting the wall or pressure sensor

real pressure is higher than the measured one

$$P \rightarrow (P + \text{mutual attraction})$$

$$\text{Mutual attraction} \propto 1/(v^2)$$

Incorporated the two effect into the gas law

$$\boxed{\left(P+\frac{a}{v^2}\right)(v-b)=RT}$$

van der Waals equation of state

Liquid

No good model for liquid yet

Can use van der Waals equation with modification

- -liquid phase, the volume $\cong$ b
- -pressure term

$$\left(P+\frac{a}{v^2}\right)\rightarrow\left(P+\frac{a}{v^2}\right)+f(b)$$

where f(b) : due to other interactions (liquid)

since v $\cong$ b : constant for liquid

$$\frac{a}{v^2}+f(b)\approx\frac{a}{b^2}+f(b)\cong const.$$

the modified van der Waals eq,

$$(P + \text{const.})\, b = RT$$

Solids

Models for solids – have more than one components
One property of one component at a time
Ex. The heat capacity of the lattice alone

Solid – a lattice of atomic masses coupled by spring

$$\text{Potential energy, } \varepsilon_P = (1/2)\, kx^2$$

When one atom vibrating – send wave down the lattice
Quantum energy of the wave: called phonon
Phonon travel throughout the solid's volume – → **phonon gas**

Metal – conduction band: electrons in the conduction band are mutually shared by all atoms – known as → **electron gas**

Example of application of the models

1. heat capacity
   let N: constant

$$dQ = dU + PdV$$

υ: degree of freedom

$$U = (1/2)\,\upsilon NkT + N\mu$$

$$dQ = (1/2)\,\upsilon Nk\,dT + N\,d\mu + P\,dV$$

change in N $d\mu$ is small

$$dQ = (1/2)\,\upsilon\,R\,dT + P\,dV$$

per mol: $dq = (1/2)\,\upsilon\,R\,dT + P\,dv \;.... \;(*)$

$R = N_A\,k$ -- gas constant

Molar heat capacity at constant volume

$$c_V = \left(\frac{\partial q}{\partial T}\right)_V = \frac{\upsilon}{2}R$$

since v= v(T,P) --- molar volume

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

from (*), at constant P ------ dP = 0

$$dq = \frac{\upsilon}{2} R dT + P \left(\frac{\partial v}{\partial T} \right)_P dT$$

$$c_P = \left(\frac{\partial q}{\partial T} \right)_P = \frac{\upsilon}{2} R + P \left(\frac{\partial v}{\partial T} \right)_P$$

or

$$c_P = c_V + P \left(\frac{\partial v}{\partial T} \right)_P$$

molar heat capacity at constant pressure

or

$$c_P - c_V = P \left(\frac{\partial v}{\partial T} \right)_P$$

for gases, change in volume at constant pressure is large

For solid & liquid, change in volume at constant pressure is smaller -----c_p & c_v nearly the same.

Example

1. Calculate c_p-c_v for an ideal gas

   Ans: Pv = RT or v = RT/P

$$c_P - c_V = P\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$c_p - c_v = P\left(\frac{\partial v}{\partial T}\right)_P = P\frac{R}{P} = R$$

2. Calculate c_p-c_v for va der Waals gas

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

a and b are constant

Ans:

$$\left(dP-\frac{2a}{v^3}dv\right)(v-b)+\left(P+\frac{a}{v^2}\right)dv=RdT$$

$$Pdv=\frac{RT-(v-b)dP}{\left[1+\frac{a}{Pv^2}\left(\frac{2b}{v}-1\right)\right]}$$

$$c_p - c_v = P\left(\frac{\partial v}{\partial T}\right)_p \frac{R}{\left[1 + \frac{a}{Pv^2}\left(\frac{2b}{v} - 1\right)\right]}$$

note: for P >> a/v^2 and v >> b

$$c_p - c_v = R \quad \text{......ideal gas}$$

for P << a / v^2 and $v \cong b$

$$c_p - c_v = \frac{R}{{}^{a}\!/_{pv^2}} \cong 0$$

.........liquid

3. Find an expression for the isothermal compressibility of an ideal gas

Ans:

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad \text{compressibility}$$

Pv = RT

Pdv = RdT – vdP

$$P\left(\frac{\partial v}{\partial P}\right)_T = -v \qquad \text{or} \qquad \kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{P}$$

4. Find an expression for the isothermal compressibility of a van der Walls gas

Ans:

$$\left(P+\frac{a}{v^{2}}\right)(v-b)=RT$$

$$\frac{1}{v}dv=\frac{RT\ -(v-b)dP}{Pv\left[1+\frac{a}{Pv^{2}}\left(\frac{2b}{v}-1\right)\right]}$$

$$\kappa=-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{T}$$

$$=\left(\frac{1}{P}\right)\frac{1-{}^{b}\!/_{v}}{\left[1+\frac{a}{Pv^{2}}\left(\frac{2b}{v}-1\right)\right]}$$

Exercise:

Suppose the equation of state for some system was

$$P^2 T^{-1/3} e^{aV} = b$$

where a and b are constants

i. write this in differential form, expressing dV in terms of dT and dP

ii. Express the isothermal compressibility of this system in terms of (T, V, P)

iii. Express the coefficient of volume expansion for this system in terms of (T, V, P)

THE END…….

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