Fall 2015 - Mid-term #1 Review - Oct. 19, 2015
Please also download the mindmaps for L1-L9 on the Downloads Page.

59-240 – MT #1 REVIEW

L1 Gases

- properties
- pressure $\boxed{\text{UNITS}}$ $\boxed{\text{TABLE}}$
- temperature
- mechanical + thermal eqb.

L2 Gas Laws

→ Boyle: $p \propto \frac{1}{V}$ OR $pV = \text{const.}$

→ Charles: $V \propto$ const. T ; $p \propto$ const. T

→ Avogadro: $n \propto V$ const. p + T

↳ $pV = nRT$ (J each side)

↳ R values $\boxed{\text{TABLE, UNITS}}$

- Dalton: mixtures

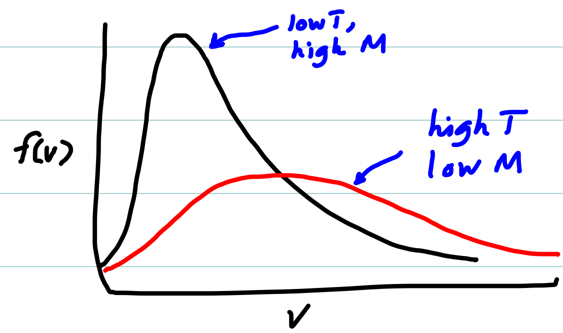
$$p = p_A + p_B + \cdots = (x_A + x_B + \cdots)p$$

$x_A = \frac{n_A}{n}$, etc.

L3 KINETIC GAS MODEL

1. hard spheres
2. elastic collisions
3. no interactions!

(L3) cont'd



$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

problems: ① $\frac{df(v)}{dv} = 0$ (c^*); ② $\langle \underline{\underline{v}} \rangle = \int_0^\infty \underline{\underline{v}}\, f(v)\, dv$; ③ $f(v)\Delta v$

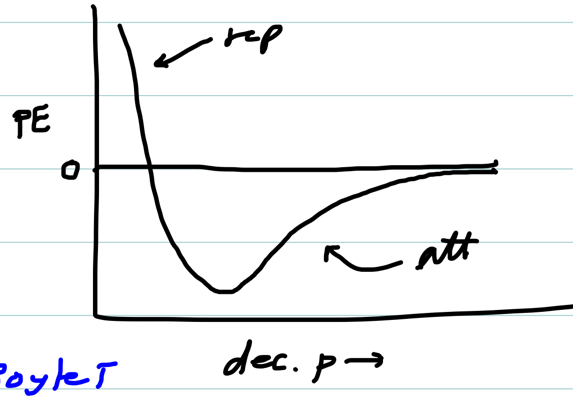
speeds: $c = \left(\frac{3RT}{M}\right)^{1/2}$ (rms) $\qquad \bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}$ (mean)

$c^* = \left(\frac{2RT}{M}\right)^{1/2}$ (most prob.) $\qquad \bar{c}_{rel} = \sqrt{2}\,\bar{c}$

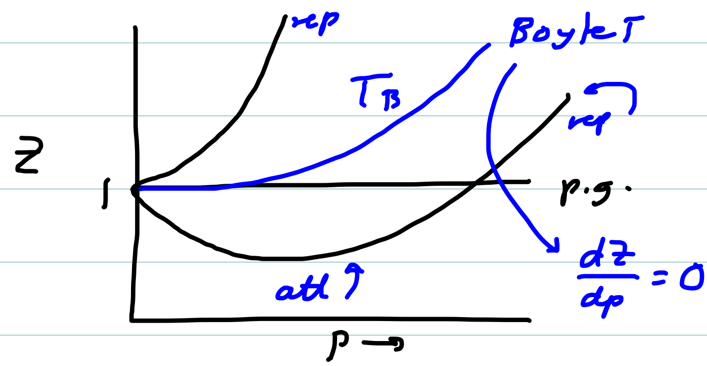
$z = \frac{\sigma \bar{c}_{rel} p}{kT}$, $\sigma = \pi d^2$; $\lambda = \frac{\bar{c}}{z}$ (UNITS!!!)

(L4) Real gases

$$Z = \frac{pV_m}{RT} = 1 \quad (p.g)$$



$Z < 1$, att., $Z > 1$, rep.



VdW: $$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$ att. forces

molec. vol.

- virial eqn's
- condensation of CO_2
- critical constants

(L5) First Law

- intro + energy scams
- system vs. surroundings; adiabatic + diathermic boundaries
- work vs. heat
- internal energy, U, STATE FTN
- $\Delta U = q + w$ OR $dU = đq + đw$

SITUATIONS:

↳ isochoric: $\Delta V = 0$, $w = 0$, $\Delta U = q_V$

↳ isobaric: $\Delta p = 0$, $\Delta U = q + w$, $\Delta H = q_p$

↳ isothermal: $\Delta T = 0$, $\Delta U = 0$ $q = -w$

↳ adiabatic: $q = 0$, $\Delta U = w$

↳ cyclic: $\Delta U = 0$, $U_i = U_f$

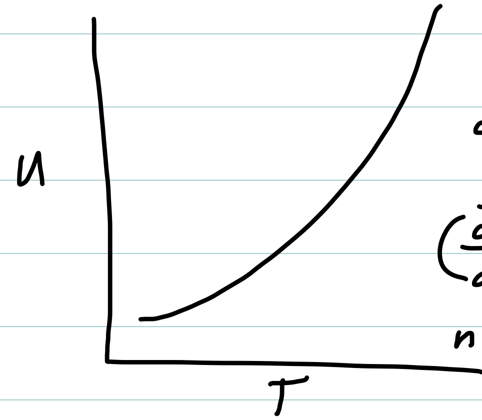
(L6) First Law, cont'd (processes + heat capacity)

$$dU = đq + đw$$

1. $w = -p_{ex}\Delta V$ const. p. exp.
2. $đw = -p\,dV$ reversible exp.
3. $w = -nRT\ln(V_f/V_i)$ isot. rev. exp.

L6 (cont'd)

- calorimetry
- heat capacity



$dU = C_V dT$

OR

$\left(\frac{\partial U}{\partial T}\right)_V = C_V$

$nC_{V,m} = C_V$

for given $q > 0$:

$\rightarrow$ large C_V, small ΔT

$\rightarrow$ small C_V, large ΔT

L7 **ENTHALPY**

$$H = U + pV = U + nRT$$

$\hookrightarrow$ const. p

$$dH = dU + d(pV) = dU + pdV + \cancel{Vdp}^{\,\rightarrow 0}$$

$$= đq + đw + pdV$$

$$= đq - p\cancel{d}V + p\cancel{d}V$$

$$dH = đq$$

$$\therefore\ \Delta H = q_p$$

$dH = C_p dT$ OR $\left(\frac{\partial H}{\partial T}\right)_p = C_p$ $\quad$ $\Delta H = C_p \Delta T$ OR $\Delta H = nC_{p,m}\Delta T$

$\Rightarrow$ temp. dep. of C_p:

$$C_{p,m}(T) = a + bT + \frac{c}{T^2}$$

$$\therefore\ \Delta H \neq C_p \Delta T$$

$\hookrightarrow$ $\Delta H = n\int_{T_i}^{T_f} C_{p,m}\, dT$

(L7) (cont'd)

↳ $C_p - C_V = nR$

↳ adiabatic changes: $q=0$, $\Delta U = w_{ad} = C_V \Delta T$

(4) rev. adiabatic. exp: $\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{1/c}$ $c = \frac{C_{V,m}}{R}$

also: pV^{γ} eqn's!

(L8) <u>Thermochem</u>

$\Delta_{vap}H^\circ$, $\Delta_r H^\circ$, $\Delta_c H^\circ$, $\Delta_f H^\circ$, etc.

COMBUSTION: $H_2O(\underline{l}) + CO_2(g)$ products

- Hess' Law
- enthalpies

QUALITATIVE FIRST LAW:

$\Delta U, \Delta H, q, w$ $>0, =0, <0$? <u>EXPLAIN</u>

⊕, ⊖ or 0

(L9) 1st Law Toolbox

$U(V,T)$ $\quad \boxed{PD} \rightarrow C_V,\ \pi_T = 0$ for p.g.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \boxed{TDE}$$

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} \quad \text{or} \quad \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T \qquad \boxed{ED}$$

why? $\boxed{\text{STATE FTN}}$

↳ same for $H(p,T)$

$\boxed{\text{EULER'S CR:}}$ $\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p = -1$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

$\boxed{IR}$ $\quad \left(\frac{\partial y}{\partial x}\right) = \frac{1}{(\partial x/\partial y)}$

⇛ How does U vary wrt T at const p?

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V \cancel{\left(\frac{\partial T}{\partial T}\right)_p}^{\,1} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$= C_V + \pi_T V \alpha$$

TRIPLETS:

p, V, T: $\quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$; $\quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

U, V, T: $\quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$; $\quad \pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$ for p.g.

H, p, T: $\quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$; $\quad \mu = \left(\frac{\partial T}{\partial p}\right)_H \quad \mu_T = \left(\frac{\partial H}{\partial p}\right)_T$ BOTH $\mu = 0$ for p.g.

MT #1

(1) — MANDATORY
(2)
(3) CHOOSE 3 of 4
(4)
(5)
(B) BONUS – TRY!

- all equal weight
- 1 easy, 2 intermed., 2 "hard"

- no pencil / red pen
- no whiteout
- no cheating
- EQ + CONST ≤ P/R UNITS

→ BRING: calc + backup
pens
student ID

FOCUS: assigned problems
in-class problems/discussions

REVIEW: derivations