THERMODYNAMICS

Reference → Introduction to Chemical
Engineering Thermodynamics,
SMITH and Van Ness

CHAPTER 1 – Introduction

Thermodynamics → "heat power, or
power developed from heat"

→ deals with transformations of
energy of all kinds from one
form to another.

NOT MICROSCOPIC!

Force

$$F = ma \quad (N)$$

$$F = \frac{1}{g_c} ma \quad (lbf) \longrightarrow g_c = 32.1740 \frac{(lbm)(ft)}{(lbf)(s^2)}$$

Temperature

$$T(°C) = \frac{5}{9}(T(°F) - 32)$$

$$T(°F) = \frac{9}{5}T(°C) + 32$$

$$T(R) = T(°F) + 459.67$$

$$T(K) = T(°C) + 273.15$$

Absolute zero → -273.15 K

<u>Kelvin Temperature</u> → based on the
ideal gas as thermometric fluid.

<u>Volume</u> → product of three lengths

Specific or "molar" volume → volume
on a per mole basis.

$$\rho = \frac{1}{}$$

<u>Pressure</u> → the normal force exerted by the fluid per unit area of the surface.

$Pa = N/m^2 = $ unit of pressure

$Psi = lbf/in^2 = $ unit of <u>pressure</u>

<u>Measuring Pressure</u> → Balance a known force on a fluid with a known surface area. $(P = F/A)$

Fluid Pressure
↓

① Dead weight gauge → a piston with weight set up on top, add weight until a balance is achieved, then

$$F = mg \quad \rightarrow \quad \boxed{P = \frac{mg}{A}}$$

② Equivalent height of a fluid column (Manometers) →

$m = Ah\rho$ $\qquad$ $P = \dfrac{F}{A} = \dfrac{mg}{A} = \rho g h \quad \rightarrow \quad \boxed{P = \rho g h}$

Most pressure gauges give readings which are the difference between the pressure of interest and the pressure of the surrounding atmosphere.

→ Gage pressure!

THUS, to get absolute pressure →

$$\boxed{P_{abs} = P_{atm} + P_{gauge}}$$

<u>WORK</u> → work is done whenever a force acts through a distance.

$$dW = Fdl$$

component of the force acting in the direction of the displacement

<u>IMPORTANT</u> → work accompanying the change in a volume of fluid. (Compression or expansion of a fluid in a cylinder like a piston)
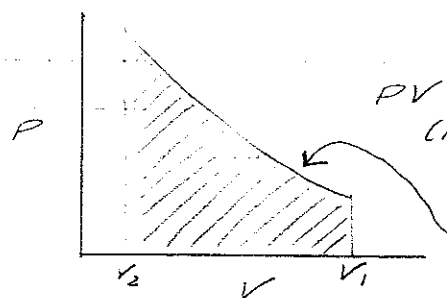
$$dW = PA \, d\left(\frac{V}{A}\right)$$

→ NOTE THAT A is a constant

THUS,

$$dW = PdV$$

Integrating → $W = \int_{V_1}^{V_2} PdV$

P

V_2 V V_1

PV diagram (Need to know this relationship!!)

WORK = the area under the curve

$J = N \cdot m$ = unit of work

ft·lbf = unit of work (ENGLISH)

<u>Energy</u>

DERIVATION OF KINETIC ENERGY

Combining Newton's Law → $F = ma$ and the definition of work → $dW = Fde$

THEN → $dW = ma\,de$

BUT → $a = \dfrac{du}{dt}$ ← velocity

THUS → $dW = m\dfrac{du}{dt}de = m\left(\boxed{\dfrac{de}{dt}}\right)du$

$\hookrightarrow u$

FINALLY → $dW = m\,u\,du$

INTEGRATING → $W = m\displaystyle\int_{u_1}^{u_2} u\,du = m\left(\dfrac{u_2^2}{2} - \dfrac{u_1^2}{2}\right)$

THUS → $W = \Delta\left(\dfrac{mu^2}{2}\right)$

→ work done on a body accelerating it from an initial velocity, u_1, to a final velocity, u_2.

← KINETIC ENERGY!!

$E_k = \dfrac{1}{2}mu^2$

$= \dfrac{mu^2}{2gc}$

↗ in English units

$\underline{W = \Delta E_k}$

$\left\{\begin{array}{l} J = N \cdot m = \text{unit of energy} \\ ft\,lbf = \text{unit of energy (ENGLISH)} \end{array}\right\}$

DERIVATION OF POTENTIAL ENERGY

Force required to raise a body → $F = ma$

$F = mg$

THEN → $W = F\,\Delta l = mg(z_2 - z_1)$

$W = mz_2g - mz_1g$

THUS → $W = \Delta(mgz)$

→ work done on a body raising it from z_1 to z_2

POTENTIAL ENERGY!!

$E_p = mzg$

<u>CONSERVATION</u>
<u>OF ENERGY</u> $\longrightarrow$ $\Delta E_P + \Delta E_K = 0$ $\longleftarrow$ BIG, IMPORTANT EQUATION!
(Mechanical) $\longrightarrow$ $\dfrac{mu_2^2}{2} - \dfrac{mu_1^2}{2} + mz_2g - mz_1g = 0$

SYSTEM $\to$ body or assemblage on which attention is focused

SURROUNDINGS $\to$ all else

Work $\to$ done by surroundings on system, or vice versa.

<u>HEAT</u> $\to$ the "something" that is transferred from a hot object to a cooler object.

Temperature is the driving force for the transfer of energy as heat.

CHAPTER 2 — The first law and other basic concepts

<u>Internal Energy</u> → U is the internal energy of a system. When energy is added to a system in the form of work, and then some of it is released as heat, what is left is the internal energy.

$$dU = dQ - dW$$

⤷ internal, whereas E_R and E_K are external

Q on system $= +$
work on system $= -$

✱✱ <u>FIRST LAW OF THERMODYNAMICS</u> ✱✱

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears in another.

$$\Delta(\text{Energy of system}) + \Delta(\text{Energy of Surr.}) = 0$$

CLOSED SYSTEM → a system which does not permit the transfer of mass between the system and its surroundings.

THEN $\Delta(\text{Energy of Surr.}) = \pm Q \pm W$

CONSTANT m, only
E_P, E_K and U
considered

$\Delta(\text{Energy of system})$
$= \Delta U + \Delta E_P + \Delta E_K$

THEN → $\Delta U + \Delta E_P + \Delta E_K = \pm Q \pm W$ $\begin{Bmatrix} Q(+) \text{ to} \\ \text{system} \\ W(-) \text{ to} \\ \text{system} \end{Bmatrix}$

with sign
convention → $\boxed{\Delta U + \Delta E_P + \Delta E_K = Q - W}$

If $\Delta E_K = \Delta E_P = 0$ (often is for closed)
                                      systems

$\Delta U = Q - W$ for finite changes
$dU = dQ - dW$ for differential changes

The Thermodynamic State and State Functions

State Functions → those which do not de-
pend on the path from one point
to another.

e.g. $\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P$

$\int_{U_1}^{U_2} dU = U_2 - U_1 = \Delta U$

Path Functions → those which depend
on the path taken, not represented
by points on a graph, but rather by
an area.

e.g. $\int dQ = Q$ $\int dW = W$

These are not referred to as changes
but as infinitesimal quantities of
heat and work.

NOTE: Q and W may not be the same
for different paths, but their
difference will be constant (ΔU!)

<u>Extensive Property</u> → internal energy, volume, depends on the quantity of the material involved.

<u>Intensive Property</u> → Temperature, pressure, independent of the quantity of material making up the system.

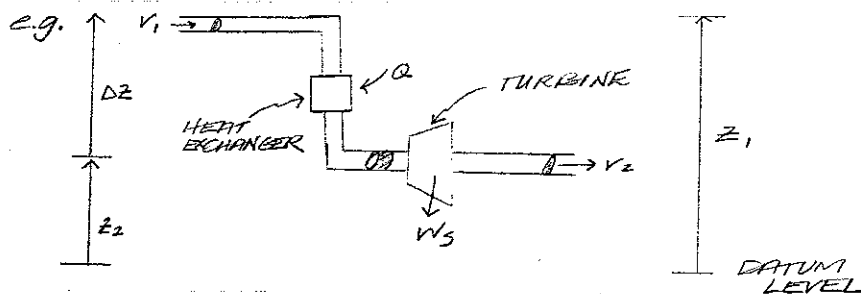<u>ENTHALPY</u> – Just another thermodynamic property.

$$H \equiv U + PV$$

U, P, V are state functions, thus so is H

Differential Form

$$dH = dU + d(PV) = \underline{dU + PdV + VdP = dH}$$

INTEGRATING →
$$\Delta H = \Delta U + \Delta(PV)$$
$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

The Steady State Flow Process

THUS → ΔE_K and ΔE_P must be considered here

FOR A UNIT MASS OF FLUID $m = 1$!!

$$\Delta E_K = \frac{1}{2}U_2^2 - \frac{1}{2}U_1^2 = \frac{1}{2}\Delta U^2$$
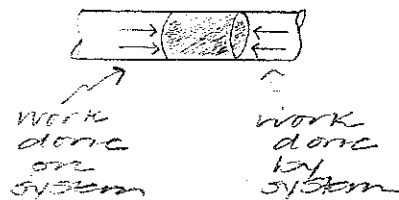
$$\Delta E_P = z_2 g - z_1 g = g\Delta z$$

THEN, substituting into the first law →

$$\Delta U + \frac{\Delta u^2}{2} + g\Delta z = Q - W$$

Types of work →

① Shaft work → work exerted through a
   piece of equipment.

② Work exchanged by fluid → the work ex-
   changed by a
   unit mass of fluid
   taken as the system
   and the fluid on
   either side of it.

work
done
on
system

work
done
by
system

Overall, this work cancels from the
initial to final point, but in an
apparatus, like the turbine, it does
not.

THUS →

① Work done on the system
   (POINT 1)   by surroundings →

$$dW = Fd\ell \quad \rightarrow \quad W = F\Delta\ell$$

$$V_1 = A_1 \Delta\ell \quad \rightarrow \quad \Delta\ell = \frac{V_1}{A_1}$$

$$F = P_1 A_1$$

$$\therefore W_1 = P_1 A_1 \frac{V_1}{A_1} = P_1 V_1 \quad \boxed{W_1 = P_1 V_1}$$

② Work done by system on
   the surroundings →
   (POINT 2)

$$V_2 = A_2 \Delta\ell \quad \rightarrow \quad \Delta\ell = \frac{V_2}{A_2} \qquad F = P_2 A_2$$

$$\therefore \boxed{W_2 = P_2 V_2}$$

$\underline{TOTAL\ WORK} \rightarrow W = W_s + P_2 V_2 - P_1 V_1$

(Done on Surr.) ... (Done on Sys.)

THEN, with First Law →

$$\Delta U + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s - P_2 V_2 + P_1 V_1$$

($\Delta(PV)$)

$$\Delta U + \Delta(PV) + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s$$

BUT → $\Delta H = \Delta U + \Delta(PV)$

$\therefore$ $\boxed{\Delta H + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s}$ { THE FIRST LAW FOR A STEADY STATE FLOW PROCESS!

IMPORTANT DERIVATION!

If ΔE_K and ΔE_P are small → $\boxed{\Delta H = Q - W_s}$

Determination of Enthalpy → this is done by using a flow calorimeter. Keeping Δu and $\Delta z = 0$, $W_s = 0$, and then adding Q →

$$\Delta H = H_2 - H_1 = Q$$

assign a basis of 0

$\therefore$ $H_2 = Q$

at some r and P

$\underline{EQUILIBRIUM} \rightarrow$ word denoting a static condition, the absence of change. The absence of any tendency toward change on a macroscopic level.

Absence of a driving force!

$\underline{The\ Phase\ Rule} \rightarrow$ Gibbs phase rule says the degrees of freedom in a system (the number of variables arbitrarily chosen)

$\boxed{F = 2 - \pi + N}$ $\pi = $ # of phases
$N = $ # of components

<u>The Reversible Process</u> → a process is said to be reversible when its direction can be reversed at any point by an infinite-simal change in external conditions.

No process is completely reversible! Energy is dissipated to molecules, it can't be retrieved.

$$W = \int_{V_1}^{V_2} P dV$$ ⟶ ⎰ This assumes a reversible process, the only way to do it, can't make calculations for a irreversible process ⎱

For a reversible process → $$W = \int_{V_1}^{V_2} P dV$$

For an irreversible process → $W = P\Delta V$

<u>Notation; constant-volume and constant-pressure processes</u>

on a molar U basis →

$d(nu) = dQ - dW$
   ↑ molar u!

reversible →
$dW = Pd(nV)$

$d(nU) = dQ - Pd(nV)$

$V = \text{CONSTANT} \quad dQ = d(nu)$

$$\boxed{dQ = n\Delta u}$$ <u>CONSTANT VOLUME</u>, <u>REVERSIBLE</u>, <u>NON-FLOW</u>

on a molar H basis →

$d(nH) = d(nu) + Pd(nV)$

$d(nu) = d(nH) - Pd(nV)$

COMBINING with previous
Equation for $d(nU) \rightarrow$ $dQ - Pd(nV) = d(nH)$
$$- Pd(nV$$

$$dQ = d(nH)$$

$$\boxed{Q = n\Delta H}$$

Heat Capacity

$$C = \frac{dQ}{dT} \rightsquigarrow \text{can define two types}$$

THUS $\rightarrow$

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \qquad \underline{V = CT} \qquad \Delta U = \int_{T_1}^{T_2} C_V \, dT$$

THUS $\rightarrow$

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P} \qquad \underline{P = CT} \qquad \Delta H = \int_{T_1}^{T_2} C_P \, dT$$

ALSO, For a reversible, constant pressure
process $\rightarrow$

$$Q = n\Delta H = n \int_{T_1}^{T_2} C_P \, dT$$

ONLY FOR <u>MECHANICALLY REVERSIBLE</u>, $\underline{P = CT}$ PROCESSES $\rightarrow$

$$Q = n\Delta H$$
$$Q = n \int_{T_1}^{T_2} C_P \, dT$$

$$W = Pn\Delta V$$

Equations of State

In a single phase region →

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

(molar)

e.g. ideal gas
$PV = RT$
holds for
low P only!

Can solve E.O.S. for P, V or T as a function of the other two variables →

① $V = f(T, P) \rightarrow dV = \left(\dfrac{\partial V}{\partial T}\right)_P dT + \left(\dfrac{\partial V}{\partial P}\right)_T dP$

② $P = f(V, T) \rightarrow dP = \left(\dfrac{\partial P}{\partial T}\right)_V dT + \left(\dfrac{\partial P}{\partial V}\right)_T dV$

③ $T = f(P, V) \rightarrow dT = \left(\dfrac{\partial T}{\partial P}\right)_V dP + \left(\dfrac{\partial T}{\partial V}\right)_P dV$

FROM ① →

volume expansivity $\quad \beta = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$

isothermal compressibility $\quad K = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$

THUS → $\dfrac{dV}{V} = \beta\, dT - K\, dP$ → Assuming β and K weak functions of T and P

$\ln V_2/V_1 = \beta(T_2 - T_1) - K(P_2 - P_1)$

__INCOMPRESSIBLE FLUID__ → occurs in the steep part of the liquid region, β and K are essentially zero!

GAS REGION ONLY!

__THE VIRIAL EQUATION__ → the equation is derived by assuming that PV is essentially as constant in this region.

POWER SERIES EXPANSION → $PV = a + bP + cP^2 + \dots$
in P

NOTE: $\lim\limits_{P \to 0} PV = $ the same value for all gases $= a$

THIS IS HOW THE ABSOLUTE T SCALE IS CREATED (Kelvin)
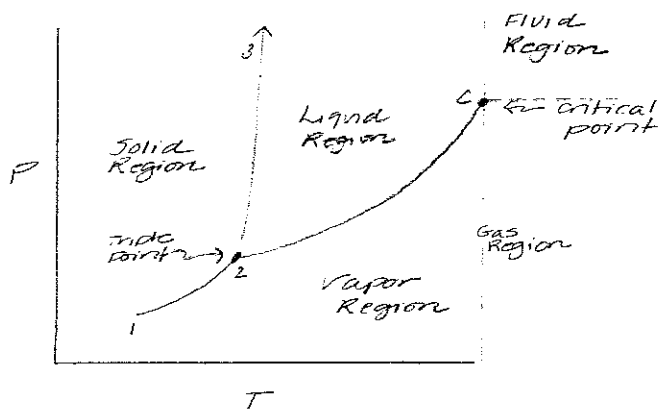
$\rightarrow (PV)^* = RT = a$

CHAPTER 3 — Volumetric Properties of Pure Fluids

PVT Behavior of Pure Substances

Use volumetric data to determine things
like internal energy (U) and entralpy (H).

Homogeneous fluids → ① liquids ⎫ but become indistinguishable at the critical point
② gases ⎭

PT Diagram (Pure Substance)
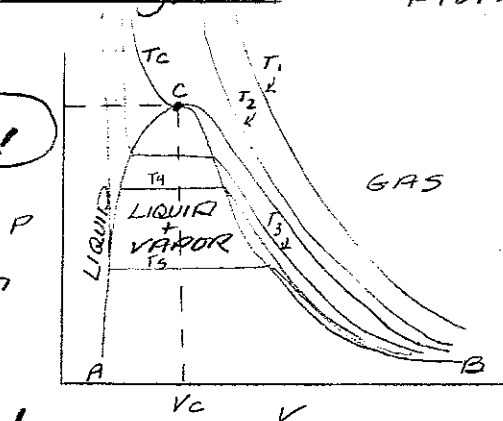

1 - 2 → Sublimation Curve

2 - 3 → Fusion curve

2 - C → Vaporization Curve

T_t = triple point = where all three phases
are in equilibrium.

At C → P_c, T_c

PV Diagram (Pure Fluid)

Decrease T, P_{sat} decreases!

In terms in the liquid region are steep because V does not Δ much with big Δ in P when liquid!

T_1, T_2 → T's greater than T_c, do not cross phase boundary

T_3, T_4, T_5 → horizontal portion is vaporization, where vapor pressure occurs

A - C → saturated liquid
C - B → saturated vapor

$$\left\{ \frac{\partial P}{\partial V} = 0 \quad \frac{\partial^2 P}{\partial V^2} = 0 \right\} \rightsquigarrow At\ P_c, T_c, V_c !$$

Replacing a with RT →

✱ ✱
$$\boxed{Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots}$$ ✱ ✱   VIRIAL
✱ ✱   ✱ ✱   E.O.S.

↳ COMPRESSIBILITY $B' = \frac{B}{RT}$, $C' = \frac{C - B^2}{(RT)^2}$, etc...
       FACTOR

OR ALSO → $Z = 1 + B/V + C/V^2 + D/V^3 + \dots = \frac{PV}{RT}$

<u>IDEAL GAS</u> → $Z = 1$! $\left(PV = RT\right)$ $\left\{\begin{array}{l}\text{ASSUMES THE}\\ \text{ABSENCE OF MOLECULAR}\\ \text{INTERACTIONS}\end{array}\right\}$

                                             LOW PRESSURE!

<u>FOR AN IDEAL GAS</u>, its macroscopic behavior is characterized by →

     ① $Z = 1$ or E.O.S. $PV = RT$
     ② $U = \mathcal{F}(T)$ only!   NOT $\mathcal{F}(T, P)$
       Hence $C_V = \mathcal{F}(T)$ only!

<u>Constant Volume Process</u>

          $\nwarrow$ molar basis

$dU = dQ = C_V\, dT$ $\Delta U = \int C_V\, dT$ $\frac{\text{IDEAL GAS}}{V = CT}$

NOTE: ΔU is the same regardless of V change, but Q is not!

<u>Constant Pressure Process</u>

$dH = dQ = C_p\, dT$ $\Delta H = \int C_p\, dT$ $\frac{\text{IDEAL GAS}}{P = CT}$

     Because $U = \mathcal{F}(T)$ $\left.\right\}$ For
       → $H = \mathcal{F}(T)$ an
         $C_p = \mathcal{F}(T)$ ideal gas only!

     FOR AN IDEAL GAS → $\left(\begin{array}{l} H = U + RT \\ H = U + PV \end{array}\right)$

     FROM → $dH = dU + R\, dT$
             $C_p\, dT = C_V\, dT + R\, dT$ ⟶ $\left\{ C_p = C_V + R \right.$

                                              ONLY FOR AN IDEAL GAS!

Constant Temperature Process

$$dU = dQ - dW = 0 \qquad \boxed{dU = 0}$$

$$\text{HENCE} \rightarrow \boxed{Q = W}$$

THEN, Knowing $\quad P = RT/V \qquad Q = W = \int P\,dV = \int RT \frac{dV}{V}$

$$\therefore \quad ① \quad Q = W = RT \ln \frac{V_2}{V_1}$$

$$\boxed{Q = W = \int RT \frac{dV}{V}}$$

SINCE
$T = CT$
$P_1 V_1 = P_2 V_2 \qquad \therefore ② \quad Q = W = RT \ln \frac{P_1}{P_2}$

$\left\{\begin{array}{l}\text{INTEGRATE AND} \\ \text{FIND } Q, W\end{array}\right\}$

The Adiabatic Process

$$dQ = 0 \qquad \therefore \qquad dU = -dW = -P\,dV$$

$$C_v\,dT = -P\,dV \rightarrow C_v\,dT = -\frac{RT}{V}\,dV$$

$\gamma = \dfrac{C_p}{C_v}$

$C_p = C_v + R$

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

$\left\{\begin{array}{l}\text{INTEGRATE, FIND} \\ \text{RELATION BETWEEN} \\ V \text{ and } T\end{array}\right\}$ $\left(\begin{array}{l}C_p = CT \\ IG \\ REV. \\ Q = 0\end{array}\right)$

$\gamma = 1.67 \quad$ monatomic gases

$\gamma = 1.4 \quad$ diatomic gases

$\gamma = 1.3 \quad$ simple polyatomic

Use $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 T_2}{V_2} \rightsquigarrow \left\{\begin{array}{l}\text{FIND RELATION} \\ \text{BETWEEN } P \text{ and } T\end{array}\right\}$

FINALLY $\rightarrow$ can find $\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = PV^{\gamma}} = \text{constant}$

$\underline{\text{WORK}} \rightarrow -dW = dU = C_v\,dT \rightarrow \boxed{W = -\Delta U = -C_v \Delta T}$

The Polytropic Process $\rightarrow$ NO specific conditions
other than mechanical reversibility are im-
posed. (NON-FLOW)

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

$$dW = P\,dV \qquad W = \int P\,dV$$

$$dU = C_v\,dT \qquad \Delta U = \int C_v\,dT$$

$$dH = C_p\,dT \qquad \Delta H = \int C_p\,dT$$

NOTE ALSO → $dQ = C_v dT + P dV$
TO FIND Q

$$Q = \int C_v dT + \int P dV$$

The work of an irreversible process → MUST cal-
culate for a reversible process, then use
an efficiency.

$$W_{ACT} = W \eta \longrightarrow \text{producing work}$$

$$W_{ACT} = \frac{W}{\eta} \longrightarrow \text{consuming work}$$

APPLICATION OF THE VIRIAL EQUATION → can truncated
to 2nd and 3rd coefficients for low to mod-
erate pressures.

FOR LOW P → truncate after 2nd term →

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} \qquad \left(\begin{array}{c}\text{volume}\\\text{Explicit}\end{array}\right)$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} \qquad \left(\begin{array}{c}\text{Pressure}\\\text{Explicit}\end{array}\right)$$

OR, for P up to 50 bar →
$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \qquad \left(\begin{array}{c}\text{Pressure}\\\text{Explicit}\end{array}\right)$$

CUBIC EQUATIONS OF STATE → need more general
equations than the virial. Ones that will define
also liquid or gases for a higher range
of pressures.

TRY → van der Waals
$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

NOTE: gives okay relation, but
messes up 2 phase region
on a P-T diagram

 → WRONG!
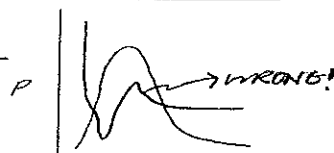
Redlich-Kwong

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

IMPORTANT INFORMATION → $\left(\frac{\partial P_c}{\partial V_c}\right)_T = \left(\frac{\partial^2 P_c}{\partial V_c}\right)_T = 0$

Use to find values of a, b in either of the above equations

GENERALIZED CORRELATIONS FOR GASES

$$T_r = T/T_c$$
$$P_r = P/P_c$$

First 2 corresponding states parameters

GASES!

THEOREM OF CORRESPONDING STATES → all gases, when compared at the same reduced T and reduced P, have approximately the same Z, and all deviate from I.G. behavior to about the same degree

W → accentric factor → 3rd corresponding states parameter, accounts for molecular structure.

BY GRAPICAL ANALYSIS → $$W \equiv -1.0 - \log (P_r^{sat})_{T_r = 0.70}$$

Pitzer Correlation → $Z = \frac{PV}{RT} = Z^0 + W Z'$ (CHARTS)

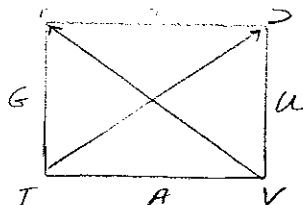ANOTHER → $\frac{BP_c}{RT_c} = B^0 + W B'$ (CHARTS)

THEN → $Z = 1 + \frac{BP}{RT}$

$= 1 + B^0 \frac{P_r}{T_r} + W B' \frac{P_r}{T_r}$

GENERALIZED CORRELATIONS FOR LIQUIDS

cubic E.O.S. are not that great for liquids

→ Rackett Correlation

LIQUIDS!

```
      G |‾‾‾‾‾‾| U
        |  ╲ ╱ |
        |  ╱ ╲ |
      T |_____| V
            A
```

CHAPTER 4 — Heat Effects → heat transfer, etc...

Sensible heat effects → characterized by temperature changes

heat effects of chemical reaction, phase transition, and the formation and separation of solutions - determined from experimental measurements made at constant temperature.

SENSIBLE HEAT EFFECTS → heat transfer to a system where there is no ① phase transition, ② no chemical reactions, ③ no changes in composition → causes a change in temperature.

Can define $H = \mathcal{F}(T, P)$ or $H = \mathcal{F}(V, P)$
                                               $H = \mathcal{F}(T, V)$

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

$$dH = C_p\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Becomes zero →
① $H \neq \mathcal{F}(P)$ (TRUE FOR IG)
② $P = CT$

HENCE → $dH = C_p\, dT$ → $\Delta H = \int_{T_1}^{T_2} C_p\, dT$

ALSO → $Q = \Delta H$ { REVERSIBLE, P = CT, NON-FLOW }

Can define $U = \mathcal{F}(T, V)$

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

$$dU = C_v\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Becomes zero →
① $U \neq \mathcal{F}(V)$ (TRUE FOR IG)
② $V = CT$

HENCE → $dU = C_v\, dT$ $\Delta U = \int_{T_1}^{T_2} C_v\, dT$

IMPORTANT CONCEPT → Need to know T dependence
of heat capacity!

(IDEAL GAS HEAT CAPACITIES)

$$\frac{C_p^{ig}}{R} = \alpha + \beta T + \gamma T^2$$

or

$$\frac{C_p^{ig}}{R} = a + bT + cT^{-2}$$

COMBINING →

$$\frac{C_p^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

one will be zero!

{ C usually zero for inorganics
D usually zero for organics }

THEN → $\dfrac{C_v^{ig}}{R} = \dfrac{C_p^{ig}}{R} - 1$

MEAN HEAT CAPACITY

$$C_{p_{mn}} = \frac{\int_{T_1}^{T_2} C_p \, dT}{T_2 - T_1}$$

→ Use in general, not just for ideal gas!

$$\frac{C_p}{R} = A + BT + CT^2 + DT^{-2}$$

Define $T_{am} = (T_1 + T_2)/2$

THEN → $\Delta H = C_{p_{mn}}(T_2 - T_1)$ { P = CT
H ≠ ℱ(P) }

can also solve for a T, but will be iterative

GAS MIXTURE HEAT CAPACITIES

$$C_{p_{mix}}^{ig} = y_A C_{pA}^{ig} + y_B C_{pB}^{ig} + y_C C_{pC}^{ig}$$

ideal gas heat capacities!

① HEAT EFFECTS ACCOMPANYING PHASE CHANGES OF PURE SUBSTANCES

TWO TYPES → ① Latent heat of Fusion (S → L)
② Latent heat of Vaporization (L → V)

NOTE: No change in T, but a transfer of heat.

Clapeyron Equation $\Delta H = T \, \Delta V \left(\dfrac{dP^{sat}}{dT} \right)$

{ ALLOWS CALCULATION OF HEAT GENERATED DURING PHASE TRANSITION }

what we want to know   SLOPE OF Psat vs. T

Determination of ΔH^{vap}

① at normal boiling point temperature
use correlation by Riedel
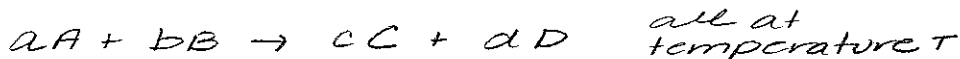
② at any temperature
use correlation by Watson

② THE STANDARD HEAT OF REACTION

Using a calorimeter to determine ΔH_{rxn} →

$$\Delta H + \cancel{\frac{\Delta u^2}{2}}^{0} + \cancel{g\Delta z}^{0} = Q - \cancel{W_s}^{0} \quad\to\quad \Delta H = Q$$

↗ heat
of reaction

"Standard" heat of reaction →

$$aA + bB \to cC + dD \qquad \text{all at temperature } T$$

standard
properties
are only a function
of Temperature

① Gases → Standard state is the pure substance
in the i.g. state at 1 bar.
② Liquids or Solids → Standard state is the actual
pure liquid or solid at 1 bar.

THE STANDARD HEAT OF FORMATION → heat of reactions
are calculated from heats of formation.
Heats of formation are determined from
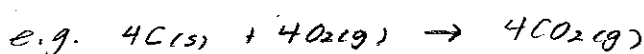experiments which involve forming the desired
species from its elements.

e.g. $C_{(s)} + O_{2(g)} \to CO_{2(g)}$
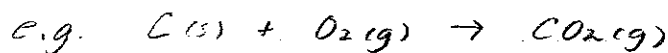
THEN $\boxed{\Delta H_{rxn}^{\circ} = \sum \gamma_i \Delta H_{f_i}^{\circ}}$

γ_i = positive
for products
γ_i = negative
for reactants

$\Delta H_{rxn}^{\circ} = \sum \gamma_i H_i^{\circ}$ ← species i

THE STANDARD HEAT OF COMBUSTION → just the heat
of reaction of a combustion reaction.

e.g. $4C_{(s)} + 4O_{2(g)} \to 4CO_{2(g)}$

reactant $\to CO_2 + H_2O$
$+ O_2$

Standard state enthalpies are only a function of temperature, therefore →

$$dH_i^\circ = C_{pi}^\circ \, dT$$

HENCE, with some manipulation → $\Delta C_p^\circ = \Sigma \gamma_i C_{pi}^\circ$
$$\Delta H^\circ = \Sigma \gamma_i H_i^\circ$$

$$d\Delta H^\circ = \Delta C_p^\circ \, dT$$

Integrating from 298.15 to T →

$\begin{pmatrix} \text{ENTHALPY} \\ \text{OF REACTION} \\ \text{AT ANY T} \end{pmatrix}$ ✻ $\boxed{\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta C_{pmn}^\circ \, (T - 298.15)}$ ✻

CHAPTER 5 — The Second Law of Thermodynamics

The efficiency of something when heat, Q, is used as an energy source is never greater than 40%. This implies that <u>heat is a form of energy intrinsically less useful and hence less valuable than an equal quantity of work or mechanical or electrical energy.</u>

STATEMENTS OF THE SECOND LAW → Places a restriction on the amount of W produced from a given Q

Just 2 of them

✱✱

① No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat adsorbed by a system completely into work.

② No process is possible which consists solely in the transfer of heat from one T level to a higher one.

──→ ⓐ It is impossible by a cyclic process to convert the heat absorbed by a system completely into work.

THE HEAT ENGINE → e.g. a steam power plant

HOW DOES A POWER PLANT WORK?
→① Liquid H_2O at ambient T is pumped to a boiler
② Heat from a fuel is transferred in the boiler to the water, converting it to superheated steam.
③ Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine.
④ Exhaust steam from the turbine is condensed by the transfer of heat to cooling water, thus a complete cycle.

<u>heat reservoirs</u> → bodies imagined capable of absorbing or rejecting an infinite quantity of heat.

for a heat engine, the first law reduces to →

$$W = Q = |Q_H| - |Q_C|$$

heat from "hot" reservoir
heat to "cold" reservoir

<u>Thermal Efficiency</u>

$$\eta = \frac{\text{net work output}}{\text{heat input}}$$

-OR- $$\eta = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

EFFICIENCY!

$$\eta = 1 - \frac{|Q_C|}{|Q_H|}$$

($Q_C = 0$ for $\eta = 1$! Does not happen)

<u>CARNOT ENGINE</u> → a heat engine which operates in a completely reversible matter.

Any "reversible" engine working between two heat reservoirs is a CARNOT engine

① A system at equilibrium with a thermal reservoir at T_C undergoes reversible adiabatic process that causes its temperature to rise to T_H.

② The system maintains contact with the hot reservoir at T_H, and undergoes a reversible isothermal process during which heat $|Q_H|$ is absorbed from the hot reservoir.

③ The system undergoes a reversible adiabatic process to bring T back to T_C.

④ Rejection of heat $|Q_C|$ to cold reservoir, at temperature T_C.

Q_H → T_H [ ] Q_C → T_C

↓ W
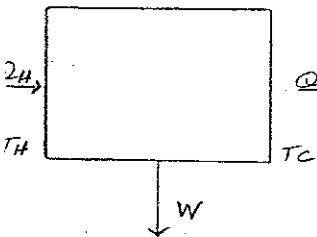
No engine can have a higher thermal efficiency than a CARNOT engine.

CARNOT CYCLE FOR AN IDEAL GAS