

<< Units & Dimensions

- > dimension - property that can be measured
- > units - specific values of dimension
 - two quantities can $+/-$ only if units are same
 - two quantities can always mult/divide.
- > base units
- > multiple units - multiple of base units
- > derived units
 - { compound units
 - equivalent of compound units

→ Unit Systems

- SI unit
- CGS system
- US customary system (American Engineering, AE)

<< Force & Weight

- $1\text{N} = 1\text{kg m/s}^2$
- $1\text{lb}_f = 32.174 \text{ lb}_m \text{ ft/s}^2$ (force on 1 lbm mass by grav. acceleration at sea level, 45° latitude)
- > weight - force exerted on the object by gravitational acceleration

$$W = mg$$

<< Dimensional Homogeneity

- > dimensional homogeneity - all additive terms on both sides of equation must have same dimension
 - derived equations must be dim homogeneous
 - dim homogeneous eq. may be invalid
- > dimensionless quantity - pure number, multiplicative combination of variables with no net dim
- > dimensionless group - \leftarrow
 - exponents, transcendental functions, and their arguments must be dimensionless quantity

<< Significant Figures

- > scientific notation - number expressed as another number between 1 and 10 and power of 10.

- > significant figures - digits from the first nonzero digit on the left to

- a) last digit on the right if there is a decimal
- b) last nonzero digit if no decimal point

/ integer or
counts have
∞ sig fig /

- scientific notation is useful to show sig. figs.

- > Multiplication/Division - result has same sig fig as the number with lowest sig. fig.

- > Addition/Subtraction - compare the positions of last sig fig of each # rel to decimal point.

the one farthest to the left is the position of the last permissible sig fig of result

<< Validating Results

- back substitution
- order-of-magnitude estimation
- test of reasonableness

<< Basic Statistics

> sample mean - $\bar{X} = \frac{1}{N} \sum_{j=1}^N X_j$

• estimates measured value

> range - $R = X_{\max} - X_{\min}$

> sample variance - $s_x^2 = \frac{1}{N-1} \sum_{j=1}^N (X_j - \bar{X})^2$

> standard deviation - $s_x = \sqrt{s_x^2}$

<< Data Analysis

> interpolation - use data to estimate values between data points

> extrapolation - use data to estimate values outside the range of data points

→ Two point Linear Interpolation

• Given two points $(x_1, y_1), (x_2, y_2)$

• slope $m = \frac{y_2 - y_1}{x_2 - x_1}$

• Interpolation: $y - y_1 = m(x - x_1) \Rightarrow y = m(x - x_1) + y_1$

→ Straight Line Fit

• use visual inspection to get linear graph (least-square fit using computer)

→ Linearization

• rearrange equation into linear form of $y = mx + b$, where x, y are expressions

• logarithm can help solve some issue

→ Logarithmic Coordinate

<< Mass & Volume

- > density - mass per unit volume
- > specific volume - volume occupied by unit mass] inverses
- > specific gravity - ratio of density of substance to density of reference substance
- $SG = \rho_{sub} / \rho_{ref}$
- l of solid & liquid typically not affected by T, P
- still effects, like Hg : $V(T) = V_0 (1 + 0.18182 \times 10^{-3}T + 0.0078 \times 10^{-6}T^2)$
T in °C at 0°C

<< Flow Rate

→ Mass & Volumetric Flow Rate

- > flow rate - rate at which material is transported through a process line
- > mass flow rate - mass/time
- > volumetric flow rate - volume/time

$$\dot{V} = \frac{m}{\rho} = \frac{\dot{m}}{\rho}$$

→ Flow rate measurement

- > flowmeter - device mounted in process line that gives continuous reading of \dot{V}
- rotameter
- orifice meter

<< Chemical Composition

→ Moles & Molecular Weight

- > atomic weight - mass of an atom on a scale that assigns ^{12}C a mass of 12.
- > molecular weight - sum of atomic weights of atoms that constitute a molecule
- > gram-mole (g-mol, mol) - amount of that species whose mass in grams is numerically equal to its molecular weight
 - kmol, lb-mol similarly defined
 - for MW = M, we have M kg/kmol, M g/g-mol, M lbm/lb-mol
 - same conversion factors as mass for moles
 - 1 mol contains $N_A = 6.02 \times 10^{23}$ molecules
 - molecular weight relates mass flow rate to molar flow rate
 - > Dalton - 1/12 mass of ^{12}C atom

<< Chemical Composition

> mass fraction - $x_A = \frac{\text{mass of } A}{\text{total mass}} = \frac{m_A}{m_t}$

> mole fraction - $y_A = \frac{\text{moles of } A}{\text{total moles}} = \frac{n_A}{n_t}$

> percent by mass = $x_A \times 100\%$

> percent by mole = $y_A \times 100\%$

• numerical value of x_A , y_A does not depend on units as long as they're consistent

$$\frac{10 \text{ g } A}{10 \text{ g total}} = \frac{10 \text{ lbm } A}{10 \text{ lbm total}}$$

• To convert a set of $x_A \leftrightarrow y_A$, set a basis of calculation.

> average molecular weight - ratio of the mass of a sample of mixture to the number of moles of all species in the sample

$$\bar{M} = \frac{m_t}{n_t} = \frac{\sum M_i}{\sum n_i} = \sum y_i M_i = \left(\sum \frac{x_i}{M_i} \right)^{-1} \quad // \quad \begin{aligned} m_t &\equiv \sum M_i \\ n_t &\equiv \sum n_i \end{aligned}$$

Proof:

$$\bar{M} = \frac{\sum M_i}{\sum n_i} = \frac{\sum M_i}{n_t} = \sum \frac{M_i}{n_t} = \sum \frac{n_i M_i}{n_t} = \sum y_i M_i$$

$$\bar{M} = \frac{\sum M_i}{\sum n_i} = \frac{m_t}{\sum n_i} = \left(\frac{\sum n_i}{m_t} \right)^{-1} = \left(\sum \frac{n_i}{m_t} \right)^{-1} = \left(\sum \frac{n_i M_i}{m_t M_i} \right)^{-1} = \left(\sum \frac{x_i}{M_i} \right)^{-1}$$

Note: total quantity need to be placed at bottom so that units can operate. if we have mol C, mol O, then there's the need to find common denominator of (mol C mol O)

Note: Here, M_i can be added at bottom because M_i is also added to the top, so the units cancels, without previous concerns.

→ concentration

> mass concentration - mass of a component per unit volume of mixture

> molar concentration - moles of a component per unit volume of mixture

> molarity - molar conc. in mol solute / L soln (mol/L)

→ ppm & ppb

• ppm = $\times 10^6$ ppm

• ppb = $\times 10^9$ ppb

<< Pressure

→ Fluid Pressure & Hydrostatic Head

> pressure - ratio of force to area on which the force acts

$$P = \frac{F}{A}$$

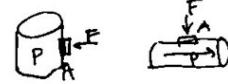
> fluid pressure - ratio of minimum force needed on a

$$P [=] Pa = N/m^2$$

> frictionless plug in a hole to keep the fluid from emerging to the area

> hydrostatic pressure - the pressure of the fluid at the base

$$P = P_0 + \rho gh$$

> hydrostatic head - height of hypothetical column of the fluid that would exert the given pressure at its base if pressure at the top $P_0 = 0$.

$$P = P_{\text{fluid}} g P_h$$

$$P_h = P_0 + h \quad (\text{mmHg})$$

→ Atmospheric, Absolute, Gauge Pressure

• Atmospheric pressure at sea level is defined as 1 atm = 760.0 mmHg

> Absolute pressure - pressure of zero corresponds to vacuum

> gauge pressure - pressure relative to atmospheric pressure

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

• -1 cm Hg gauge pressure = 1 cm Hg of vacuum

→ Fluid Pressure Measurement

• methods { elastic-element method - Bourdon tubes, bellows, diaphragms

liquid-column method - manometers

electric method - strain gauge, piezoresistive transducer, piezoelectric transducer

> Bourdon gauge - hollow tube closed at one end bent into C config. (give gauge pressure)

• P ↑, tube straightens, pointer rotates } 0 - 7000 atm

> Manometer - U-shaped tube partially filled with fluid with known density

> manometer fluid

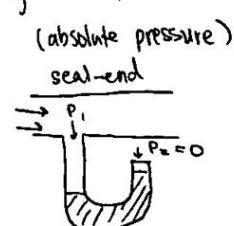
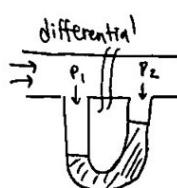
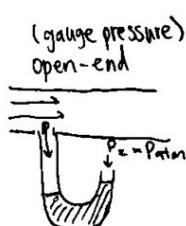
> open-end manometer - one end to measure, one to atmosphere

> differential manometer - two ends at diff point of fluid, measure pressure diff

> seal-end manometer - near-vacuum at one end

> barometer - seal-end manometer measuring atmosphere

0 - 3 atm



⇒ Pressure

→ Pressure Measurement Equations

• fluid pressure the same at two points at same height in continuous fluid

• pressure at the same height of lower surface of manometer fluid is the same in both arms

• General manometer equation

$$P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_m g h$$

• ρ_m is manometer fluid density

• Differential manometer equation

$$\cdot P_1 = P_2 = \rho$$

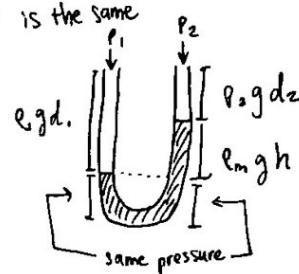
$$\cdot d_1 = d_2 + h$$

$$P_1 - P_2 = (\rho_m - \rho) gh$$

• Manometer formula for gas

$$\cdot P_m \gg P_{\text{gas}}$$

$$P_1 - P_2 = \rho_m g h = P_h$$



⇒ Temperature

• devices

- { resistance thermometer - based on electric resistance of conductor
- thermocouple - based on voltage at junction of two dissimilar metals
- pyrometer - based on spectrum of emitted radiation
- thermometer - based on volume of a fixed mass of fluid

> degree - unit temperature interval

> Celsius scale - $T_0 = -273.15^\circ\text{C}$, $T_f = 0^\circ\text{C}$, $T_b = 100^\circ\text{C}$

> Fahrenheit scale - $T_0 = -459.67^\circ\text{F}$, $T_f = 32^\circ\text{F}$, $T_b = 212^\circ\text{F}$

> Kelvin scale - $T_0 = 0\text{ K}$, same interval as Celsius

> Rankin scale - $T_0 = 0^\circ\text{R}$, same interval as Fahrenheit

→ Conversion of Temperature

$$\cdot T(\text{K}) = T(\text{ }^\circ\text{C}) + 273.15$$

$$\cdot T(\text{ }^\circ\text{R}) = T(\text{ }^\circ\text{F}) + 459.67$$

$$\cdot T(\text{ }^\circ\text{R}) = 1.8 T(\text{K})$$

$$\cdot T(\text{ }^\circ\text{F}) = 1.8 T(\text{ }^\circ\text{C}) + 32$$

→ Conversion of Temperature interval

$$\cdot \frac{1.8^\circ\text{F}}{1^\circ\text{C}} = \frac{1.8^\circ\text{R}}{1\text{K}} = \frac{1^\circ\text{F}}{1^\circ\text{R}} = \frac{1^\circ\text{C}}{1\text{K}}$$

<< Process classification

- > batch - feed charged to a vessel in the beginning, vessel content removed sometime later
 - no mass crosses system boundary in between time
- > continuous - input & output flow continuously throughout duration of process
- > semibatch - neither batch nor continuous
- > steady state - value of all variables in the process do not change over time
(except minor fluctuations about mean value)
- > unsteady state - any process variable change with time
(transient)
 - batch & semibatch
 - batch for small
 - continuous for big
 - steady state in between
 - unsteady state at beginning & end



<< Balances

→ General Balance Equation

> mass balance - balance based on conservation of mass

> balance of conserved quantity in a system :

$$\boxed{\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation}}$$

> input - enters through system boundary

> generation - produced within the system

> output - leaves through system boundary

> consumption - consumed within system

> accumulation - buildup within system

> differential balance - what happens within a system at a given time

- terms are rate

- used in continuous process

> integral balance - what happens between two instances of time

- terms are amount

- used in batch process

> Simplifying assumptions

- total mass balance : generation = 0, consumption = 0

- nonreactive species balance : generation = 0, consumption = 0

- steady-state : accumulation = 0

<< Balances

→ Balances on Continuous Steady-State Process

- accumulation = 0
- input + generation = output + consumption

→ Integral Balance on Batch Process

$$\begin{aligned} \text{• accumulation} &= \text{output} - \text{input} \\ &= \text{generation} - \text{consumption} \end{aligned}$$

$$\Rightarrow \text{output} - \text{input} = \text{generation} - \text{consumption}$$

→ Integral Balance on Semibatch Process

<< Material Balance Calculations

→ Flowcharts

> flowchart - box / symbol represent process units, lines represent input / output

- label with unknown variables and knowns
- assign variables symbols

→ Flowchart scaling & Basis of Calculation

> balanced - material balance of all system components satisfied

> scaling - procedure of changing values of all stream amount or flow rates by a proportional amount while leaving stream composition unchanged

> scaling up - final stream quantity > original quantity

> scaling down - final stream quantity < original quantity

> basis of calculation - an amount or flow rate (mass / molar) of one stream or stream component in a process

. if given, use given

. if not given, choose conveniently with stream of known composition

→ Balancing a Process (Nonreactive)

. Max # of independent equations that can be derived by writing balances on a nonreactive system equals # of chemical species in the input and output streams

. Write balances first that involve the fewest unknown variables

→ Degree of Freedom Analysis

> DOF analysis - determine if enough info is given to solve problem

$$\cdot N_{\text{df}} = N_{\text{unknowns}} - N_{\text{indep. eq.}}$$

. $N_{\text{df}} = 0$ - solvable

. $N_{\text{df}} > 0$ - underdetermined

{ . need N_{df} more variables
 . by assumptions
 . by more relations
 . underspecified problem - ∞ soln

. $N_{\text{df}} < 0$ - overdetermined

{ . incomplete flowchart
 . overspecified problem - redundant / inconsistent info

<< Material Balance Calculations

→ General Procedure for Single-Unit Process

1. Choose a basis of calculation
2. Draw a flowchart, label known & unknown
3. State problem in terms of variables
4. Express all quantities in terms of mass or moles
5. Degree of freedom analysis
6. Solve equations
7. Check solution
8. Answer the question
9. Scale solution

→ Deviation from Ideal Balance

- steady state not obtained
- faulty flow measurement { instrumental error
human error
- density of fluid differ than assumption
- slight leak in tank
- impurities in reactant
- temperature & pressure fluctuation
- chemical rxn not taken into account
- unjustified assumption of ideal behavior

<< Chemical Reaction Stoichiometry

→ Stoichiometry

➢ stoichiometric equation - statement of relative number of molecules of reactant & product of a reaction

➢ stoichiometric coefficient - # precede the chemical symbol

➢ stoichiometric ratio - ratio of stoich. coeff. in balanced rxn equation of two species.

→ Limiting & Excess Reactants

➢ stoichiometric proportion - ratio of $\frac{\text{mol A present}}{\text{mol B present}}$ equals the stoichiometric ratio of rxn

➢ limiting reactant - reactant eliminated first if a rxn proceeds to completion

➢ excess reactant - left-over reactant if rxn completes

• limiting reactant present in less than its stoch. proportion to every other reactants.

➢ stoichiometric requirement - amount needed to react completely with limiting reactant

➢ excess = $n_{\text{need}} - n_{\text{stoch}}$

➢ fractional excess = $\frac{n_{\text{need}} - n_{\text{stoch}}}{n_{\text{stoch}}} \times 100\%$

<< Chemical Reaction Stoichiometry

→ Fractional conversion, extent of reaction

> fractional conversion - $f = \frac{\text{mol reacted}}{\text{mol fed}} \times 100\%$

> stoichiometric coefficient of i th species - ν_i

- negative for reactant
- positive for product (zero for inert nonreactive species)

> extent of reaction - $\bar{z} = \frac{n_i - n_{i0}}{\nu_i}$ in mols i

• one \bar{z} per reaction

• \bar{z} is non-negative

$$\cdot n_i = n_{i0} + \nu_i \bar{z}$$

n_i - mol of species i at time t

n_{i0} - mol of species i at initial time $t=0$

ν_i - stoich coeff

→ Chemical Equilibrium

> chemical equilibrium thermodynamics - study of equilibrium composition of rxn

> chemical kinetics - study of amount of time for system to reach equilibrium

> irreversible - rxn proceed in one direction

• concentration of limiting reactant eventually $\rightarrow 0$.

• equilibrium composition: complete consumption of limiting reactant

> reversible - have forward and reverse rxn

• equilibrium $\{$ rate of fwd, reverse rxn equal

• no net composition change

→ Multiple Rxns, Yield, Selectivity

> yield = $\frac{\text{mol desired product}}{\text{mol product w/o side rxn, complete rxn}} = \frac{\text{actual}}{\text{theoretical}} \times 100\%$

> selectivity = $\frac{\text{mol desired product}}{\text{mol undesired product}}$

• extent of rxns

$$n_i = n_{i0} + \sum_j \nu_{ij} \bar{z}_j$$

<< Balances on Reactive Processes

→ Balances on Molecular & Atomic Species

- molecular balance needs generation & consumption terms
- atomic balance has simple form of input = output
 - atom not created/destroyed
 - generation = consumption = 0
- make distinction when solving problems

→ Independent Equations, Species, Reactions

- independent species
 - molecular species in the same ratio with each other \Rightarrow not independent
 - atomic species in the same ratio with each other \Rightarrow not independent
- independent reaction
 - adding or subtracting multiple of rxn gets each other \rightarrow not independent

→ Molecular Species Balance

- degree of freedom = # unknown labeled variable
 - + # independent chem. rxn.
 - # independent molecular species balance
 - # other relations

→ Atomic Species Balance

- degree of freedom = # unknown labeled variable
 - # indep. atomic balance
 - # indep. molecular balance on nonreactive species
 - # other relations

→ Extent of Rxn

- degree of freedom = # unknown labeled variable
 - + # indep. rxn
 - # indep. reactive species
 - # indep. nonreactive species
 - # other relations

→ Choosing Soln Approaches (by hand)

- molecular - simple system with 1 rxn
- atomic - 1+ rxn
- extent of rxn - equilibrium problem

<< Combustion Reaction

→ Combustion Chemistry

> natural gas - methane

> liquified petroleum gas - propane / butane

> incomplete (partial) combustion - comb. rxn where CO is formed

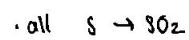
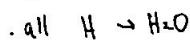
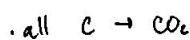
> composition on wet basis - component mol fraction of gas that contains H₂O

> component on dry basis - component mol fraction without H₂O

> flue (stack) gas - product gas that leaves the combustion furnace

→ Theoretical & Excess Oxygen & Air

> theoretical oxygen - mol / molar flow rate of O₂ needed for complete combustion of all fuel fed to the reactor.



> theoretical air - quantity of air that contains theoretical oxygen

> excess air - amount by which the air fed to the reactor exceeds the theoretical air

$$> \% \text{ excess air} = \frac{n_{\text{fed}} - n_{\text{theory}}}{n_{\text{theory}}} \times 100\% \text{ of air}$$

• theoretical air required to burn a given quantity does not depend on how much is actually burned.

• the value of percent excess of air only depends on theoretical air and air feed rate, and not how much O₂ is consumed in the reactor or whether combustion is complete or partial

→ Material Balances on Combustion Reactors

1. Mind the outlet stream

• unreacted fuel

• unreacted O₂

• H₂O, CO₂, (CO)

• N₂

2. % excess O₂ = % excess air

To get n_{feed, O_2} , calculate n_{theory, O_2} , and $n_{\text{feed}, O_2} = n_{\text{theory}, O_2} (1 + \% \text{ excess O}_2)$

3. Avoid molecular balance approach if have multiple rxns.

« Balance on Multiple Unit Process

> system - any portion of the process that can be enclosed within a hypothetical box of boundary

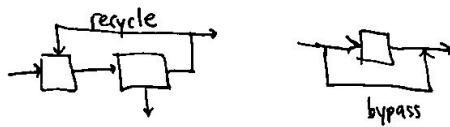
> overall balance - balance on the entire process

« Recycle & Bypass

> recycle - separate unconsumed reactant back to reactor

• purpose of recycling

- recovery of catalyst
- dilution of a process stream
- control of a process variable
- circulation of working fluid



> bypass - a fraction of the feed to a process unit is diverted around the unit and combined with output from the unit

<< Physical Properties of Process Material

- Look up
- Estimate
- Measure

<< Liquid & Solid Density

> incompressible - change in temp or pressure does not change density

- Normally, $T \uparrow$, $p \downarrow$, $V \uparrow$ expands
- experimental data is most accurate

- Experimental data first

- estimation formula

$$\left\{ \begin{array}{l} \frac{1}{P} = \sum_{i=1}^n \frac{x_i}{P_i} \\ P = \sum_{i=1}^n x_i P_i \end{array} \right.$$

(* Assume volume additivity, adds specific volume)
good for liquid with similar molecular structure

• no rule for which is the best

<< Ideal Gases

→ Ideal Gas Equation of State

> equation of state - equation that relates molar/volume quantity of a gas to temp or pressure

> ideal gas equation of state

$$PV = nRT$$

$$P\dot{V} = \dot{n}RT$$

P, T use absolute scale

> specific molar volume - $\dot{V} = \frac{V}{n}$  $\dot{P}\dot{V} = \dot{R}\dot{T}$

> ideal gas - gas modeled by ideal gas equation

- 1mol ideal gas at 0°C , 1atm occupies 22.415 L

- approximation

- good for $T > 0^\circ\text{C}$, $P < 1\text{ atm}$

- If $\dot{V}_{\text{ideal}} = \frac{RT}{P}$

$\left\{ \begin{array}{l} > 5\text{ L/mol } (80 \text{ ft}^3/\text{lbmol}) \quad \text{diatomic gas} \\ > 20\text{ L/mol } (320 \text{ ft}^3/\text{lbmol}) \quad \text{other gas} \end{array} \right.$
--

- then $|\varepsilon| < 1\%$, where $\varepsilon = \frac{X_{\text{ideal}} - X_{\text{true}}}{X_{\text{true}}} \times 100\%$, X is quantity in $PV = nRT$

<< Ideal Gases

→ Standard Temperature and Pressure

$$\frac{PV}{P_s V_s} = n \frac{T}{T_s} \Rightarrow V_A = \frac{T_A}{T_s} \frac{P_s}{P_A} \hat{V}_s n_A = \frac{T_A}{T_s} \frac{P_s}{P_A} V_s$$

• standard conditions

(Note: $n_A = n_s$ by conservation)

• 0°C, 1 atm

System	T _s	P _s	V _s	n _s	$\hat{V}_s = \frac{V_s}{n_s}$
SI	273K	1 atm	0.022415 m ³	1 mol	22.4 m ³ /kmol
CGS	273K	1 atm	22.415 L	1 mol	22.4 L/mol
U.S.	492°F	1 atm	359.05 ft ³	1 lbmol	359.05 ft ³ /lbmol

> SCM - standard cubic meters, m³(STP)> SCF - standard cubic feet, ft³(STP)

→ Ideal-Gas Mixtures

• partial pressure P_A - the pressure that would be exerted by n_A mol of A alone in the same total volume V at the same temperature T• pure-component volume - the volume that would be occupied by n_A mol of A alone at the total pressure P and temperature T of the mixture.

• ideal gas mixture - individual mixture components and the mixture as a whole behave ideally

• Partial pressure of a component in an ideal-gas mixture is the mol fraction of the component times total pressure.

$$P_A = y_A P$$

• Dalton's law - partial pressures of components of an ideal-gas mixture add up to the total pressure

$$\sum P_i = (\sum y_i) P = P \quad (\text{since } \sum y_i = 1)$$

• pure-component volume is mol frac times total volume

$$V_A = y_A V$$

• Amagat's law - pure component volume add up to total volume

$$\sum v_i = V$$

• volume fraction - $\frac{v_A}{V}$

For ideal gas, volume fraction equals mol fraction

• percent by volume - $\frac{v_A}{V} \times 100\% \quad (\%)_{v/v}$

$$\frac{v_A}{V} = y_A$$

Equations of State for Nonideal Gases

→ Critical Temperature & Pressure

> critical temperature T_c - the highest temp at which a species can coexist in two phases

> critical pressure P_c - corresponding pressure at critical temperature

> critical state - substance at T_c and P_c

> vapor - gaseous species below its critical temp.

> gas - species above its critical temp at a pressure low enough to be more like a vapor than liquid

> supercritical fluid - substance at above T_c and P_c .

→ Virial Equation of State

> Virial equation of state:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

• 1st order approx:

$$\frac{PV}{RT} = 1 + \frac{B}{V} \approx 1 + \frac{BP}{RT} \Rightarrow \boxed{\frac{PV}{RT} = 1 + \frac{BP}{RT}}$$

• good with nonpolar compound

• bad with polar compound

→ Using Virial Equation of State

1. Lookup {
 - critical temp T_c
 - critical pressure P_c
 - Pitzer acentric factor ω

2. Calculate reduced temp

$$\boxed{T_r = \frac{T}{T_c}}$$

3. Estimate parameter B :

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$\left. \right\} B = \frac{RT_c}{P_c} (B_0 + \omega B_1)$$

4. Substitute known values into virial eqn of state

<< Equations of State for Nonideal Gases

→ Cubic Equation of State

> third order equations of specific volume

→ Van der Waals

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c}$$

- $\frac{a}{V^2}$ accounts attractive forces for molecules

- b accounts volume occupied by molecules themselves

→ Soave-Redlich-Kwong (SRK)

$$P = \frac{RT}{V - b} - \frac{\alpha a}{V(V+b)}$$

$$\alpha = 0.42747 \frac{(RT_c)^{2/3}}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

- Using SRK Eqn

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2$$

- Look up T_c, P_c, ω

$$T_r = T/T_c$$

- Calculate a, b, m

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2$$

- If known T, V

- calculate T_r, α

- solve from eqn directly for P

If known T, P

- use eqn and all knowns

- use excel solver for V

If known P, V

- use eqn, T_r eqn, α eqn, and all knowns

- use excel solver for T

- eqn of state are estimations

- empirical expressions

- best in data range

<< Compressibility-Factor Equation of State

→ compressibility

$$z = \frac{P\bar{V}}{RT}$$

• $z=1$ for ideal gas

• compressibility-factor eqn

$$\hat{PV} = zRT$$

$$PV = z nRT$$

• z is different among species as T and P changes

• law of corresponding states - z of any gas at a specific value of T_r and P_r
has approx. same value.

• generalized compressibility chart - $z(T_r, P_r)$

→ Using generalized compressibility chart

1. Look up T_c, P_c

2. If gas is He or He, adjust critical constant

$$\begin{aligned} T_c^a &= T_c + 8K & \} & \text{Newton's correlation} \\ P_c^a &= P_c + 8 \text{ atm} \end{aligned}$$

3. Calculate reduced value of two variables known

$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

$$V_r^{\text{ideal}} = \frac{P_c V}{R T_c}$$

use absolute temp & pressure

4. Use compressibility chart to determine z .

5. Solve for unknown in eqn of state.

• disadvantage { not as accurate in highly nonideal condition
lack precision
hard to adapt for computer calculation

• advantage { computational simplicity
adaptability to multicomponent gas mixture

<< Compressibility-Factor Equation of State

→ Nonideal Gas Mixtures

> Kay's rule - estimates pseudocritical properties of mixture as average of pure comp.

$$> \text{pseudocritical temp: } T_c' = \sum y_i T_{c,i}$$

$$> \text{pseudocritical pressure: } P_c' = \sum y_i P_{c,i}$$

$$> \text{pseudoreduced temp: } T_r' = \frac{T}{T_c'}$$

$$> \text{pseudocritical pressure: } P_r' = \frac{P}{P_c'}$$

'use pseudocritical properties to find compressibility factor of mixture Z_m .

$$> \text{ideal pseudoreduced volume: } \hat{V}_r^{\text{ideal}} = \frac{\hat{V} P_c'}{R T_c'}$$

<< Intro to Multiphase Systems

- > phase-change operation - operations in which material is transferred from one phase to another
- > separation - separate components of mixture from one another
- > leaching - dissolving a component of a solid phase in a liquid phase
- > absorption/scrubbing - gas dissolve in solvent
- > distillation
- > liquid extraction
- > adsorption
- > crystallization
- > saturated
- > phase equilibrium - concentration of all species in each phase no longer change with time

<< Single-Component Phase Equilibrium

→ Phase Diagram

> phase diagram - plot of a system variable against another that shows the conditions at which the substance exists as a solid, liquid, or gas.

• boundary of single phase regions represent P, T at which two phase coexist.

- > vapor pressure p^* - P on vapor-liquid equilibrium
- > boiling point temp T_b - T on vapor-liquid eqm at P^*
- > normal boiling point - boiling pt at $P=1\text{ atm}$
- > melting/freezing point T_m - T on solid-liquid eqm
- > sublimation point T_s - solid-vapor eqm
- > triple point - solid, liquid, vapor phase coexist
- > critical temperature T_c - T where VLE terminates
- > critical pressure P_c - P where VLE terminates

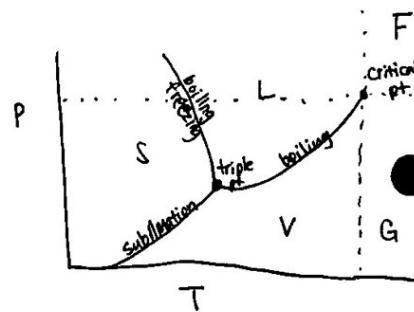
→ Estimation of Vapor Pressure

> volatility - tendency to transfer from liquid/solid to vapor

• vapor pressure \propto volatility

> Clapeyron equation

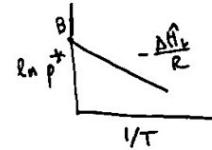
$$\frac{dp^*}{dt} = \frac{\hat{\Delta H}_v}{T} \frac{1}{V_g - V_l} \xrightarrow{V_g - V_l \propto V_g} \frac{d(\ln P^*)}{d(1/T)} = - \frac{\hat{\Delta H}_v}{R}$$



> latent heat of vaporization - $\hat{\Delta H}_v$, energy required to vaporize 1mol of liquid species

> Clausius-Clapeyron eqn

$$\ln P^* = - \frac{\hat{\Delta H}_v}{RT} + B$$



$$\ln \frac{P_2}{P_1} = - \frac{\hat{\Delta H}_v}{nR} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

<< Single-Component Phase Equilibrium

→ Estimation of Vapor Pressure

> Antoine equation

$$\log_{10} P^* = A - \frac{B}{T+C}$$

$$T = -\frac{B}{\log_{10} P^* - A} - C$$

- note units, logarithm
- note range of validity
- here, P^* [mmHg], T [$^{\circ}\text{C}$]

<< Gibbs Phase Rule

> extensive variable - depend on system size (m, n, V)> intensive variable - do not depend on system size (T, P, ρ, s_a, x, y)

> Gibbs phase Rule

- + c ² independent chem species
 - π phases at eqm
 - r independent chem rxn

$$f = 2 + c - \pi - r$$

 f degree of freedom

• dof = # intensive variables that must be specified for system at eqm for calculation

<< Single-Condensable Gas-Liquid System

- liquid \rightarrow gas : evaporation, drying, humidification

- gas \rightarrow liquid : condensation, dehumidification

- > saturated - gas contains all species molecules it can hold at specific T, P .

- > saturated vapor - molecules of species in gas phase

- > Raoult's law - If a gas at T, P contains a saturated vapor with mol frac y_i , and (single comp.) if this vapor is the only species that could condense if T is slightly lowered, then the partial pressure of the vapor in the gas equals the pure-component vapor pressure.

$$P_i = y_i P = P_i^*(T)$$

- a gas in eqm with a liquid must be saturated with the volatile component of the liquid
- partial pressure of a vapor at eqm in the gas mixture containing single condensable component cannot exceed the vapor pressure at the system temp.

$$P_i = P_i^* \Leftrightarrow \text{saturated}$$

Any attempt to increase P_i { add more vapor to gas phase } will lead to condensation
increase pressure at constant T

Single-Condensable Gas-Liquid System

> superheated vapor - vapor present in gas in less than its saturation amount.

$$P_i = y_i P < P_i^*(T)$$

- only saturated vapor can condense
- superheated vapor need to change variables to reach equality to condensate
 - $\uparrow P$ at $\Delta T=0$
 - $\downarrow T$ at $\Delta P=0$

> dew point - T at which superheated vapor becomes saturated when cooled at constant P

$$P_i = y_i P = P_i^*(T_{dp})$$

> degree of superheat - diff between temperature and dew point of gas

> evaporation - molecules from liquid surface to gas above the surface at temperature such that $P^* < P$

> boil - vapor bubbles throughout the entire liquid, but predominantly at walls at $P^* = P$.

> boiling point - T at which $P^* = P$

• saturation refers to general gas-vapor eqm

• humidity refers to air-water eqm

> relative saturation - $S_r = \frac{P_i}{P_i^*(T)} \times 100\%$,

> molal saturation - $S_m = \frac{P_i}{P-P_i} = \frac{\text{mol vapor}}{\text{mol vapor-free gas}}$

> absolute saturation - $S_a = \frac{P_i M_i}{(P-P_i) M_i} = \frac{\text{mass vapor}}{\text{mass vapor-free gas}}$

> percent saturation - $S_p = \frac{S_m}{S_m^*} \times 100\% = \frac{P_i / (P-P_i)}{P_i^* / (P-P_i^*)} \times 100\%$.

<< Multicomponent Gas-Liquid System

> absorption / scrubbing - transfer one or more species from gas to liquid

> stripping - transfer 1st species from liquid to gas

→ VLE Data

- Lookup tabulated data

→ Raoult's law & Henry's law

> phase equilibrium thermo - study of distribution of substance between equilibrated gas and liquid phase

> Raoult's law

$$P_A = y_A P = x_A P_A^*(T)$$

y - gas
x - liquid

- best when $x_A \rightarrow 1$

> Henry's law

$$P_A = y_A P = x_A H_A(T)$$

y - gas
x - liquid
 H_A - Henry's law constant

- best when $x_A \rightarrow 0$

• A doesn't dissociate, ionize, react in liquid

→ VLE Calculations for Soln Obeying Raoult's law

• Liquid mixture will have diff composition than vapor mixture

• As vaporization proceeds, composition of remaining liquid continuously changes, hence so does its vaporization temperature.

> bubble point temp - temp at which first vapor bubble forms when liquid is heated slowly at constant P.

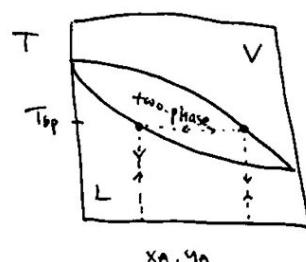
> dew point temp - temp at which first liquid droplet forms when vapor/gas is cooled slowly at constant P.

> ideal solution - solution that obeys Raoult's law and Henry's law.

→ Graphical Representations of VLE

> Txy diagram - a plot of the equilibrium temperature versus the mol frac of A, with curves drawn for both liquid phase (x_A) and gas phase (y_A) (pressure held constant)

> Pxg diagram - plot of P vs x_A and y_A (temp held constant)



<<Forms of Energy

- > kinetic energy - energy due to translational motion of the system as a whole or rotation of system about some axis.
- > potential energy - energy due to the position of the system in a potential field
- > internal energy - all energy possessed by the system other than KE or PE
 - energy due to motion of molecule relative to center of mass of system
 - energy due to rotational or vibrational motion, electromagnetic interaction
 - energy due to motion & interactions of atomic and subatomic constituents of atom
- > closed system - no mass cross system boundary
 - > heat - energy that flows as a result of temperature diff between syst. & surr.
 - always high T \rightarrow low T
 - $q > 0$ if syst \leftarrow surr.
 - > work - energy that flows in response to any driving force other than temp diff.
 - e.g. force, torque, voltage
 - $W > 0$ if syst \leftarrow surr.
 - Units of energy: J (N·m), ergs (dyne·cm), ft-lbf, kcal, cal, btu
- > first law of thermodynamics - energy can neither be created or destroyed (conservation of energy)

<<Kinetic and Potential Energy

- $E_k = \frac{1}{2}mv^2$ [J]
- $\dot{E}_k = \frac{1}{2}\dot{m}v^2$ [J/s]
- $E_p = MgZ$ [J]
- $\dot{E}_p = \dot{m}gZ$ [J/s]

<<Energy Balance on Closed System

- > closed - no mass crosses system boundary
- > open - mass crosses system boundary
- accumulation = $E_f - E_i = \text{input} - \text{output}$

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q + W}$$

- $\Delta U \approx 0$ if no T change, no phase change, no chem rxn in closed system
or if $\Delta P <$ few atm
- $\Delta E_k = 0$ if system not accelerating
- $\Delta E_p = 0$ if system not rising/falling
- $Q = 0$ if perfect insulation or syst & surr same T (adiabatic)
- $W = 0$ if no moving parts, electric current, or radiation at system boundary

<<< Energy Balance on Open System in Steady State

→ Work

> shaft work - rate of work done on process fluid by a moving part within the system

> flow work - rate of work done on the fluid at the system inlet minus

the work done by the fluid at the system outlet ($W_{fl} = (PV)_{in} - (PV)_{out}$)

• net work $\dot{W} = \dot{W}_s + \dot{W}_{fl}$

→ Specific Properties

> specific property - intensive property obtained by dividing an extensive property by the total amount of the process material.

• hat notation \hat{V}

> specific volume - $\hat{V} = \frac{V}{m} \Rightarrow V = m\hat{V}$

> specific kinetic energy - $\hat{K} = \frac{K}{m} \Rightarrow K = m\hat{K}$

> specific enthalpy - $\hat{H} = \hat{U} + PV$

• If a closed system expands (or contracts) against constant external pressure, $\Delta E_k = 0$, $\Delta E_p = 0$, and the only work done by or on the system is the work of expansion, then

$$Q = \Delta H$$

→ Open System Energy Balance

•
$$\dot{H} + \dot{E}_k + \dot{E}_p = \dot{Q} + \dot{W}_s$$

• steady state \Rightarrow no mass accumulation

• $\dot{H} = \dot{m} \hat{H}$

• if $\dot{H} = 0$, $\dot{H} = 0$.

<<< Tables of Thermodynamic Data

→ Reference State & State Properties

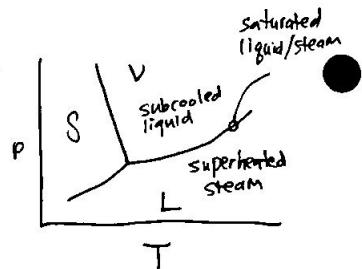
> reference state - chosen temp., pressure, state of aggregation

> state property - property of a system whose value depends only on the state of the system, and not how the system reached that state.

<< Tables of Thermodynamic Data

→ Steam Table

- > supercooled liquid - above VLE curve, to right of SLE curve
- > Saturated liquid/steam(vapor) - at VLE curve
- > superheated steam(vapor) - below VLE curve
- > steam table - compilation of physical properties of liquid water, saturated steam, superheated steam



<< Energy Balance Procedures

- For mixtures of near-ideal gases or liquids with similar molecular structures, you may assume that \hat{H} for a mixture component is the same as \hat{H} for the pure substance at same T and P

<< Mechanical Energy Balances

- > Friction loss

$$\hat{F} = \Delta \hat{U} - \frac{\dot{Q}}{m}$$

- General balance

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z + \hat{F} = \frac{\dot{W}_s}{m}$$

- Bernoulli equation

$$\begin{cases} \hat{F} \approx 0 \\ \dot{W}_s = 0 \end{cases}$$

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z = 0$$

<< Elements of Energy Balance Calculations

→ Reference States

- cannot know absolute values of \hat{U} and \hat{H}
- can determine changes $\Delta\hat{U}$ and $\Delta\hat{H}$ experimentally
- choose reference state that $\Delta\hat{U} = \hat{U} - \hat{U}_{ref}$ and let $\hat{U}_{ref} = 0$

→ Hypothetical Process Paths

- \hat{U} and \hat{H} are state properties
- when a species goes from state 1 to state 2, both $\Delta\hat{U}$ & $\Delta\hat{H}$ are independent of the path taken.
- > process path - a series of steps from initial to final state
 - add $\Delta\hat{H}_i$ of each path to get total $\Delta\hat{H}$ (path independent)

→ Procedure for Energy Balance Calculations

1. Perform all required material balance calculations
2. Write appropriate energy balance (open/closed system).

Delete any zero or negligible terms

3. Choose a reference state (phase, T, P)
4. Construct tables with initial and final states of :

- closed system : n_i/n_i , \hat{U}_i

- open system : n_i/n_i , \hat{H}_i

5. Calculate all required values and insert values in appropriate place in table

6. Calculate

$$\text{closed } \Delta U = \sum_{\text{final}} n_i \hat{U}_i - \sum_{\text{initial}} n_i \hat{U}_i \quad (\text{or } m_i)$$

$$\text{open } \Delta \dot{H} = \sum_{\text{final}} n_i \hat{H}_i - \sum_{\text{initial}} n_i \hat{H}_i \quad (\text{or } m_i)$$

7. Calculate W , ΔE_k , ΔE_p

8. Solve energy balance for unknown

$$\text{closed } \Delta U + \Delta E_k + \Delta E_p = Q + W$$

$$\text{open } \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} + \dot{W}_s$$

⇒ Changes in P at AT=0 (Isothermal)

$$\cdot \Delta \hat{U} \approx 0$$
$$\cdot \Delta \hat{H} = \Delta \hat{U} + \Delta(p\hat{V}) = \hat{V} \Delta P \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{solid, liquid}$$

$$\cdot \Delta \hat{U} = 0 \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{ideal gas}$$
$$\cdot \Delta \hat{H} = 0$$

⇒ Changes in Temperature

→ Sensible Heat & Heat Capacity

> sensible heat ~ heat that must be transferred to raise or lower the temperature of a substance or mixture of substance.

$$Q = \Delta U \quad (\text{closed syst})$$

$$Q = \Delta H \quad (\text{open syst})$$

> heat capacity at constant volume - $C_v(T) = \left(\frac{\partial U}{\partial T} \right)_v$

$$d\hat{U} = C_v(T) dT$$

$$\boxed{\Delta \hat{U} = \int_{T_1}^{T_2} C_v(T) dT}$$

ideal gas - exact
l-s - good approx
nonideal gas - valid if $\Delta V=0$

> heat capacity at constant pressure -

$$C_p(T) = \left(\frac{\partial \hat{H}}{\partial T} \right)_p$$

$$d\hat{H} = C_p(T) dT$$

$$\boxed{\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T) dT}$$

ideal gas - exact
nonideal - approx for P
nonideal gas - valid if $\Delta P=0$

$$\boxed{\Delta \hat{H} \approx \Delta P \Delta V + \int_{T_1}^{T_2} C_p(T) dT}$$

solid, liquid

→ Heat Capacity Formula

• unit C [=] J/(mol · K)

• correlation used : $C_p = a + bT + cT^2 + dT^3$

• liquid & solid :

$$\boxed{C_p \approx C_v}$$

• Ideal gas

$$\boxed{C_p = C_v + R}$$

<< Changes in Temperature

→ Estimation of Heat Capacities

> Kopp's rule - C_p of a molecular compound is the sum of contributions for each element in the compound

· good for solid & liquid near 20°C

· Estimating C_p of Mixture

· For mixture of gas or liquid, total enthalpy change \approx enthalpy changes for pure mixture components

· good for similar molecules

· For highly dilute solutions of solid or gas in liquid, neglect enthalpy change of solute

$$C_{p,mix}(T) = \sum_{\text{all comp.}} y_i C_{p,i}(T)$$

→ Energy Balances on Single-Phase Systems

1. Evaluate $\Delta\hat{U} = \int_{T_1}^{T_2} C_V dT$

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_P dT$$

2. For closed, $\Delta V=0$, calculate $\Delta U = n \Delta\hat{U}$

For closed, $\Delta P=0$, calculate $\Delta H = n \Delta\hat{H}$

For open syst., calculate $\Delta H = n \Delta\hat{H}$

3. Use energy balance to find Q or \dot{Q} .

<< Phase Change Operations

→ Latent Heat

> latent heat - specific enthalpy change associated with transition of a substance from one phase to another at $\Delta T=0$, $\Delta P=0$

> latent heat of vaporization - $\Delta\hat{H}$ for transition of $H_2O(l)$ to $H_2O(v)$ at 100°C, 1 atm.

> heat of fusion - $\Delta\hat{H}$ between solid & liquid

> heat of vaporization - $\Delta\hat{H}$ between liquid & vapor

· latent heat highly depends on T, but not so much on P.

· If closed syst., evaluate $\Delta\hat{U} = \Delta\hat{H} - \Delta(PV)$

· Solid/liquid : $\Delta\hat{U} \approx \Delta\hat{H}$

· ideal gas : $\Delta\hat{U}_v \approx \Delta\hat{H}_v - RT$

↔ Phase Change Operations

→ Estimation & Correlation of Latent Heats

> Trouton's rule - $\hat{\Delta H}_v(\text{kJ/mol}) \begin{cases} \approx 0.088 T_b(\text{K}) & \text{nonpolar liquid} \\ \approx 0.109 T_b(\text{K}) & \text{water, low molecular weight alcohol} \end{cases}$

> Chen's equation - $\hat{\Delta H}_v(\text{kJ/mol}) = \frac{T_b [0.0331 (T_b/T_c) - 0.0327 + 0.0297 \log_{10} P_c]}{1.07 - (T_b/T_c)}$

" $\hat{\Delta H}_m(\text{kJ/mol}) \begin{cases} \approx 0.0092 T_m(\text{K}) & \text{metallic element} \\ \approx 0.0025 T_m(\text{K}) & \text{inorganic compound} \\ \approx 0.050 T_m(\text{K}) & \text{organic compound} \end{cases}$

> Clausius-Clapeyron eqn - $\ln P^* = -\frac{\hat{\Delta H}_v}{RT} + B$

> Clapeyron eqn - $\frac{d(\ln P^*)}{d(1/T)} = -\frac{\hat{\Delta H}_v}{R}$

> Watson's correlation - $\hat{\Delta H}_v(T_2) = \hat{\Delta H}_v(T_1) \left(\frac{T_c - T_2}{T_c - T_1} \right)^{0.38}$

<< Heats of Reaction

> exothermic - product has lower internal energy (thus enthalpy) than reactant at given temperature and pressure.

> endothermic - product has higher V (thus H) than reactant at given T, P .

> heat of reaction $\Delta H_r(T, P)$ - enthalpy diff when stoichiometric quantities of reactants at specified T, P react completely and products are at the same T, P .

- Batch:

$$\Delta H(\text{kJ}) = \bar{z} \Delta H_r(T_0, P_0)$$

$$\bar{z} = \frac{(n_{i,\text{out}} - n_{i,\text{in}})(\text{mol } i)}{V_i (\text{mol } i)} = \frac{n_{i,r}}{V_i}$$

- Continuous:

$$\Delta H(\text{kJ/time}) = \bar{z} \Delta H_r(T_0, P_0)$$

$$\bar{z} = \frac{(n_{i,\text{out}} - n_{i,\text{in}})(\text{mol } i/\text{time})}{V_i (\text{mol } i/\text{time})} = \frac{\dot{n}_{i,r}}{\dot{V}_i}$$

- $\Delta H_r(T, P) < 0$, exothermic

- $\Delta H_r(T, P) > 0$, endothermic

- At low T and P , $\Delta H_r(T, P) \approx \Delta H_r(T)$ is nearly independent on P .

- The value of the heat of a rxn depends on how the stoichiometric equation is written.

- The value of the heat of rxn depends on phases (g, l, s) of reactant & product.

> standard heat of rxn ΔH° - heat of rxn when both reactant & product are at reference T, P (usually $25^\circ\text{C}, 1\text{atm}$)

> internal energy of rxn $\Delta U_r(T) = U_{\text{prod}} - U_{\text{react}}$

<< Hess's Law

> calorimeter - closed reactor immersed in a fluid contained in a well-insulated vessel.

> Hess's law - If the stoich eqn for rxn 1 can be obtained by algebraic operations on stoich eqn for rxns 2, 3, ..., then the heat of rxn ΔH_r° can be obtained by performing the same operations on the heats of rxns $\Delta H_{r2}^\circ, \Delta H_{r3}^\circ, \dots$

<< Heats of Formation

> formation rxn - rxn in which the compound is formed from its elemental constituents as they normally occur in nature

> standard heat of formation ΔH_f° - enthalpy change associated with the formation of 1 mol of the compound at reference T, P ($25^\circ\text{C}, 1\text{atm}$)

> Hess's law -

$$\Delta H_r^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ = \sum_{\text{prod}} |\nu_i| \Delta H_{f,i}^\circ - \sum_{\text{reactant}} |\nu_i| \Delta H_{f,i}^\circ$$

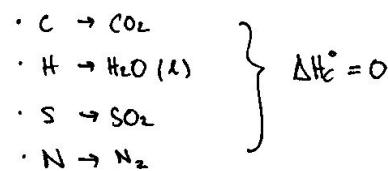
- ν_i - stoich coeff (-reactant, + prod)

- $\Delta H_{f,i}^\circ$ - standard heat of formation of species

- ΔH_f° of elemental compound = 0 (STP)

<< Heat of Combustion

→ standard heat of combustion $\hat{\Delta}H_c^\circ$ - heat of combustion of substance with O₂ to yield specified product (CO₂, H₂O) at ref T, P (25°C, 1 atm)



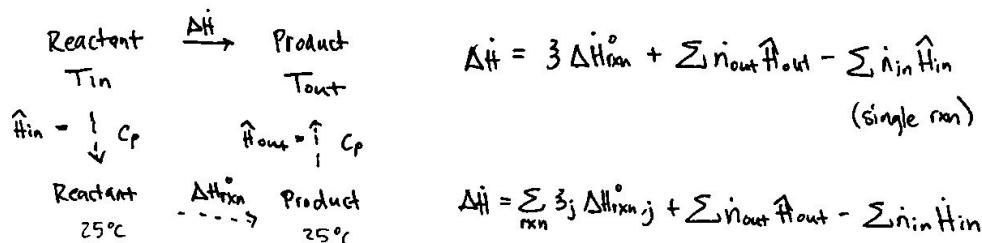
• $\hat{\Delta}H_r^\circ$ that involve only combustible substances and product can be calculated from $\hat{\Delta}H_c^\circ$

$$> \text{Hess's law} - \boxed{\hat{\Delta}H_r^\circ = - \sum_i n_i \hat{\Delta}H_c^\circ, i} = \sum_{\text{react}} |n_i| \hat{\Delta}H_c^\circ, i - \sum_{\text{prod}} |n_i| \hat{\Delta}H_c^\circ, i$$

• $\hat{\Delta}H_c^\circ$ of combustion product = 0

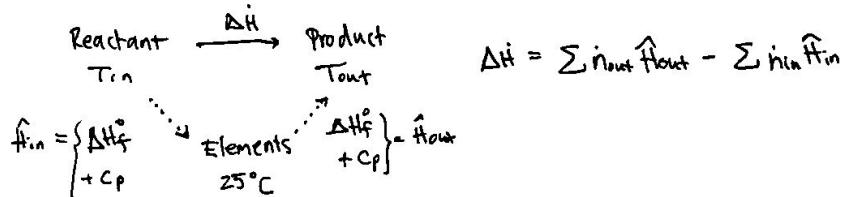
<< Energy Balance on Reactive Processes

→ Heat of Reaction Method



• Reference state: molecule at 25°C, 1 atm

→ Heat of Formation Method



• Reference state: element at 25°C, 1 atm.

<< Adiabatic Flame Temperature

→ the highest achievable T if reactor is adiabatic and all energy released by combustion goes to raising the T of combustion product.

