

CHEM E 310 Material and Energy Balances

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Units and Process Variables

| Force

Description	Equations
Units of force	$1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$ $1 \text{ lb}_f = 32.174 \text{ lb}_m \cdot \text{ft/s}^2$
Weight	$W = mg$
Gravitational acceleration	$g = 9.8066 \text{ m/s}^2$ $= 32.174 \text{ ft/s}^2$

| Mass, volume and flow rate

Description	Equations
Mass flow rate	$\dot{m} = \frac{dm}{dt}$
Volumetric flow rate	$\dot{V} = \frac{dV}{dt}$
Molar flow rate	$\dot{n} = \frac{dn}{dt}$
Density	$\rho = \frac{m}{V} = \frac{\dot{m}}{\dot{V}}$
Specific volume	$v = \frac{V}{m} = \frac{1}{\rho}$
Molar volume	$V_m = \frac{V}{n} = \frac{M}{\rho}$
Specific gravity	$SG = \frac{\rho}{\rho_{\text{ref}}}$

| Chemical composition

Description	Equations
Mole and molecular weight	$n = \frac{m}{M}$
Mass fraction	$x_A = \frac{m_A}{m}$
Mole fraction	$y_A = \frac{n_A}{n}$
Scaling factor of percent (%), parts per million (ppm), parts per billion (ppb)	$\times 100\%$ $\times 10^6 \text{ ppm}$ $\times 10^9 \text{ ppb}$
Average molecular weight	$\bar{M} = \frac{\sum m_i}{\sum n_i} = \sum y_i M_i = \left(\sum \frac{x_i}{M_i} \right)^{-1}$

Description	Equations
Mass concentration	$\rho_A = \frac{m_A}{V}$
Molar concentration	$c_A = \frac{n_A}{V}$
Molarity and molar	1 M = 1 mol/L

| Pressure

Description	Equations
Pressure	$P = \frac{F}{A}$
Hydrostatic pressure	$P = P_0 + \rho gh$
Hydrostatic head	$P = \rho g P_h$
Relationship between pressures	$P_{\text{abs}} = P_{\text{atm}} + P_{\text{gauge}}$
General manometer	$P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_a + \rho_m g h$
Differential manometer	$P_1 - P_2 = (\rho_m - \rho) g h$
Manometer for gas	$P_1 - P_2 = \rho_m g h = P_h$
SCFM (standard cubic feet per minute) and ACFM (actual cubic feet per minute)	$\dot{V}_a = \dot{V}_s \frac{P_s}{P_a} \frac{T_a}{T_s}$ (ideal gas)
Standard condition of gases	natural gas - 59°F, 1 atm other gas - 0°C, 1 atm

| Temperature

Description	Equations
Conversion of temperature	$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$ $T(^{\circ}\text{R}) = T(^{\circ}\text{F}) + 459.67$ $T(^{\circ}\text{R}) = 1.8T(\text{K})$ $T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32$
Conversion of temperature intervals	$1^{\circ}\text{C} = 1.8^{\circ}\text{F}$ $1^{\circ}\text{R} = 1.8 \text{ K}$ $1^{\circ}\text{F} = 1^{\circ}\text{R}$ $1^{\circ}\text{C} = 1.8 \text{ K}$

Fundamentals of Material Balances

| Concepts

Description	Equations
Balance equation	Accumulation = Input - Output + Generation - Consumption
Fractional excess	Fractional excess = $\frac{n_{\text{fed}} - n_{\text{stoich}}}{n_{\text{stoich}}}$

Description	Equations
Fractional conversion	Fractional conversion = $\frac{n_{\text{reacted}}}{n_{\text{fed}}}$
Fractional completion of limiting reactant	Fractional completion = $\frac{n_{\text{reacted}}}{n_{\text{fed}}} = \frac{-\nu\xi}{n_{\text{fed}}}$
Extent of reaction	$\xi = \frac{n_i - n_{i0}}{\nu_i}$
Extent of reaction in multiple reactions	$n_i = n_{i0} \sum_j \nu_{ij} \xi_{ij}$
Yield theoretical = complete rxn, no side rxn	Yield = $\frac{n_{\text{actual}}}{n_{\text{theoretical}}} \times 100$
Selectivity	Selectivity = $\frac{n_{\text{desired}}}{n_{\text{undesired}}}$
Fractional excess of air (oxygen)	Fractional excess air = $\frac{n_{\text{fed}} - n_{\text{stoich}}}{n_{\text{stoich}}}$
Quality of steam	Quality of steam = $\frac{m_{\text{vapor}}}{m_{\text{total}}}$

| Degree of freedom analysis

Description	Equations
Nonreactive process	No. unknown variables –No. independent material balance species –No. other relations (process specifications) <hr/> No. degrees of freedom
Reactive process Molecular species balance method 1 reaction system	No. unknown variables +No. independent reaction –No. independent molecular species –No. other relations <hr/> No. degrees of freedom
Reactive process Atomic species balance method >1 reaction system	No. unknown variables –No. independent reactive atomic species –No. independent nonreactive molecular species –No. other relations <hr/> No. degrees of freedom
Reactive process Extent of reaction method equilibrium problem	No. unknown variables +No. independent reaction –No. independent reactive species –No. independent nonreactive species –No. other relations <hr/> No. degrees of freedom

Single-Phase System

| Condensed phases

Description	Equations
Estimations of density of liquid mixtures	$\frac{1}{\bar{\rho}} = \sum_{i=1}^n \frac{x_i}{\rho_i}$

Description	Equations
1. Experimental data 2. Estimation formula ★ Volume additivity	$\bar{\rho} = \sum_{i=1}^n x_i \rho_i$
Incompressible approximation	$\partial \hat{V} = 0$ $\left(\frac{\partial \hat{V}}{\partial P} \right)_T = 0$ $\left(\frac{\partial \hat{V}}{\partial T} \right)_P = 0$
Volume expansivity	$\beta = \frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial T} \right)_P$
Isothermal compressibility	$K = -\frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial P} \right)_T$
Volume with change in T, P	$\ln \left(\frac{\hat{V}_2}{\hat{V}_1} \right) = \beta(T_2 - T_1) - K(P_2 - P_1)$

| Ideal gas of single component

Description	Equations
Specific molar volume	$\hat{V} = \frac{V}{n}$
Ideal gas equation of state ★ $T > 0^\circ\text{C}, P < 1 \text{ atm}$	$PV = nRT$ $P\hat{V} = RT$
Standard conditions and actual conditions	$\frac{PV}{P_s \hat{V}_s} = n \frac{T}{T_s}$
SCFM vs. ACFM ★ Ideal gas	$\dot{V}_a = \dot{V}_s \frac{P_s}{P_a} \frac{T_a}{T_s}$
Ideal gas condition	$T > 0^\circ\text{C}$ $P < 1 \text{ atm}$ $\hat{V}_{\text{ideal}} = \frac{RT}{P}$ $\begin{cases} > 5 \text{ L/mol, } 80 \text{ ft}^3/\text{lbmol} & \text{diatomic} \\ > 20 \text{ L/mol, } 320 \text{ ft}^3/\text{lbmol} & \text{other} \end{cases}$

| Ideal gas of multiple components

Description	Equations
Partial pressure	$P_i = y_i P$
Dalton's law	$\sum P_i = P$
Pure-component volume	$V_i = y_i V$
Amagat's law	$\sum V_i = V$
Volume fraction of ideal gas	$y_i = \frac{V_i}{V}$

| van der Waals equation of state

Description	Equations
van der Waals equation of state	$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2}$
Constant	$a = \frac{27R^2T_c^2}{64P_c}$
Constant	$b = \frac{RT_c}{8P_c}$
Significance of 3 real roots	$\hat{V}_{\text{highest}} = \hat{V}_{\text{sat, vapor}}$ $\hat{V}_{\text{lowest}} = \hat{V}_{\text{sat, liquid}}$ $\hat{V}_{\text{middle}} = \text{no significance}$
Significance of real and imaginary roots	$\hat{V}_{\text{real}} = \hat{V}_{\text{gas}}$ $\hat{V}_{\text{imaginary}} = \text{no significance}$

| Virial equation of state

Description	Equations
Virial equation of state	$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \dots$
First order approx. of virial equation of state	$\frac{P\hat{V}}{RT} = 1 + \frac{BP}{RT}$
Reduced temperature	$T_r = \frac{T}{T_c}$
Reduced pressure	$P_r = \frac{P}{P_c}$

| Using virial equation of state

1. Lookup T_c, P_c, ω
2. Calculate T_r
3. Estimate B by

$$1. B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$2. B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$3. B = \frac{RT_c}{P_c}(B_0 + \omega B_1)$$

4. Substitute known values into first order approximation

| Redlick-Kwong (RK) equation of state

Description	Equations
SRK equation of state	$P = \frac{RT}{\hat{V} - b} - \frac{a}{T^{0.5}\hat{V}(\hat{V} + b)}$
Constants	$a = 0.4274R^2T_c^{2.5}/P_c$ $b = 0.08664RT_c/P_c$

| Soave-Redlick-Kwong (SRK) equation of state

Description	Equations
SRK equation of state	$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$
Constants	$a = 0.4274(RT_c)^2/P_c$ $b = 0.08664RT_c/P_c$ $m = 0.48508 + 1.55171\omega - 0.1561\omega^2$ $T_r = T/T_c$ $\alpha = [1 + m(1 - \sqrt{T_r})]^2$

| Using SRK equation of state

1. Lookup T_c, P_c, ω
2. Calculate a, b, m
3. Determine the known
 1. If known T, \hat{V}
 1. Calculate T_r, α
 2. Solve from equation directly for P
 2. If known T, P
 1. Use equation and all knowns
 2. Use python to solve for \hat{V}
 3. If known P, \hat{V}
 1. Use equation, T_r, α , and all knowns
 2. Use python to solve for T

| Compressibility-factor equation of state

Description	Equations
Compressibility (Law of corresponding state)	$z = \frac{P\hat{V}}{RT}$
Compressibility-factor equation of state	$P\hat{V} = zRT$
Reduced temperature	$T_r = \frac{T}{T_c}$
Reduced pressure	$P_r = \frac{P}{P_c}$
Ideal reduced volume	$\hat{V}_r^{\text{ideal}} = \frac{P_c \hat{V}}{RT_c}$
Kay's rule of nonideal gas mixtures Pseudocritical temperature	$T'_c = \sum y_i T_{ci}$
Pseudocritical pressure	$P'_c = \sum y_i P_{ci}$
Pseudoreduced temperature	$T'_r = \frac{T}{T'_c}$
Pseudoreduced pressure	$P'_r = \frac{P}{P'_c}$
Ideal pseudoreduced volume	$\hat{V}_r^{\text{ideal}} = \frac{P'_c \hat{V}}{RT'_c}$

| Using compressibility-factor equation of state

1. Lookup T_c, P_c
2. If gas is H_2/He , adjust critical constant by Newton's correlation
 1. $T_c^a = T_c + 8 \text{ K}$
 2. $P_c^a = P_c + 8 \text{ atm}$
3. Calculate reduced value of two known variables from $T_r, P_r, V_r^{\text{ideal}}$
4. Use compressibility chart to determine z
5. Solve for unknowns from equation

Multi-Phase System

| Vapor pressure estimations

Description	Equations
Clapeyron equation	$\frac{dP^*}{dt} = \frac{\Delta \hat{H}_v}{T} \frac{1}{\hat{V}_g - \hat{V}_l}$
Clapeyron equation	$\frac{d(\ln P^*)}{d(1/T)} = -\frac{\Delta \hat{H}_v}{R}$
Clausius-Clapeyron equation	$\ln P^* = -\frac{\Delta \hat{H}_v}{RT} + B$
Clausius-Clapeyron equation	$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta \hat{H}_v}{nR} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
Antoine equation (Vapor pressure of species)	$\log_{10} P^* = A - \frac{B}{T + C}$

| Vapor liquid equilibrium (VLE) calculations

Description	Equations
Gibbs phase rule	$\mathcal{F} = 2 + c - \Pi - r$
Total vapor pressure of immiscible liquids	$P = \sum P_i^*$
Raoult's law ★ Ideal gas and solution, non-dilute x_A	$P_A = y_A P = x_A P_A^*(T)$
Henry's law ★ Ideal gas and solution, dilute x_A	$P_A = y_A P = x_A H_A(T)$
VLE of real gases φ - fugacity coefficient γ - activity coefficient	$y_i \varphi_i P = x_i \gamma_i P^*$
Partition coefficient of ideal gas (Raoult's law) ★ Ideal gas: $\varphi = 1, \gamma = 1$	$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^*}{\varphi_i P} = \frac{P_i^*}{P}$
Partition coefficient of ideal gas (Henry's law) ★ Ideal gas, Henry's law assumptions	$K_i = \frac{H_i}{P}$

| Saturation and humidity

Description	Equations
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Description	Equations
Relative saturation/humidity	$s_r = \frac{P_A}{P_A^*(T)} \times 100$
Molal saturation/humidity	$s_m = \frac{P_A}{P - P_A}$
Absolute saturation/humidity	$s_a = \frac{P_A M_A}{(P - P_A) M_A}$
Percent saturation/humidity	$s_p = \frac{s_m}{s_m^*} \times 100\%$ $= \frac{P_A / (P - P_A)}{P_A^* / (P - P_A^*)} \times 100\%$

| Bubble and dew point

Description	Equations
Superheated vapor	$P_A = y_A P < P_A^*(T)$
Saturated vapor and dew point	$P_A = y_A P = P_A^*(T_{dp})$
Degree of superheat	$T - T_{dp}$
Bubble point temperature of mixture at constant P	$P = \sum x_i P_i^*(T_{bp})$
Bubble point pressure of mixture at constant T	$P_{bp} = \sum x_i P_i^*(T)$
Dew point temperature of mixture at constant P	$\sum \frac{y_i}{P_i^*(T_{dp})} = 1$
Dew point pressure of mixture at constant T	$P_{dp} = \left[\sum \frac{y_i}{P_i^*(T)} \right]^{-1}$

Fundamentals of Energy Balances

| Closed system balance

Description	Equations
Kinetic energy	$E_k = \frac{1}{2} m v^2$
Potential energy	$E_p = m g z$
Internal energy	$U(T, V)$
Total energy	$E = U + E_k + E_p$
Work	$W = P \Delta V$
Closed system balance	$\Delta U + \Delta E_k + \Delta E_p = Q + W$
$\Delta E_k = 0$	Not accelerating
$\Delta E_p = 0$	Not changing height
$\Delta U = 0$	No phase change, chemical reaction, temperature change
$Q = 0$	Insulated system; adiabatic; temperature of system and surrounding the same
$W = 0$	No moving parts, radiation, electric current, flow

| Open system balance

Description	Equations
Work	$\dot{W} = \dot{W}_s + \dot{W}_{fl}$
Enthalpy	$H = U + PV$
Specific properties	$\hat{V} = \frac{V}{m}, \hat{V} = \frac{V}{n}$
Open system balance	$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} + \dot{W}_s$
$\Delta E_k = 0$	No acceleration; linear velocity of all streams the same
$\Delta E_p = 0$	Stream entering and leaving at same height
$\dot{Q} = 0$	Insulated; adiabatic; system and surrounding temperature the same
$\dot{W}_s = 0$	No moving parts
Friction loss	$\hat{F} = \Delta \hat{U} - \frac{\dot{Q}}{\dot{m}}$
Mechanical energy balance	$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + \hat{F} = \frac{\dot{W}_s}{\dot{m}}$
Bernoulli equation ★ $\hat{F} = 0, \dot{W}_s = 0$	$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z = 0$

Energy Balances in Nonreactive Processes

| Isothermal process

Description	Equations
Internal energy	$\Delta U = \begin{cases} = 0 & \text{(ideal gas)} \\ \approx 0 & \text{(real gas) } P < 10 \text{ bar} \\ \neq 0 & \text{(real gas) } P > 10 \text{ bar} \\ \approx 0 & \text{(condensed phases)} \end{cases}$
Enthalpy	$\Delta H = \begin{cases} = 0 & \text{(ideal gas)} \\ \approx 0 & \text{(real gas) } P < 10 \text{ bar} \\ \neq 0 & \text{(real gas) } P > 10 \text{ bar} \\ \approx \hat{V}\Delta P & \text{(condensed phases)} \end{cases}$

| Non-isothermal process

Use (hypothetical) process paths to guide the use of equations.

Description	Equations
Heat capacity at constant volume	$C_V(T) = \left(\frac{\partial \hat{U}}{\partial T} \right)_V$
Heat capacity at constant pressure	$C_P(T) = \left(\frac{\partial \hat{H}}{\partial T} \right)_P$
Heat capacity correlation	$C_P(T) = a + bT + cT^2 + dT^3$
Heat capacity relation of condensed phases	$C_P \approx C_V$

Description	Equations
Heat capacity relation of ideal gas	$C_P = C_V + R$
Heat capacity of monoatomic ideal gases	$C_V = \frac{3}{2}R, C_P = \frac{5}{2}R$
Heat capacity of polyatomic ideal gases	$C_V = \frac{5}{2}R, C_P = \frac{7}{2}R$
Kopp's rule Heat capacity of compound (table B.10)	$C_{P,\text{compound}} = \sum \nu_i C_{P,i}$
Kopp's rule Heat capacity of mixture	$C_{P,\text{mix}} = \sum y_i C_{P,i}(T)$
Change in internal energy at changing temperature	$\Delta \hat{U} = \int_{T_1}^{T_2} C_V(T) dT$
Change in enthalpy at changing temperature	$\Delta \hat{H} = \int_{T_1}^{T_2} C_P(T) dT$

| Phase change process

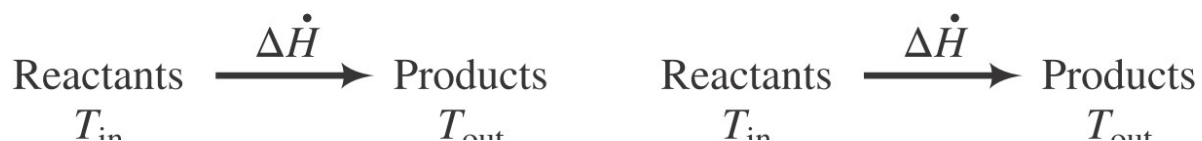
Description	Equations
Latent heat approximation of condensed phases	$\Delta U \approx \Delta H$
Latent heat approximation of ideal gas	$\Delta U_v \approx \Delta H_v - RT$

Energy Balances in Reactive Processes

| Heat of Reactions

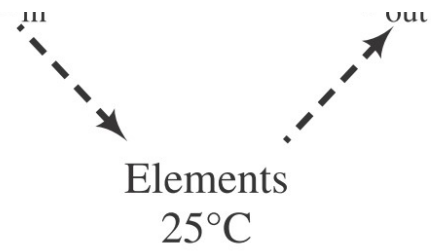
Description	Equations
Heat of reaction of batch process	$\Delta H = \xi \Delta H_{\text{rxn}}(T_1, P_1)$
Heat of reaction of continuous process	$\Delta \dot{H} = \xi \Delta \dot{H}_{\text{rxn}}(T_1, P_1)$
Endothermic reaction	$\Delta H_{\text{rxn}} > 0$
Exothermic reaction	$\Delta H_{\text{rxn}} < 0$
Hess's law and heat of formation "product minus reactant"	$\Delta H_{\text{rxn}}^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ$
Heat of formation conventions	$\Delta \hat{H}_f^\circ(\text{elemental}) = 0$
Hess's law and heat of combustion "reactant minus product"	$\Delta H_{\text{rxn}}^\circ = - \sum_i \nu_i \Delta \hat{H}_{c,i}^\circ$
Heat of combustion conventions	$\Delta \hat{H}_c^\circ(\text{O}_2) = 0$ $\Delta \hat{H}_c^\circ(\text{combustion product}) = 0$ combustion product: CO ₂ , H ₂ O, SO ₂ , N ₂
Internal energy of reaction (product $\nu > 0$; reactant $\nu < 0$)	$\Delta U_{\text{rxn}} = \Delta H_{\text{rxn}} - RT \sum_{\text{gas}} \nu_i$

| Enthalpy change of reactions





(a) Process path for heat of reaction method



(b) Process path for heat of formation method

Reaction process paths. (Elementary Principles of Chemical Processes 4e by Felder et al. p507.)

Description	Equations
Enthalpy change of heat of reaction method	$\Delta \dot{H} = \sum_{\text{rxn}} \xi \Delta H_{\text{rxn}}^{\circ} + \sum \dot{n}_{\text{out}} \hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \hat{H}_{\text{in}}$
Enthalpy change of heat of formation method	$\Delta \dot{H} = \sum \dot{n}_{\text{out}} \hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \hat{H}_{\text{in}}$