

Foundational Knowledge for ChemE 100

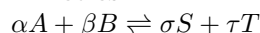
Disclaimer: you are in the engineering department. Truth is dead. Approximation reigns.
Advice: draw a diagram. It helps.

Chemistry

Conservation laws

- Mass
- Energy
- Momentum

Kinetics



Equilibrium constant:

$$K_{eq} = \frac{[S]^\sigma + [T]^\tau}{[A]^\alpha + [B]^\beta} = \exp\left(-\frac{E_a + T\Delta S}{RT}\right) \approx \exp\left(-\frac{E_a}{RT}\right)$$

Conversion factors

You can always multiply by 1.

If $1 x = 10 y$, then $\frac{1x}{10y} = \frac{10y}{1x} = 1$.

Reactions

Exothermic if $\Delta H_r^\circ < 0$

Endothermic if $\Delta H_r^\circ > 0$

Stoichiometry

Compounds are mixtures of integer numbers of atoms.

Reactions can be written with integer number of compounds.

Rate and rate constant:

$$r = k[A]^m[B]^n = A \exp\left(-\frac{E_a}{RT}\right)[A]^m[B]^n$$

Phases, States, and Transitions

Definitions:

Point: (n) A specific temperature, pressure, and composition.

Phase: (n) A distinct and homogeneous form of matter.

State: (n) The particular condition of a region of matter.

Points:

Melting point: a point where the state transitions between solid and liquid.

Boiling point: a point where the state transitions between liquid and gas.

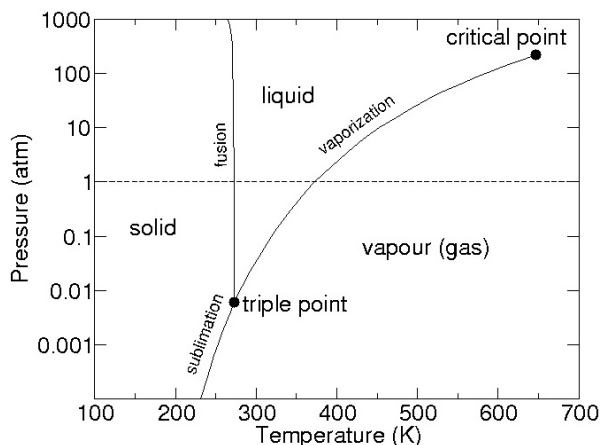
Sublimation point: a point where the state transitions between solid and gas.

Bubble point: a point where all liquid transitions into vapor.

Dew point: a point where some vapor transitions into liquid.

Triple point: a point where solid, liquid, and gas can exist.

Critical point: a point where liquid and gas have the same properties.



Left, image of H₂O PT phase diagram.
Credit: Western University, Canada.

Phase Diagrams

(I) Gibb's Phase Rule

For a given overall composition at one point (P,T) there is exactly one equilibrium composition and distribution between phases. This can be formatted as a diagram.

(II) PT Diagrams

PT diagrams give a qualitative description of system behavior. For a given overall composition, plot the phases present. Regions are drawn around areas with the same phases present.

Transition points are on lines in the chart. Tables also contain this data of melting point, boiling point, triple point, and critical point.

(III) XY Diagrams

XY diagrams give a quantitative description of system behavior. For a given P xor T, for the phases present at a given composition and T xor P. Regions are drawn around areas with the same phases present.

Transition points are horizontal lines on the chart at one temperature and pressure. The lever rule for an overall composition allows computation of phase fractions and compositions.

Physics

Mechanics:

$$\vec{v} = \frac{dx}{dt}$$

$$\vec{a} = \frac{d\vec{v}}{dt} = \frac{d^2x}{dt^2}$$

$$\vec{p} = m\vec{v}$$

$$F = \frac{d\vec{p}}{dt} = m \frac{d^2x}{dt^2} = m\vec{a}$$

Energy:

$$g \approx 9.8066 \frac{\text{m}}{\text{s}^2} = 32.174 \frac{\text{ft}}{\text{s}^2}$$

$$K = \frac{1}{2} m \|\vec{v}\|^2$$

$$U = mgx$$

$$W = \int_{x_1}^{x_2} F dx$$

Fluids:

Ideal gas law:

$$PV = nRT$$

Bernoulli Equation:

$$P_1 + \frac{1}{2} \rho v_1^2 + \rho g h_1 = P_2 + \frac{1}{2} \rho v_2^2 + \rho g h_2$$

Math

Geometry:

$$\pi = 3.14159$$

$$\sin = \frac{\text{opposite}}{\text{hypotenuse}}$$

$$\cos = \frac{\text{adjacent}}{\text{hypotenuse}}$$

$$\tan = \frac{\text{opposite}}{\text{adjacent}}$$

$$A_{\text{circle}} = \pi r^2$$

$$V_{\text{sphere}} = \frac{4\pi}{3} r^3$$

$$V \equiv \int_{x_0}^{x_1} A(x) dx$$

Euler's formula:

$$e^{ix} = \cos(x) + i \sin(x)$$

Algebra:

$$e = 2.71828$$

$$a \cdot x^2 + b \cdot x + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$y = m \cdot x + b$$

$$e^{\ln(x)} = x$$

With a system of m linear equations and n variables x_i , ($m \geq n$), the solutions are displayed in

$$\text{rref} \left(\begin{array}{cccc|c} x_1 & x_2 & \dots & x_n & \text{consts} \\ a_{11} & a_{21} & \dots & a_{n1} & c_1 \\ a_{12} & a_{22} & \dots & a_{n2} & c_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ a_{1m} & a_{2m} & \dots & a_{nm} & c_m \end{array} \right)$$

Differential Equations:

Separable:

$$f(y)y' = f(x)$$

$$\int f(y) dy = \int f(x) dx$$

Bernoulli:

$$y' + p(x)y - q(x) = 0$$

$$y = e^{-\int p(x) dx} \int e^{\int p(x) dx} q(x) dx$$

Linear second order with constant coefficients:

$$y'' + ay' + by = 0$$

$$\lambda_1^2 = \frac{-a \pm \sqrt{a^2 - 4b}}{2}$$

$$y = c_1 e^{\lambda_1 t} + c_2 e^{\lambda_2 t}$$

Chemical Engineering

Additivity:

$$\sum_i^n x_i = \sum_i^n y_i = 1$$

Conservation:

$$m_{\text{out}} = m_{\text{in}} - m_{\text{accu}}$$

Flow Rates:

m , mass; x_i mass fraction; y_i molar fraction; V volume; M molecular weight; N moles

$$\frac{dm_i}{dt} = x_i \rho \frac{dV}{dt} = M y_i \frac{dN}{dt}$$

$$\frac{dn_i}{dt} = y_i \frac{\rho}{M} \frac{dV}{dt} = y_i \frac{dN}{dt}$$

Factors for Reaction Rate:

Chemical:

- Reactants
- Catalysts

Kinetic:

- Concentration
- Temperature
- Pressure

Geometric:

- State
- Surface Area

Chapter 4: Fundamentals of Material Balances

Draw boxes for balances around units, loops, or the whole system.

Flow fractions can be presented as volume, mass, or molar flow rates.

x_i mass fraction, or mole fraction in the liquid phase

y_i mole fraction, or mole fraction in the vapor phase

Conversion:

$$n_{\text{out}} = n_{\text{in}} + \beta \xi$$

Degrees of Freedom:

$$\text{DF} = \# \text{ of variables} - \# \text{ of equations}$$

Percent:

$$\text{fraction} \times 100\% = \text{percent}$$

Chapter 5: Single Phase Systems

Compressibility factor equation of state:

The ideal gas law is an approximation. There are real gas laws, but they are complicated, and are approximations too. The compressibility factor is a simple correction.

$$PV = z \cdot nRT$$

The critical temperature, T_c , and the critical pressure, P_c , are tabulated for compounds.

Newton's corrections (for non-ideal behavior):

$$T_{c,H_2}^* = T_{c,H_2} + 8 \text{ K and } T_{c,He}^* = T_{c,He} + 8 \text{ K}$$

$$P_{c,H_2}^* = P_{c,H_2} + 8 \text{ atm and } P_{c,He}^* = P_{c,He} + 8 \text{ atm}$$

Kay's rule for a n -chemical system:

$$T_c' = \sum_i^n y_i T_{c,i} \text{ and } P_c' = \sum_i^n y_i P_{c,i}$$

The reduced temperature is, $T_r = \frac{T}{T_c}$, and the reduced pressure is, $P_r = \frac{P}{P_c}$.

The law of corresponding states claims that all gasses have the same compressibility factor, z , at the same T_r , and P_r .

The z value can be found from a graph of z as a function of P_r , with T_r isotherms drawn.

Multiphase additivity:

$$P = \sum_i^n y_i P = \sum_i^n p_i = \sum_i^n x_i p_i^*(T)$$

Absolute temperature:

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

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

Gas constants:

$$\begin{aligned} R &= 8.31446 \frac{\text{J}}{\text{mol K}} \\ &= 10.7316 \frac{\text{ft}^3 \text{ psi}}{\text{lb-mol } ^{\circ}\text{R}} \\ &= 0.0820575 \frac{\text{L atm}}{\text{mol K}} \end{aligned}$$

Standard Molar Volume:

$$1 \text{ atm} = 14.5959 \text{ psi}$$

$$273.15 \text{ K} = 459.67 ^{\circ}\text{R}$$

$$\hat{V}_s = 22.4 \frac{\text{L}}{\text{mol}} = 359 \frac{\text{ft}^3}{\text{lb-mol}}$$

Chapter 6: Multiphase Systems

Clausius-Clapeyron relation: Antoine equation:

A linear relationship that can be used to find a desired T or vapor pressure p^* if given two T/p^* pairs. Units may be $^{\circ}\text{C}$ and mmHg.

$$\ln(p^*) = -\frac{\Delta \hat{H}_v}{R} \left(\frac{1}{T} \right) + B$$

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

Raoult's law:

A relation that coordinates partial pressure, to vapor molar fraction and total pressure, to liquid molar fraction and vapor pressure at equilibrium.

$$p_i = y_i P = x_i p_i^*(T)$$

Bubble point:

The conditions where the first bubble of vapor forms from a liquid.

Temperature from Raoult's law, P given:

$$p_i = x_i p_i^*(T_{bp}) \text{ or } P = \sum_i^n x_i p_i^*(T_{bp})$$

Pressure from Raoult's law, y_i and T given:

$$P_{bp} = \frac{p_i}{y_i} = \frac{x_i p_i^*(T)}{y_i} \text{ or } \frac{1}{P_{bp}} = \sum_i^n \frac{y_i}{p_i^*(T)}$$

Dew point:

The conditions where the first droplet of liquid forms from a vapor.

Temperature from Raoult's law, x_i and P given:

$$p_i = x_i p_i^*(T_{dp}) \text{ or } P = \sum_i^n x_i p_i^*(T_{dp})$$

Pressure from Raoult's law, T given:

$$P_{dp} = \frac{x_i p_i^*(T)}{y_i} \text{ or } \frac{1}{P_{dp}} = \sum_i^n \frac{y_i}{p_i^*(T)}$$

Chapter 7: Energy and Energy Balances

Energy is neither created nor destroyed. Yet it is expensive, because it is useful, and hard to harness.
 1 kWh = \$0.12 energy 1 kg electronic grade silicon = \$50 energy 1m³ concrete = \$400 energy

Units:

Energy - 1 kJ = 239 cal = 0.239 kcal = 0.948 btu = 738 ft lb_f
 Power, ($P = E/T$) - 1 kW = 1.34 hp = 2.66E6 ft lb_f/hr

Properties:

Extensive - a property proportional to amount.
 Intensive - a property independent of amount.

Systems:

Closed - A system with no material flows. Use material totals.
 Open - A system with material flows. Use material flow rates.

Notation:

Hat, as in: \hat{V} , \hat{U} , \hat{H} , indicates a specific property.
 Dot, as in: \dot{W} , \dot{Q} , \dot{H} , indicates a flow rate.

Types of Energy:

Kinetic - $\dot{E}_k = \frac{1}{2}\dot{m}z^2$
 Potential - $\dot{E}_p = \dot{m}gz$
 Internal - U - chemical, phase, state, temperature

Reference States:

For your system, choose a temperature and pressure. Set these conditions as the zero for internal energy or enthalpy. You can choose a reference state to make calculations easier. Often choosing the conditions specified by a table, or those of one stream in a process simplify calculations.

Special Cases:

Isothermal - constant temp.
 Isobaric - constant pressure.
 Isochoric - constant volume.
 Adiabatic - no heat transfer.
 No work - no work performed.

First Law:

Accumulation = In - Out
 In and out are heat or work
 Heat = thermal energy flow
 Work = mechanical energy flow

Flow Enthalpy:

$$\Delta \dot{H} = \sum_i^{out} n_i \hat{H}_i - \sum_j^{in} n_j \hat{H}_j$$

Closed:

$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$

Open:

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

Mechanical:

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

Chapter 8: Balances on Nonreactive Processes

Appendix B of Felder and Rousseau contains: some data for internal energies and enthalpies of steam and gasses, the melting points, boiling points and enthalpies of many compounds, and a few enthalpies of mixing.

Theoretical Process Paths:

Because energies are path independent, any path between temperatures, pressures, phases and compositions can be considered. Paths may be chosen to be easily computable.

Tables:

May tabulate energy data for a given substance or mixture, temperature, pressure and phase relative to some reference condition.

Equations:

Approximate energy differences between conditions. Equations are only true for certain assumptions: check that they are fulfilled.

$$P_i, T_i, S_i \xrightarrow[\text{solids and liquids: } \Delta \hat{H} = \hat{V} \Delta P]{\text{ideal gasses: } \Delta \hat{U} \approx 0, \Delta \hat{H} \approx 0} P_f, T_i, S_i$$

$$P_i, T_i, S_i \xrightarrow[\text{solids/liquids: } \Delta \hat{H} = \Delta \hat{H}_{fus}(T, P)]{\text{liquids/gasses: } \Delta \hat{H} = \Delta \hat{H}_{vap}(T, P)} P_i, T_i, S_f$$

$$P_i, T_i, S_i \xrightarrow[\text{solids/liquids: } \Delta \hat{H} = \hat{V} \Delta P + \int_{T_1}^{T_2} C_P(T) dT]{\text{ideal gasses: } \Delta \hat{H} = \int_{T_1}^{T_2} C_P(T) dT} P_i, T_f, S_i$$

$$n_\alpha(P_\alpha, T_\alpha, S_\alpha) + n_\beta(P_\beta, T_\beta, S_\beta) \rightarrow \frac{\Delta \hat{H} = \Delta \hat{H}_{soln}(T, r)}{\text{where: } r = n_\alpha/n_\beta} n_{mix}(P_{mix}, T_{mix}, S_{mix})$$

Chapter 9: Balances on Reactive Processes

Reference conditions: the point of a known heat of reaction is often a simplifying choice.
 Theoretical process paths can be drawn between chemical species: i.e. reactions can be added.

Hess's Law:

$$\Delta \hat{H}_r^\circ = \sum_i^{prod} \nu_i \hat{H}_f^\circ - \sum_i^{react} \nu_i \hat{H}_f^\circ$$

Combustion:

$$\Delta \hat{H}_r^\circ = \sum_i^{react} \nu_i \hat{H}_c^\circ - \sum_i^{prod} \nu_i \hat{H}_c^\circ$$

Internal Energy:

Ideal gas: $\Delta \hat{U}_r \approx \Delta \hat{H}_r$
 Solid/liquid: $\Delta \hat{U}_r = \Delta \hat{H}_r + RT(\sum_i^{react} \nu_i - \sum_i^{prod} \nu_i)$