ChBE 11: Chemical Engineering Thermodynamics

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1 Measured Thermodynamic Properties and Other Basic Concepts

1.1 Preliminary Concepts - The Language of Thermo

- The **system** is the space of interest while the **surroundings** are everything else (together, system and surroundings compose the **universe**)
  - A **system boundary** separates the system and surroundings
- An **open system** is defined as one that has both mass and energy flowing across a boundary
  - The system boundary of an open system is called the **control volume**
- An **isolated system** has neither mass nor energy flowing across a boundary
- A **closed system** has no mass flowing across a boundary but energy can go through the boundary
- **Extensive properties** depend on the size of the system while **intensive properties** do not
- The **state** is the condition in which we find a system at any given time and is defined by its intensive properties
  - A **process** brings the system from one state to another
- **Adiabatic processes** have no heat transfer, **isothermal processes** have constant temperature, **isobaric processes** have constant pressure, and **isochoric processes** have constant volume
- **State functions** depend only on the state itself while path functions depend on the path taken

1.2 Measured Thermodynamic Properties

- The intensive forms of volume, are as follows:

$$v = \frac{V}{n}$$

$$\hat{v} = \frac{V}{m} = \rho^{-1}$$

- Pressure is defined as,

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

- For pressure of an ideal gas,

$$P = \frac{nRT}{V} = \frac{RT}{v}$$

1.3 Equilibrium

- **Equilibrium** is when a state has uniformity with temperature and pressure, does not change with time, does not spontaneously leave equilibrium, and has no net driving force for change (cannot be for open systems)
  - If the system is free from forced flows, it will eventually achieve equilibrium
  - The $P_{liq} = P_{vap}$ and $T_{liq} = T_{vap}$ with more than one phase present with no tendency to change
- If the system is **stable**, it will return to its original state when a small disturbance is imposed on it
- If the state of an open system does not change with time as it undergoes a process, it is said to be at **steady-state** (not at equilibrium due to net driving force)
  - A steady-state may have temperature and pressure gradients; however, the state cannot change with time
- **Mechanical equilibrium** occurs when there is a pressure balance

1.4 Independent and Dependent Thermodynamic Properties

- The **state postulate** indicates that an intensive property of a pure substance can be determined from two independent intensive properties (e.g. Temperature and Pressure)
- For an extensive property, one more specification, specifically the size of the system, must be determined
- To find the degrees of freedom, $\mathscr{F}$, the Gibbs phase rule can be used, where m is the number of components and π is the number of phases:

$$\mathscr{F} = m - \pi + 2$$

1.5 The PvT Surface and its Projections for Pure Substances

- The temperature at which a pure substance boils is also known as the **saturation temperature**
  - At 1 atm, this is the **normal boiling point**
- The critical isotherm line has $\left(\frac{\partial P}{\partial v}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$ where it goes through an inflection point
- A gas is any form of matter that fills its container while a vapor is a gas that will condense to a liquid if isothermally compressed
- The **saturation pressure** occurs when the rate of vaporization equals the rate of condensation for one species whereas the **vapor pressure** is the pressure of a single component in a vapor mixture
- A **subcooled liquid** is the state where pressure and temperature are independent properties
- A **saturated liquid** is when the liquid is "ready" to boil; any more energy input will lead to a bubble of vapor
- A **saturated vapor** is the point at which any energy that is removed would cause a drop of liquid to condense
- A **superheated vapor** exists at a higher temperature than the saturated vapor

1.6 Thermodynamic Property Tables

- The reference state used for steam tables is as a liquid at the triple point of water where internal energy and entropy are defined as zero

1.7 Lever Rule

- The **Lever Rule** states the following where the subscripts of l and v indicate the liquid and gas phases, respectively, of a mixture:

$$\text{Fraction of Vapor} = \text{Quality} = x = \frac{n_V}{n_l + n_V} = \frac{v - v_l}{v_v - v_l}$$

- As such,

$$v = x v_v + (1 - x)\, v_l$$

2 The First Law of Thermodynamics

2.1 The First Law of Thermodynamics

- The First Law states

$$\Delta E_{univ} = 0 \therefore \Delta E_{sys} + \Delta E_{surr} = 0$$

- The macroscopic kinetic energy is

$$E_K = \frac{1}{2} m \vec{V}^2$$

- The macroscopic potential energy is
$$E_P = mgz$$
- The physical definition of work is,
$$W = \int \overrightarrow{F}_E \cdot d\overrightarrow{x}$$
- Therefore, work is given by
$$w = -\int P_E \, dV$$
- A change in temperature, change in phase, and/or chemical reaction can indicate a change in U for a given chemical system
- For an ideal gas, the internal energy depends only on its molecular kinetic energy component
  - Thus, U is only a function of temperature for an ideal gas; however, for a real gas it needs a second intensive property
- Shaft work, W_S, is considered as everything that's work besides PV-work

2.2 Reversible and Irreversible Processes

- A process is **reversible** if the system can be returned to its original state without any net effect on the surroundings
- The efficiency of expansion is given by
$$\eta_{exp} = \frac{W_{irrev}}{W_{rev}}$$
- The efficiency of compression is given by
$$\eta_{comp} = (\eta_{exp})^{-1} = \frac{W_{rev}}{W_{irrev}}$$
- The system pressure can only equal the external pressure if and only if the process is reversible (and thus $w = -P\int dv$ can be used when pressure is constant)

2.3 The First Law of Thermodynamics for Closed Systems

- For a closed system,
$$\Delta U = Q + W$$
- On a differential basis,
$$dU = \delta Q + \delta W$$
- Additionally,
$$\frac{dU}{dt} = \dot{Q} + \dot{W}$$
- For an isolated system, $\Delta U = 0$ when ignoring potential and kinetic energy changes

2.4 The First Law of Thermodynamics for Open Systems

- A mole balance can be written as the following for a nonreacting system at steady-state,
$$\sum_{in} \dot{n}_{in} = \sum_{out} \dot{n}_{out}$$
- **Flow work** is the work the inlet fluid must do on the system to displace fluid within the system so that it can enter
  - The rate of flow work is given by
$$\left(\dot{W_{flow}}\right)_{in} = \dot{n}_{in} \left(Pv\right)_{in}$$

$$\dot{W} = \dot{W}_S + \dot{W}_{flow} = \left[\sum_{in} \dot{n}_{in} \left(Pv \right)_{in} - \sum_{out} \dot{n}_{out} \left(-Pv \right)_{out} \right]$$

- Enthalpy is defined as

$$h \equiv u + Pv$$

- The open system has the following balance

$$\frac{d}{dt} \left(U + E_K + E_P \right) = \sum_{in} \dot{n}_{in} \left[h + e_K + e_P \right]_{in} - \sum_{out} \dot{n}_{out} \left[h + e_K + e_P \right]_{out} + \dot{Q} + \dot{W}_S$$

- For steady-state, the left hand-side of the equation is zero
- Neglecting e_K and e_P for the inlet and outlet since the changes are small compared to internal energy

2.5 Thermochemical Data for U and H

- Heat capacity at constant volume is defined as,

$$c_v(T) \equiv \left(\frac{\partial u}{\partial T} \right)_v$$

- Therefore, at constant volume[1] for a single phase,

$$\Delta u = \int_{T_1}^{T_2} c_v \, dT = q_v$$

- Heat capacity at constant pressure is defined as,

$$c_P(T) \equiv \left(\frac{\partial h}{\partial T} \right)_P$$

- Additionally, at constant pressure for a single phase,

$$\Delta h = \int_{T_1}^{T_2} c_P \, dT = q_P$$

- For solids and liquids,

$$c_p \approx c_v$$

- For ideal gases,

$$c_P - c_v = R$$

- Using the stoichiometric coefficient of ν_i, standard[2] enthalpy of reaction is

$$\Delta h^\circ_{rxn} = \sum \nu_i \left(\Delta h^\circ_f \right)_i$$

- Note that air consists of 79 mol% $N2$ and 21 mol% $O2$
- Adiabatic flame temperature (T_{ad}) is the maximum temperature a reactor can reach for the combustion of a given fuel at constant pressure
  - Therefore, $\Delta H = Q = 0$; however, to calculate enthalpy changes, one can use this equivalent pathway:

$$0 = \Delta H^\circ_{rxn} + \sum n_i \int_{298.15K}^{Tad} c_{p,i}(T) \, dT$$

[1] The integrand limits must have absolute temperature units
[2] $^\circ \equiv 298\text{K}$ and 1bar

    * The heat of reaction for a pure substance at 25° is defined as 0

- The heat of reaction at any temperature is,

$$\Delta h_{rxn}(T) = \Delta h^{\circ}_{rxn} + \int_{298.15K}^{T} \left[\sum_{products} \nu_i c_{p,i}(T) \right] dT$$

- For other processes, including reversible isothermic processes and adiabatic expansions, see **Subsection 2.8**

2.6 Open-System Steady State Energy Balance on Process Equipment

- Cross-sectional area and velocity are related by,

$$A_1 \overrightarrow{V}_1 = A_2 \overrightarrow{V}_2$$

- Nozzles and diffusers rely on a change in the cross-sectional area to decrease the bulk flow velocity; therefore, the input stream's velocity (kinetic energy) is important to consider but the potential energy for both streams can be removed. Also, $\dot{W}_S$ and $\dot{Q}$ is typically zero. As such, since $\Delta \dot{n} = 0$ at steady state,

$$(h + e_K)_{in} = (h + e_K)_{out}$$

- Turbines and pumps (compressors) utilize shaft work. Turbines have work put out, and pumps have work put into the system. $\dot{Q}$ is typically set to zero. As such,

$$\frac{\dot{W}_S}{\dot{n}} = \Delta \left(h + e_K + e_P \right)$$

- A heat exchanger converts between Δh and Q. There is no shaft work, no change in kinetic or potential energy, so,

$$\frac{\dot{Q}}{\dot{n}} = \Delta h$$

- Throttling devices have no heat loss ($\dot{Q}$) due to the small amount of time in the device and have no shaft work. They decrease the pressure of a stream to liquify a real gas. As such,

$$\Delta h = 0$$

2.7 Thermodynamics and the Carnot Cycle

- The steps of a Carnot cycle are as follows: Isothermal expansion, adiabatic expansion, isothermal compression, and then adiabatic compression back to state one
- Since this is a cycle, $\Delta U = 0$ and therefore $-W_{net} = Q_{net}$
- The efficiency of a cycle is defined as,

$$\eta \equiv \frac{\text{net work}}{\text{heat absorbed from hot reservoir}} = \frac{W_{net}}{Q_H} = 1 - \frac{T_C}{T_H}$$

- The coefficient of performance of a refrigeration cycle is,

$$\text{COP} = \frac{Q_C}{W_{net}}$$

2.8 Summary of Calculating First Law Quantities at Steady-Sate when Shaft-Work, Kinetic Energy, and Potential Energy are Ignored for an Ideal Gas

- Always start with writing these three equations down:
  1. $W = -\int_{V_1}^{V_2} P\,dV$
  2. $\Delta U = Q + W$
  3. $\Delta H = \Delta U + \Delta\left(PV\right)$
  4. $dU = C_V\,dT$
  5. $dH = C_P\,dT$
- If it's a perfect gas, write these three down as well:
  1. $C_P - C_V = nR$
  2. $\Delta H = \int_{T_1}^{T_2} C_P\,dT$
  3. $\Delta U = \int_{T_1}^{T_2} C_V\,dT$

2.8.1 Constant Pressure (Isobaric) Heating

1. P is constant, so $W = -P\Delta V$
2. $\Delta H = Q_P = \int_{T_1}^{T_2} C_P\,dT$

2.8.2 Constant Volume (Isochoric) Heating

1. $W = 0$
2. $\Delta U = \int_{T_1}^{T_2} C_V\,dT = Q_V$
3. $\Delta H = \Delta U + V\Delta P$
   (a) Alternatively, $\Delta H = Q_P = \int_{T_1}^{T_2} C_P\,dT$

2.8.3 Adiabatic Flame Temperature (Isobaric/Adiabatic)

1. $\Delta H = Q = 0 = \Delta H^\circ_{rxn} + \sum n_i \int_{298.15K}^{Tad} c_{p,i}(T)\,dT$
2. For an alternate pathway, calculate Δh°

2.8.4 Reversible Isothermal Process in a Perfect Gas

1. $\Delta U = \Delta H = 0$
2. Rearrange the ideal-gas equation to solve for $P = \dfrac{nRT}{V}$ and substitute into the work equation to get $W = -nRT\ln\left(\dfrac{V_2}{V_1}\right) = nRT\ln\left(\dfrac{P_2}{P_1}\right)$
3. $Q = -W$

2.8.5 Reversible Adiabatic Process in a Perfect Gas with Constant Heat Capacity

1. $Q = 0$ and $\Delta U = W$
2. $\Delta U = \int_{T_1}^{T_2} C_V \, dT$
3. $\Delta H = \int_{T_1}^{T_2} C_P \, dT$
4. The final state of the gas can be found by one of the following three methods[3]:
   (a) $\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{R/c_V}$
   (b) $\left(\dfrac{P_1}{P_2}\right)^{R} = \left(\dfrac{T_1}{T_2}\right)^{c_P}$
   (c) $P_1 V_1^k = P_2 V_2^k$
      i. $k \equiv \dfrac{c_P}{c_V} \qquad (k > 1)$
         A. A process is called **polytropic** when $\gamma = k = 1$
5. To apply step 4 as one equation, we have, $\Delta U = W = \dfrac{1}{k-1}\left(P_2 V_2 - P_1 V_1\right) = \dfrac{nR}{k-1}\Delta T$

2.8.6 Adiabatic Expansion of a Perfect Gas into a Vacuum

1. $Q = W = \Delta U = \Delta H = 0$

2.8.7 Reversible Phase Change at Constant T and P

1. Q is the measured latent heat of the phase change
2. $W = -P\Delta V$
   (a) ΔV can be calculated from the densities of the two phases
   (b) If one phase is a gas, $PV = nRT$ can be used
3. $\Delta H = Q_p$
4. $\Delta U = Q + W$

[3]Note: $PV = nRT$ can be used for initial state if need be

3 Entropy and the Second Law of Thermodynamics

3.1 Directionality of Processes/Spontaneity

- Irreversible processes are distinct and show directionality
- Reversible processes do not show directionality and represent the maximum work

3.2 Entropy - The Thermodynamic Property

- Entropy is defined in terms of the heat absorbed during a hypothetical reversible process:

$$ds \equiv \frac{\delta q_{rev}}{T}$$

- Integrating yields,

$$\Delta s = \int_{q_1}^{q_2} \frac{\delta q_{rev}}{T}$$

- Also,

$$\Delta s_{univ} = \Delta s_{sys} + \Delta s_{surr}$$

- It is safe to say that

$$\Delta s_{univ} \geq 0$$

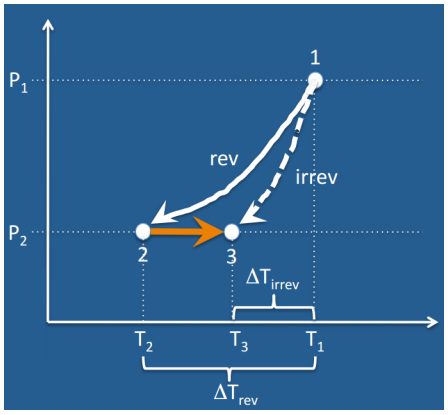
3.3 Proofs of Entropic Reversibility and Irreversibility

3.3.1 Reversible Adiabatic Ideal Gas Expansion/Compression

- Since $q_{rev} = 0$, $\Delta s_{sys} = \Delta s_{surr} = \Delta s_{univ} = 0$

3.3.2 Irreversible Adiabatic Ideal Gas Expansion

- A reversible pathway must be created to calculate the entropy change (see graph[4])

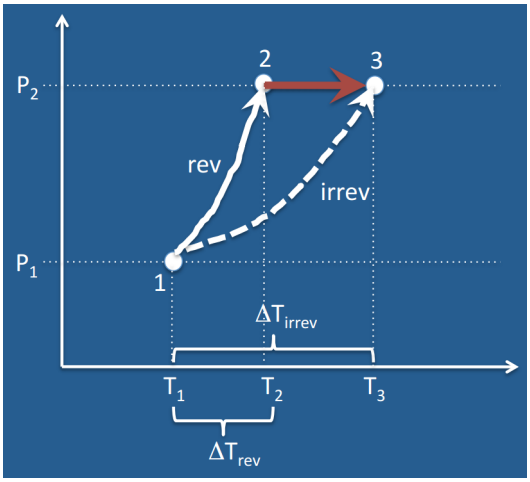


- Since reversible processes represent ideal cases, $|w_{rev}| > |w_{irrev}|$, $|\Delta u_{rev}| > |\Delta u_{irrev}|$, and $|\Delta T_{rev}| > |\Delta T_{irrev}|$
- For the reversible adiabatic portion, $\Delta s_{sys} = 0$. To calculate the irreversible value, the additional reversible isobaric pathway $(2 \rightarrow 3)$ is hypothetically considered. As such, for $2 \rightarrow 3$: $q_{rev} = \Delta h \equiv \int_2^3 c_P(T)\, dT > 0 \therefore \Delta s_{sys} = \Delta s_{univ} > 0$

[4] Property of Prof. Panzer

3.3.3 Irreversible Adiabatic Ideal Gas Compression

- A reversible pathway must be created to calculate the entropy change:



- Contrastingly to **3.2.2**, $|w_{rev}| < |w_{irrev}|$, $|\Delta u_{rev}| < |\Delta u_{irrev}|$, and $|\Delta T_{rev}| < |\Delta T_{irrev}|$ since compression effectiveness is based on minimizing that amount of work put into the system
- However, an analogous reversible isobaric pathway is created, so the result is the same as **3.2.2**. Thus, $q_{rev} = \Delta h \equiv \int_2^3 c_P(T)\,dT > 0 \therefore \Delta s_{sys} = \Delta s_{univ} > 0$

3.3.4 Reversible Isothermal Ideal Gas Expansion/Compression

- Due to the definition of entropy, $\Delta s_{sys} \neq 0$. Also, $\Delta s_{surr} = -\Delta s_{sys}$ since the surroundings absorb the q_{rev}. As such, $\Delta s_{univ} = 0$

3.3.5 Irreversible Isothermal Ideal Gas Expansion/Compression

1. For an ideal gas, $T = T_{surr} = \dfrac{Pv}{R}$
2. $\Delta s_{sys} = \int \dfrac{\delta q_{rev}}{T} = \dfrac{q_{rev}}{T}$
   (a) $\Delta u = q_{rev} + w_{rev}$
      i. Since $\Delta u = 0$ for isothermal processes, $q_{rev} = -w_{rev} = nRT \ln\left(\dfrac{V_2}{V_1}\right) = -nRT \ln\left(\dfrac{P_2}{P_1}\right)$
3. $\Delta s_{surr} = \dfrac{-q_{rev}}{T_{surr}} = \dfrac{w_{rev}}{T_{surr}}$ (this will be opposite sign of Δs_{sys} but smaller magnitude)
4. $\Delta s_{univ} = \Delta s_{sys} + \Delta s_{surr} > 0$

3.3.6 Reversible Carnot Engine

- For a Carnot cycle,
$$\frac{P_1}{P_4} = \frac{P_2}{P_3} \rightarrow \frac{P_2}{P_1} = \frac{P_3}{P_4}$$
- For the surroundings,
$$\Delta s_{surr} = -\frac{q_H}{T_H} - \frac{q_C}{T_C} = 0$$
- Additionally,
$$\frac{q_H}{q_C} = -\frac{T_H}{T_C}$$

- As such,
$$\eta = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H}$$
- For the refrigerator,
$$COP = \frac{T_C}{T_H - T_C}$$
- For an irreversible Carnot engine, $\Delta s_{surr} = \Delta s_{univ} > 0$

3.4 The Second Law of Thermodynamics for Open Systems

- For an open system,
$$\left(\frac{dS}{dt}\right)_{univ} = \left(\frac{dS}{dt}\right)_{sys} + \left(\frac{dS}{dt}\right)_{surr} \geq 0$$
  - At steady-state, $\left(\frac{dS}{dt}\right)_{sys} = 0$
- At constant temperature and steady state,
$$\Delta \dot{S}_{univ} = \Delta \dot{S}_{surr} = \sum_{out} \dot{n}_{out} s_{out} - \sum_{in} \dot{n}_{in} s_{in} - \frac{\dot{Q}}{T_{surr}}$$
- When there is one stream with outlet and inlet molar flow rates being the same,
$$\dot{n}\Delta s - \frac{\dot{Q}}{T_{surr}} \geq 0$$

3.5 Calculating Entropy for Closed Systems

3.5.1 Cyclic Process

- $\Delta s = 0$ since it is a state function

3.5.2 Reversible Adiabatic Process

- Since $dq_{rev} = 0$, $\Delta s = 0$
- Note: Even for irreversible adiabatic processes, $\Delta s_{surr} = 0$ even though $\Delta s_{sys} = \Delta s_{univ} \neq 0$

3.5.3 Reversible Isothermal Process

$$\Delta s = \frac{q_{rev}}{T} \text{ (isothermal)}$$

If it's an ideal gas,

$$\Delta s = -R \ln\left(\frac{P_2}{P_1}\right) \text{ (isothermal, perf. gas)}$$

3.5.4 Reversible Isobaric Process

$$\Delta s = \int_{T_1}^{T_2} \frac{c_P(T)}{T} dT \text{ (Const. } P\text{, no phase change)}$$

3.5.5 Reversible Isochoric Process

- Since $\Delta v = 0$, $w = 0$. Therefore, $\Delta u = q$ and thus
$$\Delta s = \int_{T_1}^{T_2} \frac{c_V(T)}{T}\, dT \text{ (Isochoric)}$$

3.5.6 Reversible Phase Change at Constant T and P

- At constant temperature, $\Delta s = \dfrac{q_{rev}}{T}$
- q_{rev} is the latent heat of the transition in this case
- Since P is constant, $q_{rev} = q_P = \Delta h$. Therefore,

$$\Delta s = \frac{\Delta h}{T} \text{ (rev. phase change at const. } T \text{ and } P)$$

3.5.7 Change of State of a Perfect Gas - "The Catch-All"

Using c_V for an ideal gas,

$$\Delta s = \int_{T_1}^{T_2} \frac{c_V(T)}{T} dT + R \ln\left(\frac{V_2}{V_1}\right) \text{ (perf. gas)}$$

Using c_P for an ideal gas,

$$\Delta s = \int_{T_1}^{T_2} \frac{c_P(T)}{T} dT - R \ln\left(\frac{P_2}{P_1}\right) \text{ (perf. gas)}$$

If c_P is not temperature dependent,

$$\Delta s = c_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) \equiv c_P \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{V_1 T_2}{V_2 T_1}\right) \text{ (perf. gas, const. } c_P)$$

If c_V is not temperature dependent,

$$\Delta s = c_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) \equiv c_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1 T_2}{P_2 T_1}\right) \text{ (perf. gas, const. } c_V)$$

3.5.8 Mixing of Different Inert Perfect Gases

The general equation can be written as the following for each substance i,

$$\Delta S_{mix} = \sum n_i R \ln\left(\frac{V_f}{V_i}\right)$$

For a perfect gas at constant temperature and external pressure (P_i is partial pressure of substance i),

$$\Delta S_{mix} = -R \sum n_i \ln\left(\frac{P_i}{P_{tot}}\right) \equiv -R \sum n_i \ln\left(y_i\right)$$

3.5.9 Joule Expansion

$\Delta S \neq 0$ for a Joule Expansion. Instead, the following is true,

$$\Delta S_{sys} = \Delta S_{univ} = nR \ln\left(\frac{V_2}{V_1}\right) \equiv -nR \ln\left(\frac{P_2}{P_1}\right) \text{ (Joule Expansion)}$$

3.5.10 Finding if an Isothermal Process is Reversible or Irreversible for an Ideal Gas

- Simply calculate the ΔS_{sys} as if it were a reversible isothermal process
- Then, calculate ΔS_{surr} using $Q_{surr} = -Q$ from $\Delta U = Q + W = 0 \therefore Q = -W$
- Sum the two entropy values to see if ΔS_{univ} is zero or not

3.6 Mechanical Explosions

- Since a mechanical explosion happens so quickly, the process is considered to be adiabatic with $\Delta n = 0$ so that $\Delta U = W$
- The pressure after the explosion will reach one atmosphere
- The process is considered reversible only to find the maximum work and damage of the explosion ($\Delta S_{univ} = 0 \therefore S_1 = S_2$)

Example:
A $V_1 = 1m^3$ tank containing superheated steam at 20 MPa and 1000°C bursts. Estimate the damage caused by the explosion.

1. From the steam tables, $\hat{s}_1 = 7.4925\,kJ/kg\,K$, $\hat{u}_1 = 4003.1\,kJ/kg$, and $\hat{v}_1 = 0.0289666\,m^3/kg$
   (a) Therefore, the mass is $m = \dfrac{V_1}{\hat{v}_1} = 34.52\,kg$
2. Since $\hat{s}_1 = \hat{s}_2$, use this to find $\hat{u}_2$ at 1 atm
   (a) Since $\hat{s}_2 = 7.4925\,kJ/kg\,K$ and 1 atm can only be found in the superheated water vapor table, this is the condition of the water
      i. Interpolate to yield: $\hat{u}_2 = 2546\,kJ/kg$
3. Perform the energy balance to yield the answer
   (a) $\Delta U = m\,(\hat{u}_2 - \hat{u}_1) = -50.3\,MJ$

3.7 The Mechanical Energy Balance and Bernoulli Equation

$$\frac{\dot{W}_s}{\dot{n}} = \int_{P_1}^{P_2} v\,dP + MW\left(\frac{\overrightarrow{V_2}^2}{2} - \frac{\overrightarrow{V_1}^2}{2}\right) + MW \cdot g \cdot \Delta z$$

- The mechanical energy balance can only be used for reversible processes at steady state with one stream in or out. It also only works for an isothermal or adiabatic process
- The Bernoulli Equation is (no $\dot{W}_S$; nozzle, diffuser):

$$0 = \int_{P_1}^{P_2} v\,dP + \Delta e_K + \Delta e_P$$

- For turbines or compressors/pumps (no Δe_K, Δe_P):

$$\frac{\dot{W}_S}{\dot{n}} = \int_{P_1}^{P_2} v\,dP$$

- Recall that $\dfrac{\dot{W}_S}{\dot{n}} = \Delta h$ for adiabatic processes
- Efficiencies can be described as:

$$\eta_{turbine} = \frac{\text{actual } \dot{W}_S}{\text{reversible } \dot{W}_S}$$

$$\eta_{compressor} = \eta_{turbine}^{-1} = \frac{\text{reversible } \dot{W}_S}{\text{actual } \dot{W}_S}$$

3.8 Vapor-Compression Power and Refrigeration Cycles

3.8.1 The Rankine Cycle

- The Rankine cycle consists of the following steps: turbine, condenser, compressor, boiler
- The fluid enters the turbine (adiabatic and reversible) as superheated vapor where $\dot{W}_s = \dot{m}\Delta\hat{h}$ and $\hat{s}_1 = \hat{s}_2$
  - Only vapor is sent through to avoid blade erosion
- The condenser brings the superheated vapor to the saturated liquid water state at constant pressure. Thus, $\dot{Q}_C = \dot{m}\Delta\hat{h}$
- The compressor (adiabatic and reversible) raises the pressure of the liquid via $\dot{W}_c = \dot{m}\Delta\hat{h} = \dot{m}\hat{v}_l\Delta P$ (if $\hat{v}_l$ is constant) and $\hat{s}_3 = \hat{s}_4$
  - Only liquid is sent through since it's difficult to pump a 2-phase mixture
- The boiler then brings the saturated liquid water back to the superheated vapor at constant pressure given by $\dot{Q}_H = \dot{m}\Delta\hat{h}$,where the final $\hat{h}$ is state 1
- Additionally, the net work is,
$$w_{net} = |\dot{W}_S + \dot{W}_C| = |q_H + q_C|$$
- The efficiency of the cycle is given by,
$$\eta_{\text{ Rankine}} = \frac{|\dot{W}_{net}|}{\dot{Q}_H} = \frac{|\Delta h_{turbine} + \Delta h_{comp}|}{\Delta h_{boiler}}$$
- Since the heat absorbed is proportional to the amount of fuel consumed,
$$q_{rev} = \int T\, ds$$
- For the Rankine Cycle, $P_1 = P_4 > P_2 = P_3$

3.8.2 The Vapor-Compression Refrigeration Cycle

- The refrigeration cycle is a backwards Rankine cycle: evaporator, compressor, condenser, expansion valve
- The refrigerant should boil at a lower temperature than water at a pressure above ambient pressure (usually chlorofluorocarbons)
- The heat transfer at T_C for the evaporator is $\dot{Q}_C = \dot{n}\Delta h$
- The refrigerant is then compressed to a high pressure where $\dot{W}_c = \dot{n}\Delta h$ and $s_3 = s_2$ if it's reversible
- The condenser then brings the refrigerant to the liquid phase via $\dot{Q}_H = \dot{n}\Delta h$
- The high-pressure liquid is then irreversibly expanded in a valve back to state 1. This is a throttling process where $h_4 = h_1$
- The COP for the cycle is,
$$\text{COP} = \frac{\dot{Q}_C}{\dot{W}_C} = \frac{h_2 - h_1}{h_3 - h_2}$$

3.9 The Zeroth Law and Third Law

- The Zeroth Law states that if two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other
  - Temperature, an intensive property, is defined from this since it determines thermal equilibrium
- The Third Law states that the entropy of a system approaches zero as the temperature approaches zero
  - Another interpretation is that no finite sequence of cyclic processes can realistically succeed in cooling a body to zero Kelvins

3.10 Molecular View of Entropy

- From a statistical mechanics perspective,

$$\frac{\text{Population in energy level E}}{\text{Population in energy level 0}} = e^{-\beta E}$$

- The constant β is defined as

$$\beta = \frac{1}{k_B T}$$

- There is an inverse exponential filling of higher energy states
- The molecular view of entropy is[5],

$$s = k \ln W$$

4 Equations of State and Intermolecular Forces

4.1 Equations of State

4.1.1 Non-Ideality Improvements

- The Ideal Gas equation can be improved by using the dimensionless compressibility factor,

$$Pv = zRT$$

- Reduced properties (unitless) can account for intermolecular forces,

$$T_r = \frac{T}{T_c} \qquad P_r = \frac{P}{P_c}$$

- The Principle of Corresponding States states that on the microscopic level, the dimensionless potential energy function is the same for many species while the compressibility factor at T_r and P_r is the same for many species at the macroscopic level
- The van der Waals equation of state is,

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

- For the van der Waals equation of state,

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c} \qquad b = \frac{RT_c}{8P_c}$$

4.1.2 Van der Waals-like Equations

- The Redlich-Kwong (RK) equation states,

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

$$a = \frac{0.42748R^2T_c^{2.5}}{P_c} \quad b = \frac{0.08664RT_c}{P_c}$$

- Even more accurate, the Peng-Robinson equation states,

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

$$a = 0.45724\frac{R^2T_c^2}{P_c} \quad b = 0.07780\frac{RT_c}{P_c} \quad \alpha(T) = \left[1+\kappa\left(1-\sqrt{T_r}\right)\right]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

[5] W is the number of microstates

4.1.3 Virial Equations

- For pressures less than 15 bar,

$$z = 1 + \frac{BP}{RT} = \frac{Pv}{RT}$$

$$B = \frac{B_r R T_c}{P_c}$$

$$B_r = B^{(0)} + \omega B^{(1)}$$

$$B^{(0)} = 0.083 - 0.422 T_r^{-1.6} \quad B^{(1)} = 0.139 - 0.172 T_r^{-4.2}$$

- The Generalized Compressibility (Lee-Kessler) equation is (use Tables C1/C2),

$$z = z^{(0)} + \omega z^{(1)}$$

4.1.4 Liquids and Solids

- For a saturated liquid, the Rackett Equation applies:

$$v^{l,sat} = \frac{RT_c}{P_c} (0.29056 - 0.08775\omega)^{\left[1+(1-T_r)^{2/7}\right]}$$

- For general liquids and solids the thermal expansivity and compressibility constants are as follows, respectively:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \kappa \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

4.2 Determination of Parameters for Mixtures

- For a two-component mixture,

$$a_{mix} = y_1^2 a_1 + 2 y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2$$

$$b_{mix} = y_1 b_1 + y_2 b_2$$

5 Thermodynamic Web

5.1 Differential Quantities

5.1.1 Basic Thermodynamic Quantities

The total differential, dz, for $z(x, y)$ is defined as:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -1$$

The basic thermodynamic relationships are:

$$H \equiv U + PV \qquad A \equiv U - TS \qquad G = H - TS$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Additionally, for a closed system in equilibrium,

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \text{ (Closed, Eq.)} \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P \text{ (Closed, Eq.)}$$

5.1.2 The Gibbs Equations

$$du = T\,dS - P\,dv$$

$$dh = T\,dS + v\,dP$$

$$da = -P\,dv - S\,dT$$

$$dg = v\,dP - S\,dT$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$
$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Furthermore,

$$\beta\,(T,P) \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa\,(T,P) \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Procedure:

1. Write out the corresponding Gibbs Equation
2. Set the designated variable as constant
3. Solve for the desired relation

5.1.3 The Maxwell Relations

The Maxwell Relations can be derived by applying the basic Euler's Reciprocity to the derivative forms of the equations of state. The Euler Reciprocity is[6],

$$\frac{d^2z}{dx\,dy} = \frac{d^2z}{dx\,dy}$$

For instance,

$$\frac{\partial^2 G}{\partial T\,\partial P} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial T}V\right)_P = \left(\frac{\partial V}{\partial T}\right)_P$$

This must equal $\frac{\partial^2 G}{\partial P\,\partial T} = -\left(\frac{\partial S}{\partial P}\right)_T$ via the Euler Reciprocity

Some relationships are shown below:

$$\frac{\partial^2 U}{\partial S \partial V} : \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \text{ and } \frac{\partial^2 H}{\partial S \partial P} : \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\frac{\partial^2 A}{\partial T \partial V} : \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \text{ and } \frac{\partial^2 G}{\partial T \partial P} : \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

[6]It is important to note that the operator in the denominator of the derivative is performed right to left

5.1.4 Dependence of State Functions on T, P, and V

1. Start with the Gibbs equation for dU, dH, dA, or dG
2. Impose the conditions of constant T, V, or P
3. Divide by dP_T, dV_T, dT_V, or dT_P
4. Use a Maxwell relation or heat-capacity equation to eliminate any terms with entropy change in the numerator

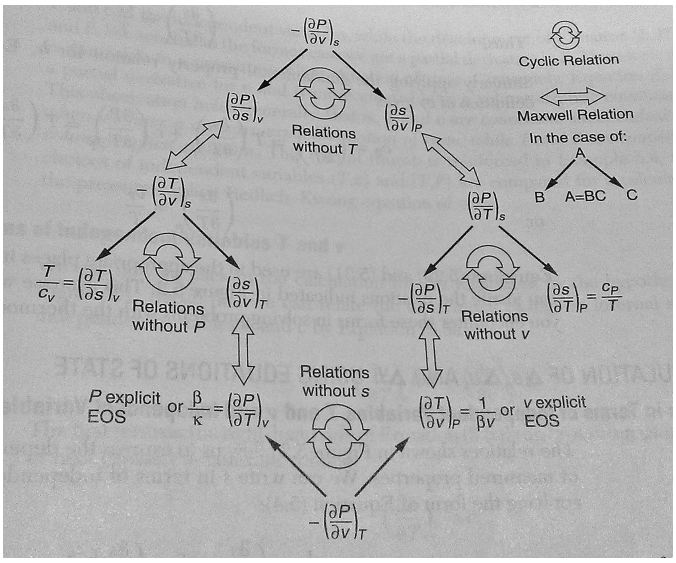
Here are a few examples:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = \frac{\alpha T}{\kappa} - P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha + V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$$

5.1.5 Thermodynamic Web - Summary



5.2 Thermodynamic State Functions for Real Fluids

$$\Delta s = \int \frac{c_P}{T} dT - \int \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Delta s = \int \frac{c_v}{T} dT + \int \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\Delta u = \int c_v dT + \int \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$\Delta h = \int c_P dT + \int \left[-T\left(\frac{\partial v}{\partial T}\right)_P + v\right] dP$$

- Hypothetical paths must be used. A key feature of these is hypothetically converting a real gas to an ideal one by increasing the volume to $v = \infty$ or decreasing the pressure to $P = 0$. Then, the necessary changes can be imposed followed by bringing the system to the real final state

- Alternatively. a two-step path can be used that doesn't utilize ideal gas properties,

$$c_v^{real} = c_v^{id} + \int_\infty^{v_1} \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_v \right] dv$$

$$c_P^{real} = c_p^{id} - \int_0^{P_1} \left[T \left(\frac{\partial^2 v}{\partial T^2} \right)_P \right] dP$$

$$\Delta u = \int_1^2 \left\{ c_v^{id} + \int_\infty^{v_1} \left[T \left(\frac{\partial^2 P}{\partial T^2} \right)_v dv \right] \right\} dT + \int_1^2 \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

5.3 Departure Functions

- The departure function is defined as (using enthalpy as an example), $\Delta h_{T,P}^{dep} = h_{T,P} - h_{T,P}^{id}$
  - Departure functions are based on Lee-Kessler data

$$\Delta h = -\Delta h_{T_1,P_1}^{dep} + \int_{T_1}^{T_2} c_P^{id} dT + \Delta h_{T_2,P_2}^{dep}$$

$$\frac{\Delta h_{T_r,P_r}^{dep}}{RT_c} = \left[\frac{\Delta h_{T_r,P_r}^{dep}}{RT_c} \right]^{(0)} + \omega \left[\frac{\Delta h_{T_r,P_r}^{dep}}{RT_c} \right]^{(1)}$$

$$\Delta s = -\Delta s_{T_1,P_1}^{dep} + \left[\int_{T_1}^{T_2} \frac{c_P^{id}}{T} dT - R \ln \left(\frac{P_2}{P_1} \right) \right] + \Delta s_{T_2,P_2}^{dep}$$

$$\frac{\Delta s_{T_r,P_r}^{dep}}{R} = \left[\frac{\Delta s_{T_r,P_r}^{dep}}{R} \right]^{(0)} + \omega \left[\frac{\Delta s_{T_r,P_r}^{dep}}{R} \right]^{(1)}$$

5.4 Joule-Thomson Expansions and Liquefaction

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_h$$

- Liquefaction involves a reversible compressor (constant s), an isobaric cooler, and a JT-expansion valve (constant h), and then a separator for the liquid and vapor streams
- For a J-T Expansion,

$$\mu_{JT} = \frac{\left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]}{c_P^{id} - \int_{P_{id}}^{P_{real}} \left[T \left(\frac{\partial^2 v}{\partial T^2} \right)_P \right] dP}$$

6 Phase Equilibria I

6.1 Pure Species Phase Equilibrium

- Combination of the first and second laws yields the following for a closed system,

$$0 \geq (dG_i)_{T,P}$$

- The Clapeyron Equation states,

$$\frac{dP}{dT} = \frac{\Delta h}{T \Delta v}$$

- Assuming that $v_l \ll v_v$, that $v_l \approx 0$, and that $v_v = \frac{RT}{P}$, we obtain the Clausius-Clapeyron Equation that states,

$$\frac{dP^{sat}}{dT} = \frac{P^{sat}\Delta h_{vap}}{RT^2}$$

- If Δh_{vap} is considered independent of temperature,

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta h_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

  - This can be used to find effects of pressure on phase transitions since normal boiling points have a fixed P_1 and T_1
  - The Clausius-Clapeyron Equation can be used even for solid temperatures and pressures to find heats of sublimation
    - The equation works on phase boundaries with two data points for the same phase

- This can be re-arranged to yield the experimental Antoine equation that states,

$$\ln P^{sat} = A - \frac{B}{C+T}$$

6.2 Partial Molar Quantities

- The arbitrary partial molar quantity, K, is defined as,

$$\bar{K}_i \equiv \left(\frac{\partial K}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

- Therefore,

$$K = \sum_i n_i \bar{K}_i$$

- This should not be confused with the intensive k, which is,

$$k = \frac{K}{n_T} = \sum x_i \bar{K}_i$$

  - Note: k_i is the intensive property of a substance if it existed as a pure substance while $\bar{K}_i$ is what it contributes to the solution
  - If $\bar{K}_i - k_i$ is zero, the species behave in the mixture to how they behave as pure substances
  - $\bar{K}_i = k_i$ as $x_i \to 1$
  - $\bar{K}_i = \bar{K}_i^{\infty}$ as $x_i \to 0$

6.3 The Gibbs-Duhem Equation and Mixing Quantities

- The Gibbs-Duhem Equation states the following for constant temperature and pressure,

$$0 = \sum n_i d\bar{K}_i$$

  - It means that the a substance's partial molar properties cannot be independently changed (dependent on other substance's partial molar properties in the mixture)

- Additionally,

$$\Delta k_{mix} = k - \sum x_i k_i = \sum x_i \left(\bar{K}_i - k_i\right)$$
$$\Delta K_{mix} = K - \sum n_i k_i = \sum n_i \left(\bar{K}_i - k_i\right)$$
$$\left(\Delta \bar{K}_{mix}\right)_i = \bar{K}_i - k_i$$

- Positive deviations occur when the dissolution process is not energetically favorable such that $\Delta v_{mix} > 0$ and $\Delta h_{mix} < 0$
- Negative deviations occur when the dissolution process is energetically favorable (i-j interactions are stronger than i-i or j-j) such that $\Delta v_{mix} < 0$, $\Delta h_{mix} < 0$, and $P_i < P_{i,}^{id}$
- Enthalpy of solution is,

$$\Delta \tilde{h}_S = \frac{\Delta h_{mix}}{x_{solute}}$$

6.4 Analytical Determination of Partial Molar Properties

- Compute $\bar{K}_i = \left(\frac{\partial K}{\partial n_i}\right)_{T,P,n_j}$ by brute force

6.5 Determination Partial Molar Properties for a Binary Mixture

- For a binary mixture, $k = x_1\bar{K}_1 + x_2\bar{K}_2$, so:

$$k = \bar{K}_1 + x_2\frac{dk}{dx_2}$$

  - Graphically, the first term is the intercept, and the derivative is the slope of the tangent line at x_2 if data is plotted as k vs. x_2
  - This form allows you to construct a tangent curve at a specific constrained mole fraction using the point-slope formula of $(y - y_0) = m\,(x - x_0)$, and to extrapolate at $x = 1$ and $x = 0$ to find $\bar{K}_2$ and $\bar{K}_1$, respectively
    - Graphically, you can approximate $\bar{K}_1$ as the y-intercept of a k vs. x_2 plot and $\bar{K}_2$ as the y-intercept of a k vs. x_1 plot (or, more simply, the value of v at $x_2 = 1$ on the tangent line for a k vs. x_2 plot)

- The above method can be conveniently written in the following form:

$$\bar{K}_1 = k - x_2\left.\frac{dk}{dx_2}\right|_{x_1,x_2}$$

$$\bar{K}_2 = k + (1 - x_2)\left.\frac{dk}{dx_2}\right|_{x_1,x_2} = k + x_1\left.\frac{dk}{dx_2}\right|_{x_1,x_2} = k - x_1\left.\frac{dk}{dx_1}\right|_{x_1,x_2}$$

6.6 Mixing Quantities for Ideal Mixtures

- Entropy of mixing for a regular (ideal) solution,

$$\Delta s^{id}_{mix} = -R\sum_i y_i \ln y_i$$

- Mixing quantities of enthalpy and molar volume is,

$$\Delta h^{id}_{mix} = \Delta v^{id}_{mix} = 0$$

- Therefore,

$$\Delta g^{id}_{mix} = RT\sum y_i \ln y_i$$

7 Phase Equilibrium II: Fugacity

7.1 The Fugacity

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_T = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \bar{V}_i \therefore d\mu_i = \left(\frac{RT}{P}\right)dP$$

- From this, chemical potential can be expressed as the following for ideal gases,

$$\mu_i - \mu_i^\circ = RT\ln\left[\frac{P}{P^\circ}\right] = RT\ln\left[\frac{p_i}{P_i^\circ}\right]$$

  - However, this expression breaks down when $y_i \to 0$ or $P \to 0$

- Fugacity is defined as the following and is for real gases,

$$\mu_i - \mu_i^\circ \equiv RT\ln\left[\frac{\hat{f}_i}{\hat{f}_i^\circ}\right] \to \hat{f}_i = \hat{f}_i^\circ \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right)$$

- The reference state is some low pressure (typically 1 bar)

- For an ideal gas,

$$\lim_{P\to 0}\left(\frac{\hat{f}_i}{p_i}\right) \equiv 1$$

- The fugacity coefficient is defined as,

$$\hat{\varphi}_i \equiv \frac{\hat{f}_i}{p_{i,sys}} = \frac{\hat{f}_i}{y_i P_{sys}}$$

  - Fugacity is defined relative to the system's partial pressure and not the partial pressure of the reference state
  - If $\varphi < 1$ attractive forces dominate, and if $\varphi > 1$ repulsive forces dominate

7.2 Fugacity of a Pure Gas

7.2.1 Mathematical Definition

- If we choose the reference state as a low enough pressure that the gas behaves ideally (e.g. 1 bar) such that $\hat{f}_i^\circ \to P$ and $\varphi_i^\circ \to 1$,

$$g_i - g_i^\circ \equiv RT \ln\left[\frac{f_i^v}{P_{low}}\right]$$

$$\varphi_i^v \equiv \frac{f_i^v}{P_{sys}}$$

7.2.2 Using Steam Tables

- From the tables in the back of the book, there are h, s, T, and P, which can be used to find g in order to solve for f_i

7.2.3 Equation of State

- Using an equation of state,

$$g_i - g_i^\circ = \int_{P_{low}}^{P} v_i dP = RT \ln\left[\frac{f_i^v}{P_{low}}\right]$$

  - If the equation of state cannot be solved for v, then one can differentiate the equation of state with respect to P at constant T to change the variable of integration from dP to dv and thus the integral bound from pressure to molar volume
    - The lower bound molar volume can be found from $\dfrac{RT}{P_{low}}$ since it is ideal in this case

7.2.4 Generalized Correlations

- Similar to departure functions, we have,

$$\log \varphi_i = \log \varphi_i^{(0)} + \omega \log \varphi^{(1)}$$

  - Since φ_i is dependent only on reduced quantities, one can use the Lee-Kessler tables to find φ_i
  - Once you find φ_i, multiply it by the pressure the vapor is at to find f_i

7.3 Fugacity of a Species in a Gas Mixture

7.3.1 Equation of State

$$\mu_i - \mu_i^\circ = RT \ln\left[\frac{\hat{f}_i^v}{y_i P_{low}}\right] = \int_{P_{low}}^{P} \bar{V}_i dP$$

- To find $\bar{V}_i$, apply $\left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ to the equation of state

7.3.2 The Lewis Fugacity Rule

- The Lewis Fugacity rule is an approximation for the more rigorous $\hat{f}_i^v = y_i \hat{\varphi}_i P$ via the assumption that $\hat{\varphi}_i^v \approx \varphi_i^v$
- From this rule comes the following approximations:

$$\hat{f}_i^v \approx y_i \varphi_i^v P \therefore \hat{f}_i^v = y_i f_i$$

  - Can be used when there is low pressure or high temperature, mostly i in the mixture, or the chemical nature of all species in the mixture are similar
  - When using this method, T_r and P_r are for substance i (not pseudocritical) where the pressure used to find P_r is the partial pressure of i such that $P_i = y_i P$

7.3.3 Ideal Gas Mixture Assumption

- Alternatively, one can assume an ideal gas mixture to simply have $\hat{\varphi}_i = 1$ such that $\hat{f}_i^v = y_i P$

7.4 Fugacity in the Liquid Phase

7.4.1 Activity Coefficient and Reference States

- When the mixing rules of a liquid mixture are the same for an ideal gas, the solution is said to be ideal
- Recall that an ideal solution follows $\Delta v_{mix}^{id} = \Delta h_{mix}^{id} = 0$, $\Delta s_{mix}^{id} = -R \sum y_i \ln y_i$ and $\Delta g_{mix}^{id} = RT \sum y_i \ln y_i$
  - Additionally, $\hat{f}_i^{id} = x_i f_i^{id}$
  - There are equal intermolecular potentials between all species in solution
- When there is mostly i in mixture, the Lewis-Randall State applies. However, when there is mostly j in solution, Henry's Law applies for substance i. Therefore,

$$f_i^{id} = f_i^\circ = f_i \quad \text{(Lewis Rule: } i\text{-}i\text{interactions)}$$

$$f_i^{id} = f_i^\circ = \mathcal{H}_i \quad \text{(Henry's Law: } i\text{-}j\text{interactions)}$$

  - Therefore, i is a solute when applying Henry's Law and a solvent when applying Lewis' Rule
- The activity coefficient is defined as,

$$\gamma_i = \frac{\hat{f}_i^l}{\hat{f}_i^{id}} = \frac{\hat{f}_i^l}{x_i f_i^\circ}$$

  - The reference state for the liquid phase is when all intermolecular interactions are the same
- Additionally,

$$\gamma_i^{\text{Henry}} = \frac{\gamma_i}{\gamma_i^\infty}$$

- Therefore,

$$\hat{f}_i^l = x_i \gamma_i f_i = x_i \gamma_i^{\text{Henry's}} \mathcal{H}_i$$

- The activity of species i in liquid is given by,

$$a_i \equiv \frac{\hat{f}_i^l}{f_i^\circ}$$

- This leads to,

$$a_i = x_i \gamma_i$$

7.4.2 Pure Species Fugacity

$$f_i^l = \varphi_i^{sat} P_i^{sat} \exp\left[\int_{P_i^{sat}}^{P} \left(\frac{v_i^l}{RT}\right) dP\right]$$

- Poynting Correction: v_i^l is typically assumed to be constant
  - The correction is about 1 for $P < 100$ bar
  - If $P_i^{sat}(T)$ is low then $\varphi_i^{sat} = 1$ such that $f_i^l = P_i^{sat}$
  - If the liquid mixture is ideal then $\gamma_i = 1$
- The Antoine Equation is used to find P_i^{sat}

7.4.3 Pressure and Temperature Dependence of Henry's Constant

- The pressure dependence of Henry's Constant is,

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial P}\right)_T = \frac{\bar{V}_i^{\infty}}{RT}$$

- This integrates to,

$$\mathcal{H}_i = \mathcal{H}_i^{1\,bar} \exp\left(\int_{1\,bar}^{P} \frac{\bar{V}_i^{\infty}}{RT} dP\right)$$

  - If the partial molar volume is not available, it can be approximated as the pure species molar volume
- The temperature dependence of Henry's Constant is,

$$\left(\frac{\partial \ln \mathcal{H}_i}{\partial T}\right)_P = \frac{h_i^v - \bar{H}_i^{\infty}}{RT^2}$$

- The above can be rearranged to $\left(\frac{\partial \ln \mathcal{H}_i}{\partial (1/T)}\right)_P = \frac{\bar{H}_i^{\infty} - h_i^v}{R}$

7.4.4 Thermodynamic Relations Between γ_i

- The Gibbs-Duhem Equation states that $\sum x_i d \ln \gamma_i = 0$. Therefore, for a binary mixture,

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1}\right) = 0$$

  - As such, γ_i values are not independent of one another

7.4.5 Excess Quantities

- Excess Gibbs' energy is defined as $g^E \equiv g - g^{id}$
  - Furthermore,

$$g^E = \sum x_i \bar{G}_i^E = RT \sum x_i \ln \gamma_i = \Delta g_{mix} - \Delta g_{mix}^{id} = \Delta g_{mix} - RT \sum x_i \ln x_i$$

- Partial molar excess Gibbs' energy is defined as

$$\bar{G}_i^E \equiv \bar{G}_i - \bar{G}_i^{id} = RT \ln \gamma_i$$

- The thermodynamic consistency test states that

$$0 = \int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1$$

7.4.6 Models for γ_i using g^E

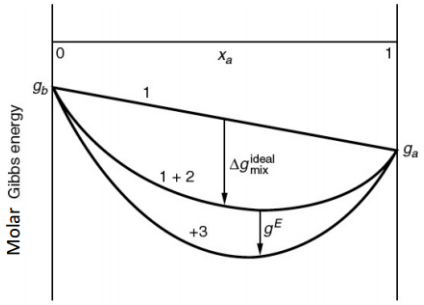
- The two conditions that must be satisfied by g^E expressions are that $g^E = 0$ at $x_i = 1$ and that it must obey the Gibbs-Duhem Equation
- One symmetric model is the Two-Suffix Margules
- Other common models are asymmetric and can be found in Table 7.1

7.4.7 Expressing Molar Gibbs Energy of a Solution

- To find g^E, recall that $\Delta g_{mix} = g - \sum_i x_i g_i$ and $\Delta g^{id}_{mix} = RT \sum_i x_i \ln x_i$.
- Therefore,

$$g = \sum x_i g_i + RT \sum x_i \ln x_i + g^E$$

- The plot below shows g where each number corresponds to one of the three terms of the equation above



- Sometimes, the system can minimize its free energy by splitting into two phases

7.4.8 Temperature and Pressure Dependence of g^E

$$\left(\frac{\partial g^E}{\partial P}\right)_{T,n_i} = v^E = \Delta v_{mix}$$

$$\left(\frac{\partial \left(\frac{g^E}{T}\right)}{\partial T}\right)_{P,n_i} = \frac{-h^E}{T^2} = -\frac{\Delta h_{mix}}{T^2}$$

8 Phase Equilibria III: Phase Diagrams

8.1 Vapor-Liquid Equilibrium

- The following statement relates vapor and liquid nonideality, $y_i \hat{\varphi}^v_i P = x_i \gamma^l_i f^\circ_i$
- Raoult's Law is a simplification for ideal gases/solutions at low pressure and when intermolecular forces are approximately the same: $y_i P = x_i f_i \rightarrow y_i P = x_i P^{sat}_i$ where $P = \sum_i x_i P^{sat}_i$ for a multiphase system
- For non-ideal liquids, a Lewis/Randall state can be used such that $y_i P = x_i \gamma_i P^{sat}_i$ where $P = \sum_i x_i \gamma_i P^{sat}_i$ for a multiphase system
  - A helpful diagram for this is on Page 373
- Recall that the VLE requirement of $\hat{f}^l_i = \hat{f}^v_i$ can be rewritten as,

$$y_i \hat{\varphi}^v_i P = x_i \gamma^l_i \left[\varphi^{sat}_i P^{sat}_i \exp\left(\int_{P^{sat}_i}^{P} \left(\frac{v^l_i}{RT}\right) dP\right)\right]$$

8.2 Bubble Point and Dew Point

8.2.1 Ideal Liquid

- If you're looking for the bubble point and pressure is known, one can find y_i and P_i^{sat} from Raoult's Law and T from the Antoine Equation once P_i^{sat} is found
- If you're looking for the dew point and pressure is known, one can find x_i and P_i^{sat} from Raoult's Law and T from the Antoine Equation once P_i^{sat} is found
- If you're looking for the bubble point and temperature is known, one can find y_i and P from Raoult's Law once P_i^{sat} is obtained from the Antoine equation
- If you're looking for the dew point and temperature is known, one can find x_i and P from Raoult's Law once P_i^{sat} is obtained from the Antoine equation
- What's important to note here is that the second equation for dew point calculations will be $1 = \sum \frac{y_i P}{P_i^{sat}}$ since the sum of the liquid mole fractions is 1

8.2.2 Nonideal Liquid

- See Page 378

8.3 Azeotropes

- The azeotrope is where the P_x and P_y curves go through a maximum or minimum at $x_i \neq 0$
- At the azeotrope, $x_i = y_i$
- Also, $P = \gamma_i P_i^{sat}$ such that $\frac{\gamma_a}{\gamma_b} = \frac{P_b^{sat}}{P_a^{sat}}$ at the azeotrope
- One cannot purify past an azeotrope via simple distillation
  - Instead, a temperature/pressure change or addition of a third component is needed

8.4 Solubility of Gases in Liquids

- Applying Henry's law to a fugacity equilibrium yields $y_i \hat{\varphi}_i P = x_i \gamma_i^{\text{Henry's}} \mathcal{H}_i$
  - If the gas is assumed to be ideal then $y_a P = x_a \mathcal{H}_a$ and $y_b P = x_b P_b^{sat}$ where a is the gas and b is the liquid phase
    - Therefore, $P = x_a \mathcal{H}_a + x_b P_b^{sat}$

8.5 Liquid-Liquid Equilibrium (LLE)

- For LLE, $\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \therefore x_i^{\alpha} \gamma_i^{\alpha} = x_i^{\beta} \gamma_i^{\beta}$ with Lewis/Randall reference
- Therefore, there are two sets of equations: $x_a^{\alpha} \gamma_a^{\alpha} = x_a^{\beta} \gamma_a^{\beta}$ and $x_b^{\alpha} \gamma_b^{\alpha} = x_b^{\beta} \gamma_b^{\beta}$ where $x_a^{\alpha} + x_b^{\alpha} = 1$ and $x_b^{\alpha} + x_b^{\beta} = 1$
- For fluid stability, $\left(\frac{\partial^2 g}{\partial x_i^2} \right)_{T,P} > 0$
- A binodal curve is the curve found when the two sets of equations above are solved using a g^E model for γ_i^j
- The upper-consulate temperature is the value above which the liquid mixture no longer separates into two phases at any composition
- The lower-consulate temperature is the value below which phase separation is impossible at any composition

- A spinodal curve is the solution of where the fluid is unstable, which is reliant on the g^E model chosen since this influences the value of g
- For a binodal and spinodal curve plot, see Page 398
- For a $x_i\gamma_i$ vs. x_a plot, see Page 401

8.6 Vapor-Liquid-Liquid Equilibrium (VLLE)

- Here, $\hat{f}_i^v = \hat{f}_i^\alpha = \hat{f}_i^\beta$ such that $y_i P = x_i^\alpha \gamma_i^\alpha P_i^{sat} = x_i^\beta \gamma_i^\beta P_i^{sat}$
  - An ideal gas mixture occurs at P and P_i^{sat}

8.7 Colligative Properties

- Let i be the Van't Hoff Factor, which is the amount of moles of ions a solute dissociates into in solution
  - For instance, $i = 2$ for $NaCl$. If the substance is covalent (e.g. glucose), $i = 1$
- Boiling point elevation equation is $T - T_{boil} \approx \dfrac{RT_{boil}^2}{\Delta h_{vap}} x_b i$
  - This is based on the assumptions that the solute is dilute enough that the liquid can be treated as an ideal solution, that $\ln(1 - x_b) \approx -x_b$, and that Δh_{vap} is independent of temperature
- Freezing point depression equation is $T_{melt} - T \approx \dfrac{RT_{melt}^2}{\Delta h_{fus}} x_b i$
- The osmotic pressure is given by $\Pi = \dfrac{x_b RT}{v_a} = \dfrac{C_b RT}{MW_b}$, where C_b has units of kg/m^3

9 Chemical Reaction Equilibrium

9.1 Equilibrium for a Single Reaction

- At low temperatures the system is said to be under kinetic control while it is under thermodynamic control occurs at higher temperatures when the activation energy is not an issue
- Let moles be related to extent of reaction via $n_f = n_i + \nu_i \xi$
- At equilibrium $\dfrac{dG}{d\xi} = \sum \mu_i \nu_i = 0$
- Therefore, $\ln \prod \left(\dfrac{\hat{f}_i}{f_i^\circ} \right)^{\nu_i} = -\dfrac{\sum \nu_i g_i^\circ}{RT} = -\dfrac{\Delta g_{rxn}^\circ}{RT}$
  - More simply, $\prod \left[\dfrac{\hat{f}_i}{f_i^\circ} \right]^{\nu_i} = \exp\left[\dfrac{-\sum \nu_i g_i^\circ}{RT} \right] = \exp\left[\dfrac{-\Delta g_{rxn}^\circ}{RT} \right] \equiv K$
- K is a function of temperature such that: $\ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta h_{rxn}^\circ}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ where Δh_{rxn}° is assumed to be independent of temperature

9.2 Gas Phase Reactions (Single Reaction)

9.2.1 Equations

- Recall that for an ideal gas mixture $\hat{f}_i = y_i P$ where the nonideal Lewis Fugacity Rule produces $\hat{f}_i = y_i \varphi_i P$
  - Therefore, $\prod \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} = \left(\frac{P}{1\,bar}\right)^{\nu} \prod (y_i)^{\nu_i} = K$
- Also, $y_i = \frac{n_i^\circ + \nu_i \xi}{n^\circ + \nu \xi}$

9.2.2 Walkthrough

1. Calculate Δg_{rxn}° from tabulated data
2. Calculate K° using $\Delta g_{rxn}^\circ = -RT \ln(K^\circ)$ and convert to K non-standard via the temperature dependent equation
3. Use the stoichiometry of the reaction to express mole numbers in terms of initial mole number and equilibrium extent of reaction
4. Analyze reaction conditions
   (a) This is simply the creation of an I.C.E. table
   (b) If the reaction is at fixed temperature and pressure, use $P_i = y_i P = \frac{n_i}{n_{tot}} P$
      i. A simplified equation under constant temperature and pressure for an ideal system is the following, where all moles and mole fractions are amounts at equilibrium:
      $$K^\circ = \frac{(y_C)^c (y_D)^d}{(y_A)^a (y_B)^b} \cdot \left(\frac{P}{P^\circ}\right)^{\nu_i} = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b} \cdot \left(\frac{P}{n_{Total} \cdot P^\circ}\right)^{\nu_i}$$
   (c) If the reaction is at fixed temperature and volume, use $P_i = \frac{n_i RT}{V}$
      i. A simplified equation under constant temperature and volume for an ideal system is, where all moles are amounts at equilibrium:
      $$K^\circ = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b} \cdot \left(\frac{RT}{P^\circ V}\right)^{\nu_i}$$
5. Substitute the P_i values into the equilbrium-constant expression and solve for ξ_{eq}
6. Calculate the equilibrium mole numbers from ξ_{eq} and the expressions for n_i

9.3 Liquid Phase Reaction (Single Reaction)

- $\prod \left[\frac{\hat{f}_i}{f_i^\circ}\right]^{\nu_i} = \prod \left(\frac{x_i \gamma_i f_i}{f_i^\circ}\right)^{\nu_i} = K$
  - When pressure is low, $\prod (x_i \gamma_i)^{\nu_i} = K$
  - For an ideal solution, $\prod (x_i)^{\nu_i} = K$

9.4 Multiple Reactions

- Here, there are two unknowns of ξ_1 and ξ_2, two equations of K_1 and K_2 can be solved
- $y_i = \frac{n_i^\circ + \sum_{k=1}^{R} \nu_{ik} \xi_k}{n^\circ + \sum_{k=1}^{R} \nu_k \xi_k}$
- The new Gibbs Phase Rule is that $\mathscr{F} = m - \pi + 2 - R$ where R is the number of independent chemical reactions

9.5 Equilibrium Shifts

1. Increasing pressure at constant volume by adding inert gas will not change the equilibrium composition since partial pressures are the same
2. Adding an inert gas while holding temperature and pressure constant will shift the reaction to the side of greater moles
   (a) This is analogous to decreasing pressure at constant temperature
3. Adding a reactant or product gas at constant temperature and volume will shift the equilibrium to the side opposite of the addition since other partial pressures don't change
4. Adding a reactant or product gas at constant temperature and pressure changes other partial pressures, so there is no simple rule
   (a) For example, if we have $N2(g) + 3H2(g) \rightleftharpoons 2NH3(g)$, we can establish equilibrium at constant temperature and pressure. Then, we can add some $N2$ at constant total pressure. The partial pressure of $N2$ will go up while the other partial pressures go down. Under certain conditions, equilibrium will shift to the left to produce more of the added gas even though this goes against intuition
5. Decreasing volume at constant temperature will be the same as increasing the pressure at constant temperature. It will shift the reaction to the side of lower moles of gas
6. An increase in temperature at constant pressure will shift the equilibrium to the direction in which the system absorbs heat from the surroundings via the van't Hoff equation

10 Electrochemistry

- $E = E^\circ - \dfrac{RT}{zF} \ln \Pi \left[\dfrac{\hat{f}_i}{f_i^\circ} \right]^{\nu_i}$ where $E^\circ = \dfrac{-\Delta g_{rxn}^\circ}{zF}$
  - The variable z is the number of moles of electrons transferred in balanced cell reaction (unitless) and $F = 96485 \dfrac{C}{mol}$
- The major assumption is that the reaction is reversible