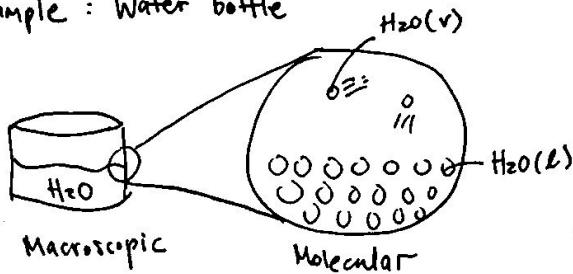


<< Intro to Thermo

- Example : Water bottle



- How do we describe the behavior of the water?

- Molecular Scale

- For each Molecule , { position \leftrightarrow
orientation \curvearrowright
velocity \rightarrow
chemical nature H_2O } } hard to use, nonintuitive
(doable with molecular dynamics simulation)

- Macroscopic Scale

- System as a whole { volume of container
of phases
temperature
pressure } } easy to use
hard to explain

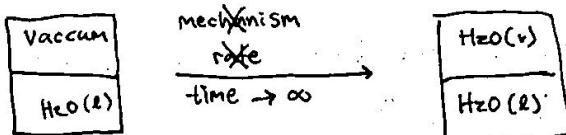
> Thermodynamics - the bridge between molecular & macroscopic scales

(Def.) - a framework that allows us to understand & define
the behavior of molecules in a system at equilibrium
from its measurable macroscopic properties, and vice versa

Thermo predicts group behavior, NOT individual molecules

e.g. H_2O @ $4^\circ C$, 1 atm \leftarrow on average as a group

Thermo predicts equilibrium behavior, NOT how or the rate
(mechanism)



Why is thermo useful?

explicit : predict state of matter at e.g. N_2/O_2 $\xrightarrow{-200^\circ C}$ $\square \rightarrow N_2(v)$ $\square \rightarrow O_2(l)$

implicit : knowing energetics & molecular behavior is important

<< Definitions

- > system - a group of molecules of interest
- > control volume - physical space occupied by the system
- > boundary - separates system from surroundings
- > surroundings - everything outside the boundary that is not the system
- > universe - system + surrounding

<< Types of Systems

- > Isolated system - no exchange of Mass or energy

- usually fixed volume



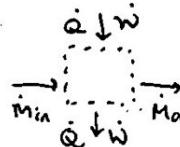
- > Closed system - exchange energy, but NO mass



- > Open system - exchange mass & energy

- usually steady state

- often fixed volume



<< Thermo Properties

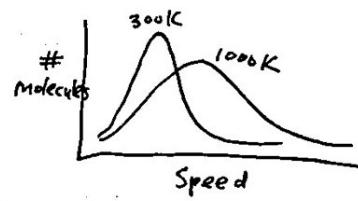
- > continuum approximation - describable molecular behavior using measurable thermo properties (T, P), rather than calculating them from individual molecules (avg behavior)

- > temperature - "degree of hotness"

- Molecularly, molecule's translational speed

$$\bar{KE} = \frac{1}{2} M V^2$$

- > Maxwell-Boltzmann distribution : $\bar{KE} = \frac{3}{2} k_B T$



- > Pressure - "molecules push back" ; $P = \frac{F}{A}$

- molecularly, molecules hitting the wall



$$F = Mg \quad F = PA \Rightarrow P = \frac{Mg}{A}$$

<< Types of Properties

- > state properties - value does not depend on route took to reach the state

- e.g. V, N, U, T, P, g (quality)

- > quality - fraction of molecule in a phase

- > non-state properties - describe a pathway or constant ; path dependent

- e.g. W, Q

<< Type of Properties

> extensive properties - scale linearly with # of material in a system

- e.g. N, m, V, U

> intensive properties - do not change by changing # of material

- e.g. $T, P, \rho, v = \frac{V}{n}, \hat{v} = \frac{V}{m}$

- extensive properties can be normalized to remove dependence on system size

- molar volume - $v = \frac{V}{n}$

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

phase-intensive
 $\rho_v(T_v)$

system-intensive
 $\rho_{\text{total}} = \frac{M_{\text{total}}}{V_{\text{total}}}$

<< Phase / System-Intensive Property

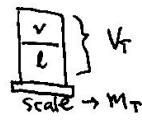
> phase-intensive - constant within the phase

> system-intensive - constant within the system

> quality (q) - relative fraction of one phase (usually vapor) out of the total

[Ex] How much $M_{\text{H}_2\text{O}}$ is in container?

Given $T, P \rightarrow \rho_v, \rho_L$



$$\rho_T = \frac{m_T}{V_T} = \frac{m_T}{V_v + V_L} = \frac{m_T}{\frac{m_v}{\rho_v} + \frac{m_L}{\rho_L}}$$

$$\frac{1}{\rho_T} = \frac{\frac{m_L}{\rho_L} + \frac{m_v}{\rho_v}}{m_T} = \frac{m_L}{m_T} \left(\frac{1}{\rho_L} \right) + \frac{m_v}{m_T} \left(\frac{1}{\rho_v} \right) = (1-q) \left(\frac{1}{\rho_L} \right) + q \left(\frac{1}{\rho_v} \right)$$

• quality is useful for "lever rule" (weighted avg) of intensive variables.

- e.g. $v, h, s, u, \hat{v} = \frac{1}{\rho}$

$$V_T = V_v q + V_L (1-q)$$

- System-intensive var is weighted avg of phase-intensive var

<< Phase

- > Phase - a group of atoms/molecules @ eqm that is macroscopically homogeneous over a state-determined length scale
 - at eqm - $t \rightarrow \infty$
 - Macro homo - have same properties
 - state-determined len scale - method of preparation doesn't matter

<< Degrees of Freedom

Ex1 Isolated system, 1 phase, ideal

$$\dot{Q} = 0 \quad dV = 0$$

$$\dot{W} = 0 \quad dm = 0$$

$$dn = 0$$



constant

U - total energy

V - volume

n - # of molecules

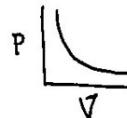
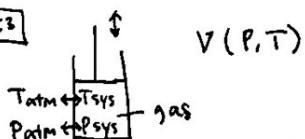
$$\cdot T \propto KE \Rightarrow dT = 0, T(U, V, n), T(u, v)$$

$$\cdot P = \frac{F}{A} \Rightarrow dP = 0, P(U, V, n), P(u, v)$$

> State Postulate - for a system with a single unreactive molecular species, which exists as a single phase @ eqm, we must specify the value of two independent phase-intensive state properties to uniquely & adequately define the intensive thermo state of system.

Ex2 Ideal gas law $PV = nRT \Rightarrow P \propto V = RT$

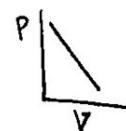
Ex3



Ex4

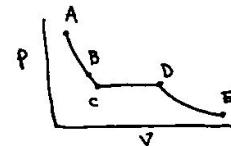
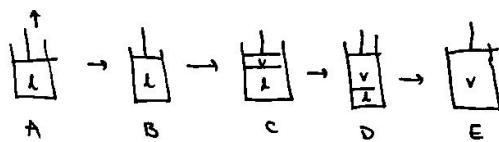


$$dV \rightarrow \text{large } dP \text{ (incompressible)}$$



*** Degrees of Freedom

- pure vapor : Define $v, T \Rightarrow P$
- pure liquid : Define $v, T \Rightarrow P$
- VLE of expanding liquid : pressure P is fixed, being the saturation pressure



- molar volume v is system intensive, but not phase intensive

$$v(T) = \gamma v_g + (1-\gamma) v_l$$

- $P(T)$ is also set by temperature

<< Gibbs Phase Rule

$$F = 2 + c - p - r \quad \text{"CPR"}$$

- c - # of species / components
- p - # of phases @ eqm
- r - # of independent rxns
- F - degree of freedom, # phase intensive var

[Ex1] Cup of ice water @ 10°C , 1 atm

$$F = 2 + c - p - r = 2 + 1 - 2 - 0 = 1$$

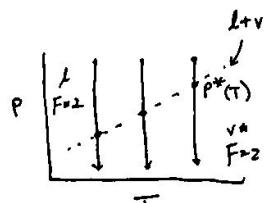
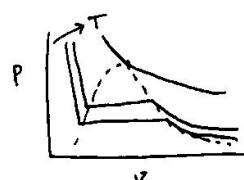
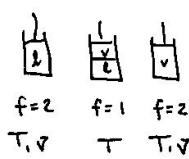
$F = 1$, but given 2 properties (T, P), \rightarrow over-determined system

[Ex2] Soln of ethanol & water.

$$F = 2 + c - p - r = 2 + 2 - 1 - 0 = 3$$

$F = 3$, given 0 property \rightarrow under-determined system

<< Thermodynamic Data



> triple point - all 3 phases coexist ($F = 2 + 1 - 3 - 0 = 0$)

> critical point - can't distinguish vapor & liquid

<< Quality

EX1 $V = 2L$ $V_L = 1 \text{ L/mol}$ $\gamma = ?$ $V = \frac{V}{n} = 2 \text{ L/mol}$

$n = 1 \text{ mol}$ $V_v = 5 \text{ L/mol}$

$$V = \gamma V_g + (1-\gamma) V_L$$

$$\gamma = \frac{V - V_L}{V_v - V_L} = \frac{2 - 1}{5 - 1} = 0.25$$

<< Thermodynamic Data

(or other prop.)

> tie line - constant P line connecting molar volume of 2 phases

• In two phase region,

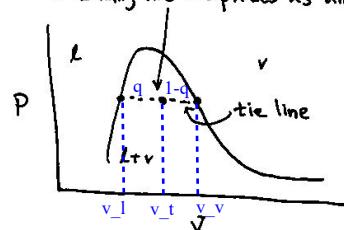
$$F = 2 + c - p - r = 2 + 1 - 2 - 0 = 1$$

$$\cdot \text{All liquid } V_T = V_L \quad (\gamma = 0)$$

$$\cdot \text{All vapor } V_T = V_v \quad (\gamma = 1)$$

$$\cdot \text{TWO phase } V_T = \gamma V_v + (1-\gamma) V_L$$

this is the system molar volume (weighted avg)
it actually has two phases as directed by tie line



<< Thermodynamic Processes

> Isobaric - constant pressure

> Isothermal - constant temperature

> Isoenthalpic - constant enthalpy h

> Isoentropic - constant entropy s

> Isochoric - constant volume

• Why do we need two tables, one based on two param, one based on one param (T/P)?

• Depending on # of phase, we have diff dof, therefore diff tables.

• e.g. only liq, only vapor, l+v (saturated)

Example of Using Thermo Data

Ex1 0.1g H₂O in 1000cm³ sealed rigid container @ 60°C

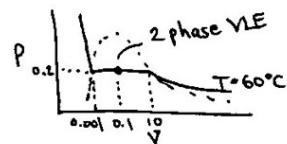
What phases are present? In what quantity @ eqm?

I Calculate known intensive properties

$$T = 60^\circ\text{C}$$

$$\begin{aligned} m &= 0.1\text{g} \\ V &= 1000\text{ cm}^3 \end{aligned} \quad \left. \begin{aligned} \hat{V} &= \frac{1000\text{ cm}^3}{0.1\text{g}} = 0.1\text{ m}^3/\text{kg} \end{aligned} \right\}$$

II Determine location on phase diagram (graph / table)



T	P	\hat{v}_l	\hat{v}_v
60°C	0.2 atm	0.001 m ³ /kg	7.67 m ³ /kg

NIST Fluid

- try one phase prop. first if discontinuity occurs for desired data,
- try sat. two phase prop.

III Find relative amount in each phase (lever rule get quality)

$$\hat{v} = \hat{v}_v q + (1-q) \hat{v}_l$$

$$q = \frac{\hat{v} - \hat{v}_l}{\hat{v}_v - \hat{v}_l} = \frac{0.1 - 0.001}{7.67 - 0.001} = 0.013 \quad (\text{table})$$

$$q = \frac{0.1 - 0.001}{10 - 0.001} \approx 0.01 \quad (\text{graph})$$

Ex2 Liquid refrigerant 134a @ 10bar, 25°C



What is T_f? How much original liq leave as vapor?

1 P=1bar, two phase : F = 2 + c - p - r = 2 + 1 - 2 - 0 = 1

2 NIST Fluid, sat, Pinterval $\Rightarrow T_f = -26.4^\circ\text{C}$

3 Open system + steady state + adiabatic : q=0, $\Delta h=0$

From T_f, P_f $\Rightarrow \hat{h}_c, \hat{h}_v$ NIST Fluid, sat, Pinterval $\Rightarrow \hat{h}_c = 165.4 \text{ kJ/kg}, \hat{h}_v = 382.6 \text{ kJ/kg}$

From T_i, P_i $\Rightarrow \hat{h}_T = \hat{h}_{\text{before valve}}$ NIST Fluid, isobaric $\Rightarrow \hat{h}_T = 234.6 \text{ kJ/kg}$

$$q = \frac{\hat{h}_T - \hat{h}_c}{\hat{h}_v - \hat{h}_c} = 0.319$$

<< Gibbs Phase Rule of Multicomponent

- 1 component, 1 phase : $F = 2 + 1 - 1 - 0 = 2$ e.g. T, P
- 1 component, 2 phase : $F = 2 + 1 - 2 - 0 = 1$ e.g. T
- 2 component, 1 phase : $F = 2 + 2 - 1 - 0 = 3$ e.g. T, P, x_i
- c component, 1 phase : $F = 2 + c - 1 - 0 = 1 + c$ e.g. T, P, composition var

<< Composition Variables

- Within a phase, multiple components :

$$\begin{aligned} > \text{mole fraction } x_i &= \frac{n_i}{\sum_j n_j} \Rightarrow \sum_j x_j = 1 \\ > \text{mass fraction } \hat{x}_i &= \frac{m_i}{\sum_j m_j} \Rightarrow \sum_j \hat{x}_j = 1 \end{aligned} \quad \left. \begin{array}{l} \text{phase-intensive} \\ \text{composition variable} \end{array} \right\}$$

EX1 phase with A \neq B.

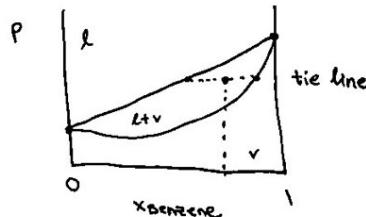
$$x_A = \frac{n_A}{n_A+n_B}, \quad x_B = \frac{n_B}{n_A+n_B}, \quad x_A = 1 - x_B$$

- Only $(c-1)$ independent variable needed to fully define the composition of a phase.

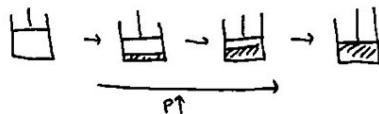
<< Favorable Mixing

EX2

	Benzene	Toluene
Top	80°C	111°C
structure		

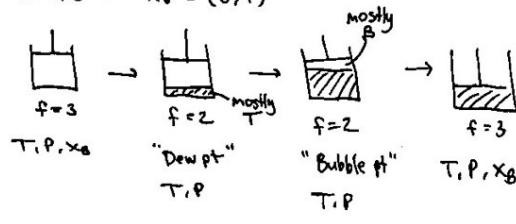


- pure benzene: $x_b = 1$



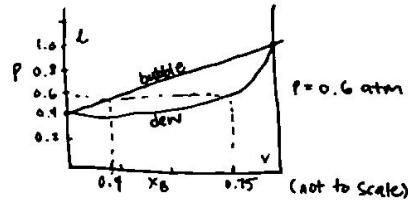
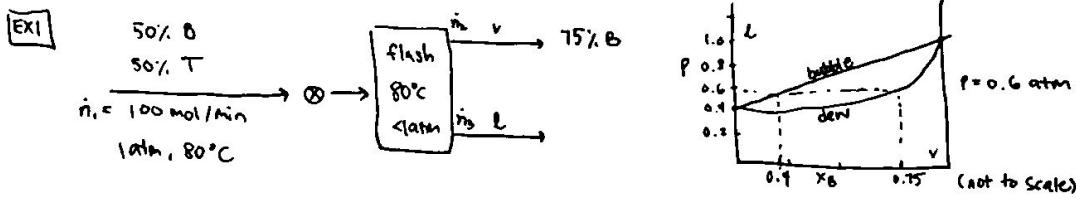
- pure toluene: ~~x_b~~ $x_b = 0$

- mixture: $x_b \in (0,1)$



x_b is system intensive

Example of Favorable Mixing



What pressure will achieve this separation? How much vapor is produced?

- $P = 0.6 \text{ atm}$. From product fraction $x_B = 75\%$, reach the dew point curve, and read the pressure.
- $x_{B1} = 0.4$. By tie line, we determine the fraction of B in liquid.
- Overall : $n_1 = n_2 + n_3$
- benzene : $n_{10} = n_{20} + n_{30}$

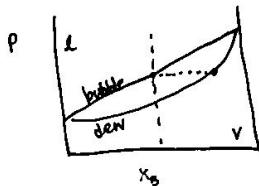
$$x_B, n_1 = x_{B1} n_2 + x_{B3} n_3$$

$$x_{B1} = x_{B2} \frac{n_2}{n_1} + x_{B3} \frac{n_3}{n_1} \quad \left(\frac{n_2}{n_1} = \frac{n_v}{n_l} = q, \quad \frac{n_3}{n_1} = \frac{n_1 - n_2}{n_1} = 1 - q \right)$$

$$x_{B1} = x_B = q + x_{B3} (1-q)$$

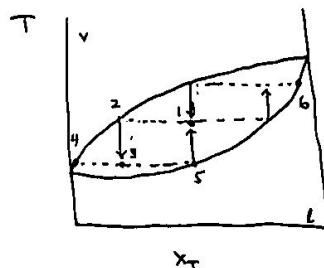
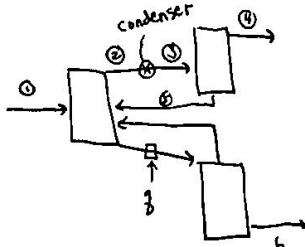
$$q = \frac{x_{B1} - x_{B3}}{x_{B2} - x_{B3}} = \frac{0.5 - 0.4}{0.75 - 0.4} = 0.29$$

- Quality works for mole fraction too
- Quality \neq mole fraction
 - quality - between phase
 - mole fraction - within a phase
- High purity stream results in lower flow rate (tradeoff!)



- Known initial x_B , to get high purity $B(v)$, it should be on the bubble pt curve. Since it just started to bubble, the flow rate of vapor is low.

- Want high purity & molar flowrate, use more flash stages

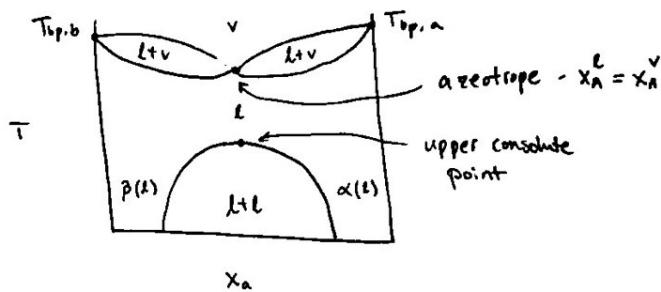


$$x_{10} = x_{10} q + x_{00} (1-q)$$

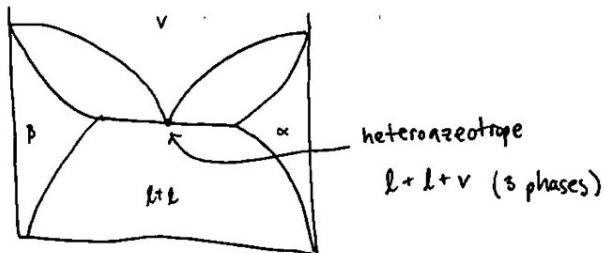
Quality works for whole system or individual stages

Ex2 Thermo Data for Nonideal Mixtures

Ex2 Less favorable Mixing of Butanol & H₂O



Ex3 Even less favorable mixing



To calculate moles in each phase, we need 3 equations at heteroazeotrope.

$$n = n_\alpha + n_\beta + n_v$$

$$x_B \cdot n = x_{\alpha,\alpha} n_\alpha + x_{\beta,\beta} n_\beta + x_{v,v} n_v$$

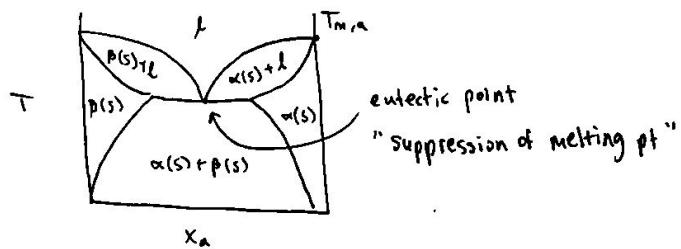
$$h_A \cdot n = h_{\alpha,\alpha} n_\alpha + h_{\beta,\beta} n_\beta + h_{v,v} n_v$$

When referring to two liquids, fraction f is used instead of quality q.

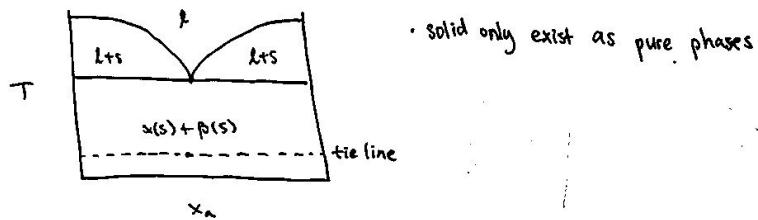
$$x_B = f^\alpha x_\alpha^\alpha + (1-f^\alpha) x_\alpha^\beta \quad , \text{ where } f^\alpha = \frac{n^\alpha}{n}$$

“Thermo Data for Solids”

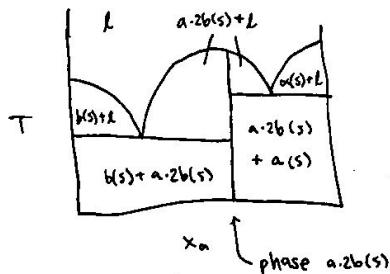
→ Solid Phase Diagram (Favorable Mixing)

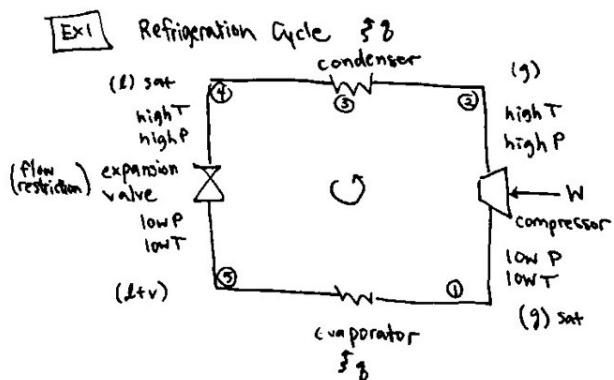


→ Poor mixing



→ Hydrates (More complex solid phase)

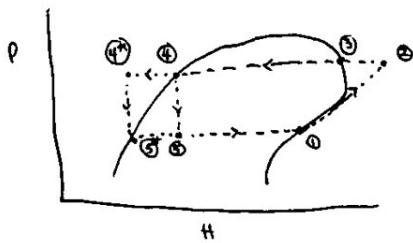




- Which way does the cycle operate?
- Where is the condenser & evaporator?

- Since compressor goes from low P to high P, the cycle operates counterclockwise.
- Since work is added via compressor, T is increased. To drop T, condenser is needed at the top. So evaporator is needed at bottom to raise T.

► Trace the cycle in P-H diagram.



> expansion valve - $\Delta P < 0 / P \downarrow$ / high P \rightarrow low P (flow restriction) adiabatic $q=0$, $\Delta H=0$ (open sys)	} work done
> compressor - $\Delta P > 0 / P \uparrow$ / low P \rightarrow high P - $\Delta T > 0 / T \uparrow$ / low T \rightarrow high T (ΔH)	
> condenser - $\Delta P = 0$ - $\Delta T < 0 / T \downarrow$ / high T \rightarrow low T	} work done
> evaporator - $\Delta P = 0$ - $\Delta T > 0 / T \uparrow$ / low T \rightarrow high T	

1. Known ④ is sat liq, it needs to be on the eqm curve
2. Expansion valve / flow restriction is adiabatic ($q=0$), in open system, $\Delta H=0$.

Therefore ② will have same H but lower pressure.

3. Evaporator is isobaric, so no change in P. With $\Delta T > 0$, $\Delta H > 0$.

Since it becomes a saturated vapor, it is also on the eqm curve.

4. Compressor increase P and T, and the vapor becomes superheated.

5. The condenser finally isobarically decreases T, returning to sat liq.

In the condenser, the gas is condensed to liquid, so ③ is on eqm curve

- In application, ④ is typically cooled to subcooled liquid. Label on P-H diagram as ④'.

• Condenser is isobaric. With lower T, H is lower.

- Why is ④' subcooled better than ④? Given H values:

$$H_1 = 621.7 \text{ kJ/kg}$$

From ④ \rightarrow ①, heat removed is $\Delta H = H_1 - H_4 = 177.9 \text{ kJ/kg}$

$$H_2 = 653.1 \text{ kJ/kg}$$

④' \rightarrow ①, heat removed is $\Delta H = H_1 - H_{4'} = 183 \text{ kJ/kg}$

$$H_4 = 443.8 \text{ kJ/kg}$$

But the work used is the same: $\Delta H = H_2 - H_1 = 31.4 \text{ kJ/kg}$

$$H_{4'} = 438.7 \text{ kJ/kg}$$

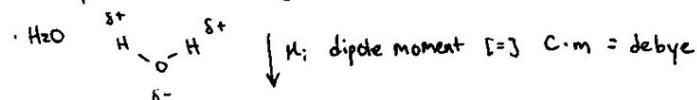
④ \rightarrow ④'

• More heat is removed using the same work.

<< Internal Energy & Attractive Forces

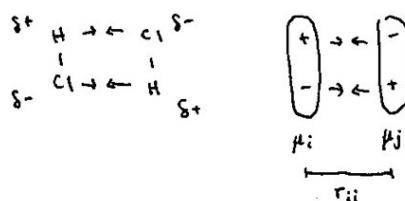
- Context: Why do phases form?
- Answer: Attractive forces between molecules (without them, everything will be gas)
- Attractive forces between neutral molecules: "van der Waals"
 - Keeson (dipole-dipole)
 - Debye (dipole-induced dipole)
 - London dispersion (induced dipole-induced dipole)

> dipole - separation of charge



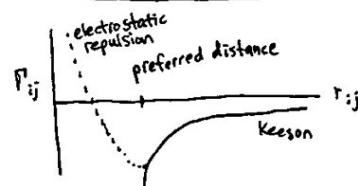
neutral overall

→ Keeson (dipole-dipole)



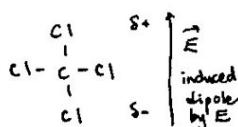
Γ_{ij} = potential energy to separate molecules

$$\Gamma_{ij} = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{r_{ij}^6 k_B T}$$



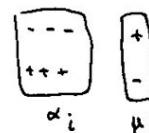
→ Debye (dipole-induced dipole)

e.g. CCl_4



α_i - polarizability, how easily e- cloud is distorted by \vec{E}

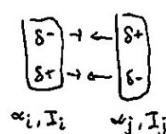
$$\Gamma_{ij} = -\frac{\alpha_i \mu_j^2}{r_{ij}^6}$$



→ London dispersion force (induced-dipole-induced-dipole)

spontaneously form dipole to lower overall energy

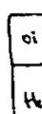
I_i - ionization energy



$$\Gamma_{ij} = -\frac{3}{2} \frac{\alpha_i \alpha_j}{r_{ij}^6} \frac{1}{\frac{1}{I_i} + \frac{1}{I_j}}$$

Keeson (dipole-dipole) is the strongest of van der Waal forces

These interactions are attractive



H_2O (dipole)

oil (induced)

H_2O & oil are attracted...

BUT!

H_2O (dipole)

H_2O (dipole)

they are each prefer to attract to each other.

⇒ phase separation

<< Lennard-Jones Model

- empirical model of potential energy
- ϵ - depth of potential well
- σ - distance at which attractive & repulsive forces cancel

$$\Gamma = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

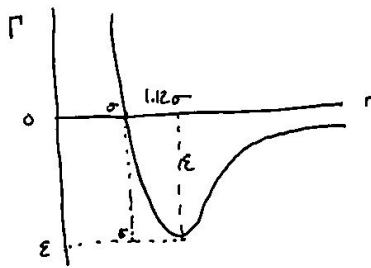
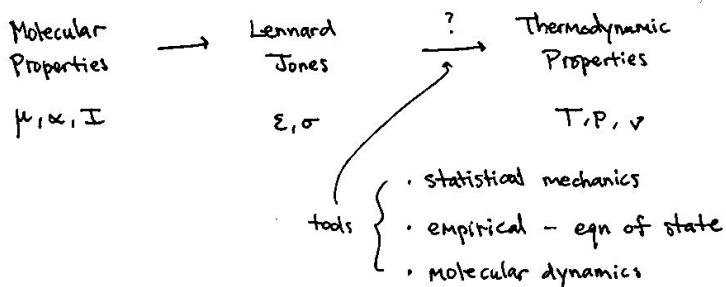
/ \

 empirical van der Waals

 repulsion attraction

- $r(\Gamma_{\min}) = 2^{1/6}\sigma = 1.12\sigma$
- distance between molecules

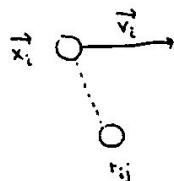
→ Bigger picture



... Classical Molecular Dynamics Simulation

- track molecular motion in an isolated system

 (no mass & energy exchange)



After some dt :

$$\frac{dx_i}{dt} = \vec{v}_i$$

$$\vec{F}_i = \sum_j \vec{F}_{ij} \quad (j \text{ is other molecule})$$

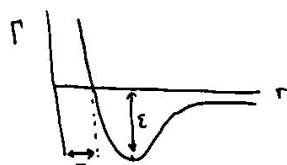
$$\frac{d\vec{v}_i}{dt} = \frac{\vec{F}_i}{m}$$

$$\vec{F}_{ij} = \frac{d\vec{r}_{ij}}{dt} \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|^3} \quad (\text{by LJ potential})$$

\vec{r}_{ij}

→ Dimensionless Parameters

- nondimensionalize parameters are easier to work with



$$r' = \frac{r}{\sigma}$$

$$T' = \frac{k_b T}{\epsilon}$$

$$P' = \frac{\sigma^3}{\epsilon} P$$

$$E' = \frac{U}{\epsilon}$$

$$t' = \frac{t}{\sigma \sqrt{m/\epsilon}}$$

$$T = \frac{KE}{n} = \frac{\text{kinetic energy}}{\# \text{ molecules}} \Rightarrow KE = nT \quad (\text{could be dimensional or dimensionless})$$

→ Potential Energy

Ex1 In a frozen system of 492 molecules, what is the potential energy? Assume hexagonal packing.



• $KE = 0$ (frozen)

• For each pair, $PE = -\epsilon$ (LJ potential)

• Amount of interactions: $\frac{1}{2}(\# \text{ Molecules})(\# \text{ neighbors})$

$$\# \text{ interactions} = \frac{1}{2}(492)(6) \approx 1500$$

$$PE = \frac{1500(-\epsilon)}{\epsilon} = -1500 \quad \Rightarrow \quad U = KE + PE = -1500$$

Ex2 Energy $\Delta U = 850$ is added to the system. Given $T = 0.435$, $n = 492$,

How much is KE and PE?

$$\Delta KE = nT = (492)(0.435) = 214, \quad KE = 0 + 214 = 214$$

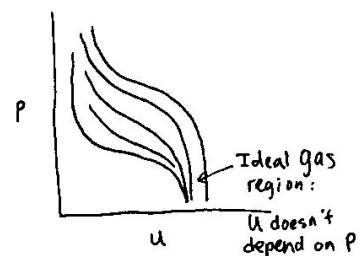
$$U = -1500 + 850 = -650$$

$$\Delta PE = \Delta U - \Delta KE = +850 - 214 = 636$$

$$PE = PE + \Delta PE = -1500 + 636 = -864$$

→ Temperature Dependence

- In ideal gas region, total internal energy U does not depend on pressure
- no potential energy - molecules too far apart to interact
- $U = KE + PE = Tn + (\text{molecular interaction of LJ potential})$
- $U = f(T)$ for ideal gas



«« Equation of State (EOS)

- context: empirical model translating molecular behavior to bulk behavior

- Ideal gas law:

$$PV = RT$$

- van der Waals EOS:

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

- attraction reduces pressure (a term)

- potential energy $e_p \propto p$ (more nearest neighbor, more PE)

$$e_p = -\frac{a}{V}$$

$$d(E_p) = -F_x dx = -PA dx = -P dV$$

$$P = -\frac{d(E_p)}{dV} = -\frac{d(e_p)}{dV}$$

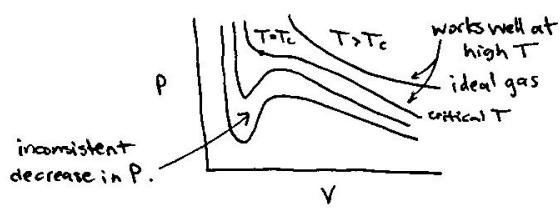
$$P|_{e_p=0} = -\frac{d(e_p)}{dV} = -\frac{d}{dV}(-\frac{a}{V}) = -\frac{a}{V^2} \rightarrow P|_{e_p=0} = -\frac{a}{V^2}$$

- molecules have size (relevant at high P , low V) (b term)

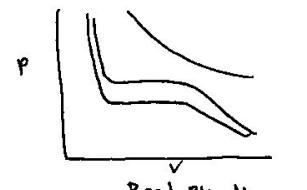
- $V_{actual} = V - b$, where b is vol occupied by molecule

- assume single phase gas

- Only works at high T , especially near T_c



PV-diagram according to van der Waals



Real PV-diagram

- real pressure doesn't decrease at low V .

→ Fitting van der Waals EOS

- Either lookup a and b , or * use math relationship with physical properties (T_c, P_c)

$$\text{At } T_c \text{ it's critical pt: } \left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

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

$T_c, P_c \rightarrow \text{NIST, Table A.1}$

- In summary, find T_c, P_c , calculate a, b , use EOS.

$$\text{solve for } P: \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{solve for } V: \quad V^3 - \left(\frac{RT}{P} + b\right)V^2 + \frac{a}{P}V - \frac{a}{P}b = 0$$

<< Principle of Corresponding States

- > All fluids deviate from ideal gas behavior to roughly the same degree when compared to their reduced temperature & pressure (T_r, P_r)
 - around critical pt, all fluids behave similarly
 - away from critical pt, behave similar to others

<< Compressibility Factor

> Reduced temperature -
$$\bar{T}_r = \frac{T}{T_c}$$

> Reduced pressure -
$$\bar{P}_r = \frac{P}{P_c}$$
 Pv/RT

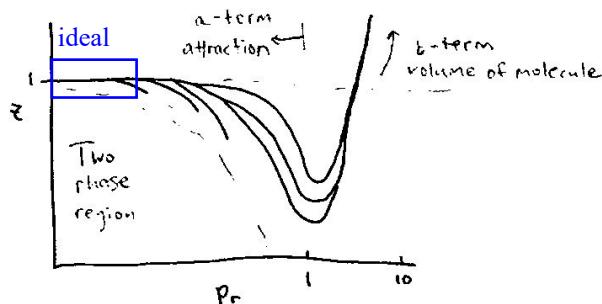
> compressibility factor -
$$\bar{z} = \frac{V_{\text{real}}}{V_{\text{ideal}}} = \frac{V_r T}{P}$$

- how much volume a fluid has relative to how much it would have without molecular interactions

- $\bar{z} = 1$ for ideal gas
- $\bar{z} \rightarrow$ van der Waals EOS:

$$\cdot z = \frac{\bar{z}}{\bar{z} - \frac{1}{8} \frac{P_r}{T_r}} - \frac{27 \bar{P}_r}{64 T_r^2 \bar{z}}$$

• vdW Compressibility chart



- Lines on low P_r terminates since it enters 2-phase region
- Decrease in z for small P_r is caused by a -term of attraction (potential energy)
- At low pressure, $z \rightarrow 1$, ideal gas
- Increase in z for large P_r is caused by b -term

<< Using vdW EOS

EX1 Find molar volume v of butane at 235°C , 60 bar, given $T_c = 425\text{K}$, $P_c = 38\text{bar}$, $R = 8.314 \times 10^{-2} \frac{\text{L bar}}{\text{mol K}}$

$$T = 235^\circ\text{C} = 508\text{K}$$

$$a = \frac{27}{64} \frac{(RT_c)^2}{P_c} = \frac{27}{64} \frac{[(8.314 \times 10^{-2} \frac{\text{L bar}}{\text{mol K}})(425\text{K})]^2}{38\text{ bar}} = 13.9 \frac{\text{L}^2 \text{bar}}{\text{mol}^2}$$

$$b = \frac{RT_c}{8P_c} = \frac{(8.314 \times 10^{-2} \frac{\text{L bar}}{\text{mol K}})(425\text{K})}{8(38\text{ bar})} = 0.116 \text{ L/mol}$$

$$\text{Solve for } v \text{ in the vdW EOS: } v^3 - \left(\frac{RT}{P} + b\right)v^2 + \frac{a}{P}v - \frac{a}{P}b = 0$$

$$\Rightarrow v = 0.442 \text{ L/mol}$$

EX2 What is the molar potential energy of butane?

$$e_p = -\frac{a}{v} = \frac{-13.9 \frac{\text{L}^2 \text{bar}}{\text{mol}^2}}{0.442 \text{ L/mol}} = -31.45 \frac{\text{L bar}}{\text{mol}}$$

<< Departure Function for vdW EOS

- Ideal gas has no PE, but only KE.
- Real gas has PE (intermolecular force). It's the diff between internal energy of real gas and ideal gas

$$e_p = u_{\text{real}}(T, P) - u_{\text{ideal}}(T, P=0)$$

> departure function - relative importance of attractive interaction to kinetic energy

$$\boxed{\frac{e_p}{RT_c} = \frac{u_{\text{real}}(T, P) - u_{\text{ideal}}(T, P=0)}{RT_c}}$$

For vdW EOS:

$$\frac{e_p}{RT_c} = -\frac{a}{RT_c v} = -\frac{27}{64} \frac{(RT_c)^2}{P_c} \frac{1}{RT_c v} = -\frac{27}{64} \frac{RT_c}{P_c v} \frac{T}{T} \frac{P}{P} = -\frac{27}{64} \frac{P_r}{T_r} \frac{R T}{P} = -\frac{27}{64} \frac{P_r}{z T_r}$$

$$\boxed{\frac{e_p}{RT_c} = -\frac{27 P_r}{64 z T_r}}$$

<< Using Departure Functions

Ex3 Find molar volume v of butane at 235°C , 60 bar. (same as Ex1!)

$$T = 235^\circ\text{C} = 508\text{K} \quad T_c = 425\text{K} \quad Tr = \frac{T}{T_c} = \frac{508\text{K}}{425\text{K}} = 1.2$$

$$P = 60\text{bar} \quad P_c = 38\text{bar} \quad Pr = \frac{P}{P_c} = \frac{60\text{bar}}{38\text{bar}} = 1.6$$

From compressibility chart, $\bar{z} = 0.6$

$$v = \frac{\bar{z}RT}{P} = \frac{(0.6)(8.3 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1})(508\text{K})}{60\text{bar}} = 0.422 \text{ L/mol}$$

Ex4 What is the molar potential energy of butane? (same as Ex2!)

From departure function chart, using $Tr, Pr,$

$$\frac{u - u^{\text{IG}}}{RT_c} = \frac{e_p}{RT_c} = -0.9$$

$$e_p = -0.9 RT_c = -31.8 \text{ L} \cdot \text{bar/mol}$$

<< Lee-Kesler EOS

- based on compressibility EOS, with improved compressibility factor \bar{z} .

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

> acentric factor ω - Molecules with strong interactions or oblong shapes have lower Pr than they should.

> Find $z^{(0)}, z^{(1)}$: Koretsky Fig 4.13, 4.14, Table C.1, C.2

> Find ω : tabulated, or $\omega = -1 - \log_{10}(Pr^{\text{sat}}(Tr=0.7))$

> enthalpy departure functions

$$\frac{h - h^{\text{IG}}}{RT_c} = \left(\frac{h - h^{\text{IG}}}{RT_c} \right)^{(0)} + \omega \left(\frac{h - h^{\text{IG}}}{RT_c} \right)^{(1)}$$

> Find departure function ${}^{(0)}$ and ${}^{(1)}$: Koretsky Fig 5.5, 5.6, Table C.3, C.4

> $h = u + Pv$

> relation between internal energy and enthalpy departure function.

$$\frac{u - u^{\text{IG}}}{RT_c} = \frac{h - h^{\text{IG}}}{RT_c} + Tr(1-\bar{z})$$

<< First Law of Thermo

> the energy in an isolated system cannot increase or decrease

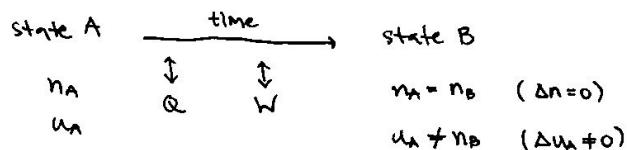
- e.g. universe

- energy cannot be created / destroyed

- conservation of energy

<< Closed System

> closed system - no exchange of mass, but can exchange energy in the form of heat / work.



> heat Q - net flow of thermal energy (from diff of energy) into the system

> Work W - net work done on the system

> 1st law of thermo -
for closed system

$$\Delta U = Q + W$$

$$\Delta U = q + w$$

$$\Delta \hat{U} = \hat{q} + \hat{w}$$

→ Types of work

> work - energy transfer from movement & nonthermal sources

> Pv work w - deformation of control volume or boundary layer

$$w = \int_{x_1}^{x_2} F dx = \int_{x_1}^{x_2} P A dx = - \int_{V_1}^{V_2} P dV$$

$$w = \int_{V_1}^{V_2} P dV$$

- requires reversible process

- no change in entropy

- practically slow change

> shaft work w_s - work delivered by things not heat related

- motor-delivered

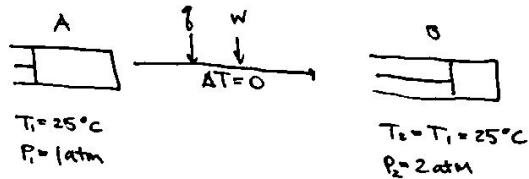
$$\boxed{d\delta}$$

- current energy generation

$$\boxed{I} \quad p = IV$$

« Isothermal Process

Ex1 Ideal gas @ 1 atm, 25°C. Isothermally compressed to 2 atm. Find Δu , q , w .



$$\begin{aligned} \Delta U &= \cancel{e_p} + e_k \\ &= e_k(T) \end{aligned} \quad (\cancel{e_p} = 0 \text{ for ideal gas}, e_k = f(T))$$

Since $\Delta T = 0$, $\boxed{\Delta U = 0}$

First law: $\Delta U = q + w = 0$

$$q = -w = + \int_A^B P dV$$

Method 1

rewrite P in terms of v

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

$$W = - \int_A^B \frac{RT}{v} dv \rightarrow \text{need } v_A \text{ and } v_B$$

Method 2

rewrite dv in terms of dP

$$v = \frac{RT}{P} \Rightarrow dv = -\frac{RT}{P^2} dP$$

$$W = - \int_A^B P dV = + \int_A^B \frac{RT}{P^2} dP = RT \ln P \Big|_{P_A}^{P_B}$$

$$= RT \ln(2) = 1.7 \text{ kJ/mol}$$

$$q = -w = -1.7 \text{ kJ/mol}$$

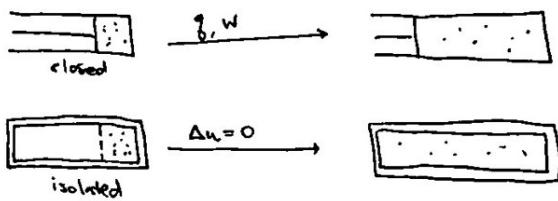
« Isoenergetic Process

Ex2 Ideal gas go through isoenergetic process of compression. Find ΔT , q , w .

$$\Delta U = 0 \Rightarrow \Delta T = 0 \quad (\text{isoenergetic} = \text{isothermal} \text{ only for ideal gas})$$

$$\left. \begin{array}{l} w > 0 \\ q < 0 \end{array} \right\} q = -w$$

⇒ Path Dependence of Heat & Work



$$\Delta U = 0, q = -w$$

$$w < 0, q > 0$$

$$\Delta U = 0, \Delta n = 0, \Delta V = 0$$

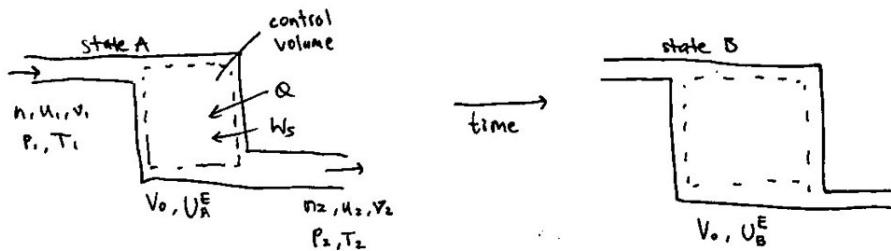
$$w = 0, q = 0$$

} same final
T,P.

⇒ First Law for Open System

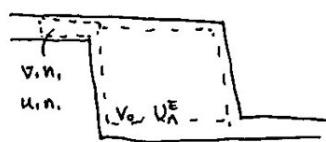
→ Eulerian control volume

- Fixed Volume V_0 , no PV work
- Open System



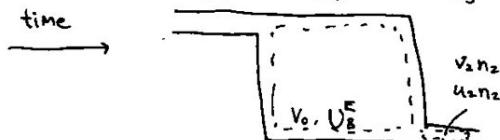
→ Lagrangian control volume

- tracks particular amount of particles
- closed system



$$V_A^L = V_0 + v_1 n_1$$

$$U_A^L = U_A^E + u_1 n_1$$



$$V_B^L = V_0 + v_2 n_2$$

$$U_B^L = U_B^E + u_2 n_2$$

→ Enthalpy

> enthalpy - energy carried by a fluid when crossing system boundary

$$h = u + Pv$$

• u - internal energy - energy carried by molecules themselves

• Pv - mechanical energy carried by molecules

• not PV Work! PV Work is $P\Delta V$.

• Pv is a state property

<< Deriving First Law for Open System

- Goal: Determine ΔU^E

$$\cdot \Delta U^E = U_B^E - U_A^E$$

$$= (U_B^L - u_{2n_2}) - (U_A^L - u_1 n_1) \quad \text{Lagrangian ctrl vol}$$

$$= U_B^L - U_A^L + u_1 n_1 - u_2 n_2$$

$$= \Delta U^L + u_1 n_1 - u_2 n_2 \quad \boxed{\text{I}}$$

$$\cdot \Delta U^L = Q + W_s + W_{PV} \quad \boxed{\text{II}} \quad \text{First law for closed syst.}$$

$$\cdot W_{PV} = W_1 + W_2 + W_3$$

$$\cdot W_1 = - \int_A^B P dV^L = P_1 (V_1 n_1 - 0) = P_1 V_1 n_1$$

$$\cdot W_2 = 0 \quad (\Delta V = 0)$$

$$\cdot W_3 = - \int_A^B P dV^L = - P_2 (V_2 n_2 - 0) = - P_2 V_2 n_2$$

$$\Rightarrow W_{PV} = P_1 V_1 n_1 - P_2 V_2 n_2 \quad \boxed{\text{III}}$$

$$\cdot (\boxed{\text{II}} \rightarrow \boxed{\text{III}}) \rightarrow \boxed{\text{I}}:$$

$$\begin{aligned} \Delta U^E &= Q + W_s + P_1 V_1 n_1 - P_2 V_2 n_2 + u_1 n_1 - u_2 n_2 \\ &= Q + W_s + h_1 (u_1 + P_1 v_1) - n_2 (u_2 + P_2 v_2) \\ &= Q + W_s + n_1 h_1 - n_2 h_2 \\ &= Q + W_s + H_1 - H_2 \end{aligned}$$

• Generalize to multiple streams:

$$\Delta U = Q + W_s + \sum_{in} n_i h_i - \sum_{out} n_j h_j$$

First law for open system

$$\frac{dU}{dt} = Q + W_s + \sum_{in} n_i h_i - \sum_{out} n_j h_j$$

Time dependent

$$\dot{Q} = \dot{Q} + \dot{W}_s + \sum_m \dot{n}_i h_i - \sum_{out} \dot{n}_j h_j$$

@ steady state

↔ Open System Example

Ex1 Ideal gas 25°C, 1 atm adiabatically expand to 1 atm. Find Δh , Δu , ΔT , W_{pr} , W_s , g .

$$\xrightarrow{T_1 = 25^\circ C} \textcircled{S} \xrightarrow{P_1 = 1 \text{ atm}} P_2 = 1 \text{ atm}$$

open system balance

$$0 = \cancel{\dot{Q}} + \dot{W}_s + \dot{n}_i h_i - \dot{n}_o h_o$$

$$\dot{n}_i h_i = \dot{n}_o h_o$$

$$h_i = h_o \quad (\text{since } \dot{n}_i = \dot{n}_o)$$

$$\boxed{\Delta h = 0}$$

$$\text{adiabatic} \Rightarrow \boxed{g = 0}$$

$$\text{no mechanical work} \Rightarrow \boxed{W_s = 0}$$

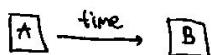
$$\text{no change in volume in system} \Rightarrow \boxed{W_{pr} = 0}$$

For ideal gas, $h = f(T)$ since $h = u + Pv = u + RT = u(T) + R(T)$

$$\Rightarrow \boxed{\Delta T = 0} \Rightarrow \boxed{\Delta U = 0}$$

↔ Summary of 1st Law

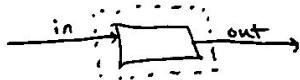
→ Closed System



$$\Delta U = U_B - U_A = Q + W \quad (\Delta u = u_B - u_A = q + w)$$

$$W_{pr} = - \int_{V_A}^{V_B} P dV \quad (w_{pr} = - \int_{V_A}^{V_B} P dv)$$

→ Open System



$$0 = \dot{Q} + \dot{W}_s + \sum \dot{n}_i h_i - \sum \dot{n}_o h_o$$

$$h = u + Pv$$

First Law Analysis

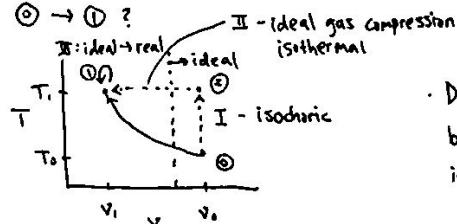
- What if we want to find u or h at arbitrary new condition?

1. perform an experiment
2. Lookup data on NIST
3. Use a model (vdW, Lee-Kesler)

- * 4. Construct a convenient hypothetical path to new state

EX1 How does u change from $\textcircled{0} \rightarrow \textcircled{1}$?

ref state
 T_0, V_0, u_0



- Does not choose other path because we want to assume ideal gas.

I Isochoric path to still be in ideal gas region.

$$\Delta u_I = \delta q + \delta w^0$$

$$\Delta u_I = \delta q$$

Since $du = \left(\frac{\partial u}{\partial T}\right)_v dT = C_v dT$, where $C_v = \left(\frac{\partial u}{\partial T}\right)_v$

$$\Delta u_I = \int_{T_0}^{T_1} C_v dT$$

II Isothermal path, assume ideal gas

$$\Delta T = 0 \rightarrow \Delta u = 0 \quad (\text{since } \Delta u = e_p + e_k; e_p = 0 \because \text{ideal gas}; e_k(T) = 0 \text{ since } \Delta T = 0)$$

III Ideal gas \rightarrow real gas

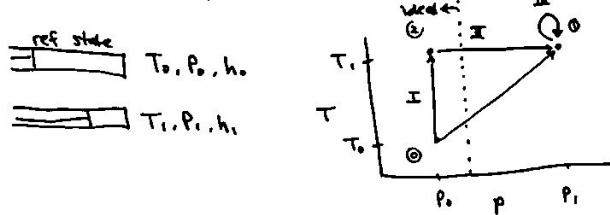
• Use departure function (Lee-Kesler) : $\frac{u_{\text{real}} - u_{\text{ideal}}}{RT_c}$

$$\Delta u_{\text{III}} = RT_c \frac{u_{\text{real}} - u_{\text{ideal}}}{RT_c} \quad (\text{vdW, Lee-Kesler})$$

• Overall, with C_v data & PVT (L-K EOS), we can solve for Δu .

$$\Delta u = \Delta u_I + \Delta u_{\text{II}} + \Delta u_{\text{III}}$$

<< First Law Analysis

[Ex] How does h change from $\textcircled{0}$ to $\textcircled{1}$?**[Ex]** Isobaric, ideal gas

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT = c_p dT \quad \text{, where } \boxed{c_p = \left(\frac{\partial h}{\partial T}\right)_P}$$

$$\text{so } \Delta h_I = \int_{T_0}^{T_1} c_p dT$$

[Ex] Isothermal, assume ideal gas

$$\Delta T = 0 \Rightarrow \Delta h = 0 \quad (h = u + Pv = u(T) + RT = f(T))$$

[Ex] Ideal gas \rightarrow real gas

- Use departure functions

$$\Delta h_{II} = h_{\text{real}} - h_{\text{ideal}} = RT_c \left(\frac{h_{\text{real}} - h_{\text{ideal}}}{RT_c} \right)$$

<< Relationship between Heat Capacities of Ideal Gas

- Assume ideal gas

$$h = u + Pv$$

$$\frac{\partial h}{\partial T} = \frac{\partial u}{\partial T} + \frac{\partial}{\partial T}(Pv) = \frac{\partial u}{\partial T} + \frac{\partial}{\partial T}(RT)$$

$$\frac{\partial h}{\partial T} = \frac{\partial u}{\partial T} + R$$

$$\boxed{c_p = c_v + R}$$

$$\frac{c_p}{R} = \frac{c_v}{R} + 1$$

<< Incompressible Liquids & Solids

$$u = e_p + e_k \quad (e_p = -\frac{a}{V})$$

$$u = e_p(v(T)) + e_k(T)$$

$$u = u(T)$$

$$h(T) = u(T) + Pv_0 \quad (\text{where } v = v_0 \approx \text{const, small})$$

 \rightarrow Low Pressure

$$h(T) \sim u(T)$$

$$\Delta u = \Delta h = \int_{T_0}^{T_1} c_p(T) dT$$

 \rightarrow High Pressure

$$\begin{aligned} \Delta h &= \Delta h_I + \Delta h_{II} \\ &= \int_{T_0}^{T_1} c_p(T) dT + v_0(p_1 - p_0) \end{aligned}$$

<< Phase Change

$$\Delta h = \Delta u + \Delta(Pv)$$

$$\begin{aligned} &= \Delta u + P_0 \Delta v \quad (w = - \int_{V_0}^{V_1} P_0 dV = P_0 \Delta V) \\ &= \Delta u - w \end{aligned}$$

$$\boxed{\Delta h = q_b}$$

$$\Delta h_{\text{vap}}^0(T_b) = h_g - h_s$$

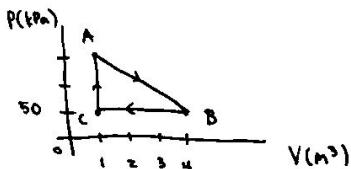
$$\Delta h_{\text{melt}}^0(T_m) = h_L - h_S$$

$$\Delta h_{\text{subl}}^0(T_s) = h_g - h_S$$

$$\Delta h_{\text{rm}}^0(T_b) = h_{\text{prod}} - h_{\text{react}}$$

<< Ideal Gas Cycle

Ex1 67.5 mol monoatomic ideal gas. Find T at each state.



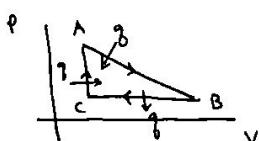
$$PV = nRT$$

$$T_A = \frac{PV}{nR} = \frac{(150\text{kPa})(1\text{m}^3)}{(67.5\text{mol})(8.314/\text{mol}\cdot\text{K})} \times \frac{10^3\text{Pa}}{1\text{kPa}} = 267\text{K}$$

$$T_B = 356\text{K}$$

$$T_C = 89\text{K}$$

Ex2 What are direction of heat flow?



Note that work is area under curve for Pv diagram.

$$\begin{aligned} \text{A} \rightarrow \text{B} &: \Delta T > 0 \Rightarrow \Delta U > 0 \\ &\Delta V > 0 \Rightarrow W < 0 \end{aligned} \quad \left. \begin{aligned} q &> 0 \\ q &> 0 \end{aligned} \right\} q > 0$$

$$\begin{aligned} \text{B} \rightarrow \text{C} &: \Delta T < 0 \Rightarrow \Delta U < 0 \\ &\Delta V < 0 \Rightarrow W > 0 \end{aligned} \quad \left. \begin{aligned} q &< 0 \\ q &< 0 \end{aligned} \right\} q < 0$$

$$\begin{aligned} \text{C} \rightarrow \text{A} &: \Delta V = 0 \Rightarrow W = 0 \\ &\Delta T > 0 \Rightarrow \Delta U > 0 \end{aligned} \quad \left. \begin{aligned} q &> 0 \\ q &> 0 \end{aligned} \right\} q > 0$$

Ex3 Calculate values of q in each process.

$W = - \int P dV = \text{area under curve with sign!}$

$$\text{A} \rightarrow \text{B} \quad \Delta U = ncv\Delta T = n\frac{3}{2}R\Delta T = (67.5\text{mol})\left(\frac{3}{2}\right)(8.314\text{J/K}\cdot\text{mol})(356-267)\text{K} = 75761\text{J}$$

$$W = -[\frac{1}{2}(150-50)\text{kPa}(4-1)\text{m}^3 + (50\text{kPa})(4-1)\text{m}^3] = -300000\text{J}$$

$$q = \Delta U - W = 376\text{kJ}$$

$$\text{B} \rightarrow \text{C} \quad \Delta U = n\frac{3}{2}R\Delta T = -224759\text{J}$$

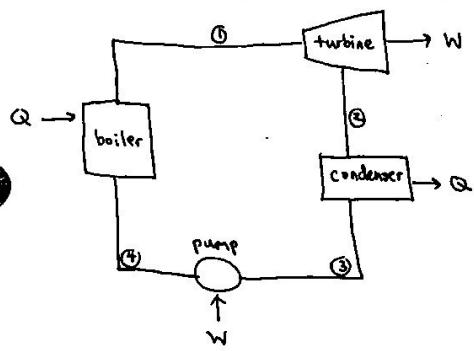
$$W = -[-(50\text{kPa})(4-1)\text{m}^3] = 150000\text{J}$$

$$q = \Delta U - W = -375\text{kJ}$$

$$\text{C} \rightarrow \text{A} \quad \Delta U = n\frac{3}{2}R\Delta T = 149839\text{J}$$

$$W = 0$$

$$q = \Delta U = +50\text{kJ}$$

<< Open Rankine Cycle (H₂O)

③ saturated liquid (condenser always produce)

↓ **pump** $q=0, \Delta S=0, W=\Delta H>0, \Delta P>0$

④ liquid

↓ **boiler** $\Delta P=0, q=\Delta H>0, W=0, \Delta T=0$

① super heated vapor

↓ **turbine** $W<0, q=0, \Delta S=0, \Delta P<0$
 $W=\Delta H$

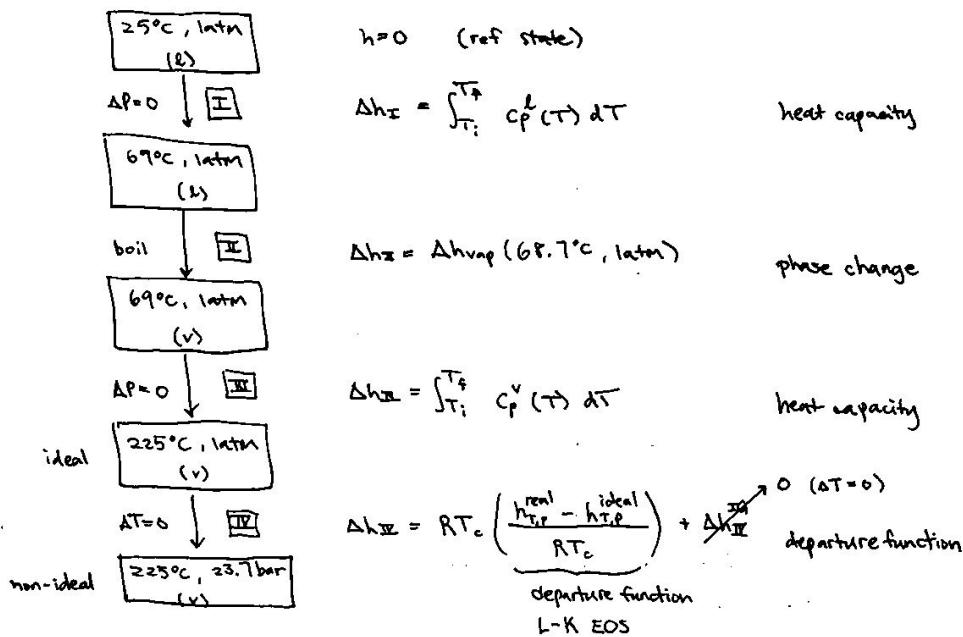
② vapor + liquid

↓ **condenser** $\Delta P=0, \Delta T=0, q=\Delta H<0$

<< First Law Analysis Example

[Ex] Find molar enthalpy h of gaseous n-hexane at 225°C , 23.7 bar. ($\Delta h_{\text{vap}}(68.7^\circ\text{C}, 1\text{atm}) = 28.86 \text{ kJ/mol}$)

- System is well-determined: $F = 2 + c - p - r = 2 + 1 - 1 - 0 = 2$, given 2 properties.
- From database, $\Delta h = 61.0 \text{ kJ/mol}$ ($h=0$ at 25°C , 1 atm liquid)
- From NIST, $\Delta h = 52.113 \text{ kJ/mol}$ ($h=0$ at $T_b = 68.71^\circ\text{C}$, sat liquid>)
- To calculate from known values, define reference state as 25°C , 1 atm.



$$\boxed{\text{I}} \quad \Delta h_{\text{I}} = \int_{298\text{K}}^{342\text{K}} c_p^l(T) dT = \int_{298\text{K}}^{342\text{K}} RA dT = [RT]_{298\text{K}}^{342\text{K}} \quad A = 23.7$$

$$= (8.341 \text{ J/(mol·K)})(23.7)(342 - 298)\text{K} = 8.61 \text{ kJ/mol}$$

$$\boxed{\text{II}} \quad \Delta h_{\text{II}} = \Delta h_{\text{vap}}(68.7^\circ\text{C}, 1\text{atm}) = 28.86 \text{ kJ/mol}$$

$$\boxed{\text{III}} \quad \Delta h_{\text{III}} = \int_{342\text{K}}^{498\text{K}} c_p^v(T) dT = \int_{342\text{K}}^{498\text{K}} R(A + BT + CT^2) dT = R \left[AT + B \frac{T^2}{2} + C \frac{T^3}{3} \right]_{342\text{K}}^{498\text{K}} \quad A = 3.025$$

$$= 29.36 \text{ kJ/mol} \quad B = 53.72 \times 10^{-3}$$

$$\boxed{\text{IV}} \quad \Delta h_{\text{IV}} = RT_c \left(\frac{h_{T,p}^{real} - h_{T,p}^{ideal}}{RT_c} \right) = (8.341 \text{ J/mol}^{-1}\text{K}^4)(507.4\text{K})(-1.66) = -7.0 \text{ kJ/mol}$$

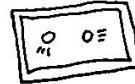
$$T_c = 507.4\text{K} \quad T_r = \frac{T}{T_c} = \frac{498}{507.4} = 0.98 \quad \left(\frac{h^r - h^i}{RT_c} \right)^{(0)} = -1.3, \quad \left(\frac{h^r - h^i}{RT_c} \right)^{(1)} = -1.3$$

$$P_c = 29.69 \text{ bar} \quad P_r = \frac{P}{P_c} = \frac{23.7}{29.69} = 0.8 \quad \left(\frac{h^r - h^i}{RT_c} \right)^{(0)} = (-)^{(0)} + \omega (-)^{(1)} = -1.66$$

$$\Delta h_{\text{total}} = \sum_i \Delta h_i = 59.8 \text{ kJ/mol}$$

see Statistical Mechanics

- we have described system of aggregates (average) behavior of molecules
- EOS - "mean field theory" - avg behavior of molecules
- To fully capture molecular behavior, we need to account for fluctuations with statistics.
- Isolated system has system invariants of N, V, U
- E_k, E_p are fluctuating
- T, P are time averages
- e.g. $\bar{T} = \frac{\langle E_k \rangle}{N} = \frac{1}{N} \frac{1}{t_2-t_1} \int_{t_1}^{t_2} E_k(t) dt$
- Each time step has diff instantaneous E_k that time avg to the same avg $\langle E_k \rangle$
- How much time needed for time avg?
- Depend on system
- slow molecules \rightarrow more time
- more molecules \rightarrow less time

 \rightarrow Configurations

> Ergodic hypothesis - molecular configurations acquired by a system of constant N, V, U over a finite time are statistically representative of all possible configurations sharing these same values of N, V, U .

> Configuration (microstate) - a specific microscopic arrangement of a thermodynamic system that the system might occupy.

> State - specific macroscopic property of system (e.g. N, V, U)

- large # of configurations for a state
- because molecular positions are quantized, # of config is finite

> multiplicity Ω - # of unique system configurations sharing the same N, V, U (microcanonical partition function)

 \rightarrow Ergodic Hypothesis

- Each microstate has a diff set of instantaneous properties, f

> time average - $\langle f \rangle = \lim_{t_2 \rightarrow \infty} \frac{1}{t_2-t_1} \int_{t_1}^{t_2} f(t) dt$

- t_j - time spent in config. j

- p_j - probability of being in config j

$$\cdot p_j = \frac{t_j}{t_2-t_1}$$

$$\cdot \sum_{j=1}^{\Omega} p_j = \frac{1}{t_2-t_1} \sum_{j=1}^{\Omega} t_j = 1$$

> ensemble average ($\langle f \rangle$) - averaging over # of config rather than time.

$$\cdot \langle f \rangle = \frac{1}{t_2-t_1} \sum_{j=1}^{\Omega} p_j f_j t_j = \sum_{j=1}^{\Omega} p_j f_j = \langle f \rangle \Rightarrow \boxed{\langle f \rangle = \langle f \rangle}$$

by Ergodic Hypothesis
→ ignore time, consider microstates

<< Statistical Mechanics (cont.)

→ Assumptions for $\langle f \rangle = \langle f' \rangle$

1. Macroscopic Reversibility

1. The dynamics of particles & fields is time reversible

2. Motion cannot be biased towards one direction in time

• no device can treat molecules differently at equilibrium

• No Maxwell's demon

2. Equal Probability Postulate

→ For an isolated system with fixed N, V, U , all system configuration are equally probable.

$$P_j = \frac{1}{\Omega} \quad \Rightarrow \quad \langle f \rangle = \frac{1}{\Omega} \sum_{j=1}^{\Omega} f_j$$

<< Multiplicity as a state property

# Molecules	Microstate 1	release ↔ X ↔ $P = \frac{1}{2^N}$	Microstate 2
1	Ω_0		$2\Omega_0$
2	Ω_0^2		$(2\Omega_0)^2 = 2^2\Omega_0^2$
N	Ω_0^N		$(2\Omega_0)^N = 2^N\Omega_0^N$

- Microstate 1 is one subset of microstate 2.
- probability of all molecules end up at bottom from microstate 2 → 1 is

$$P = \frac{\Omega_0^N}{2^N\Omega_0^N} = \frac{1}{2^N} \quad \text{very very small}$$

<< Second Law of Thermodynamics

> The multiplicity of an isolated system can never spontaneously decrease; it can only increase

- multiplicity is hard to use
 - large number
 - neither intensive nor extensive
 - intensive : $S_{A+B} = S_A = \Omega_B$ Nope!
 - extensive : $S_{A+B} = S_A + S_B$ Nope!
 - probabilistic : $S_{A+B} = S_A S_B$ Yes!
- working in log scale make things extensive.

$$\ln(S_{A+B}) = \ln(S_A) + \ln(S_B)$$

> entropy = $S = k_B \ln(\Omega)$

- natural log of # of configurations of a system
- $S_{A+B} = S_A + S_B$ (extensive)
- $S_{A+B} = S_A = S_B$ (intensive) $S = \frac{S}{N}$

<< Configurational Entropy

> config entropy - entropy that only depends on arrangement of non-interacting molecules

$$\Omega = (V_0 \bar{\Omega}_0)^N = V_0^N \bar{\Omega}_0^N$$

$$S_0 = k_B \ln(\Omega) = k_B \ln((V_0 \bar{\Omega}_0)^N) = N k_B \ln(V_0 \bar{\Omega}_0)$$

$$= n N k_B \ln(V_0 \bar{\Omega}_0)$$

$$S_0 = n R \ln(V_0 \bar{\Omega}_0)$$

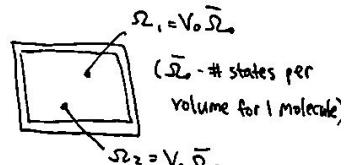
$$[N = n N_A]$$

$$[R = N_A k_B]$$

• Change volume from V_0 to arbitrary V :

$$S = n R \ln(V \bar{\Omega}_0) = n R \ln\left(\frac{V}{V_0} V_0 \bar{\Omega}_0\right) = n R \ln(V_0 \bar{\Omega}_0) + n R \ln\left(\frac{V}{V_0}\right) = S_0 + n R \ln\left(\frac{V}{V_0}\right)$$

$$\Rightarrow \Delta S = n R \ln\left(\frac{V}{V_0}\right), \quad [S = S_0 + \Delta S]$$



<< AS for ideal gas

- $\Delta S = nR \ln \left(\frac{V}{V_0} \right) \quad , \quad S(T, V) = S_0(T, V_0) + \Delta S$
- $\Delta S = -nR \ln \left(\frac{c}{c_0} \right) \quad , \quad S(T, c) = S_0(T, c_0) + \Delta S \quad , \text{ where } C = \frac{1}{V}$
- $\Delta S = -nR \ln \left(\frac{P}{P_0} \right) \quad , \quad S(T, P) = S_0(T, P_0) + \Delta S \quad , \text{ since } P = \frac{nRT}{V}$

* Also works for dilute solutions of noninteracting solute molecules in a solvent.

$$S_i(T, c_i) = S_i(T, c_i^0) - R \ln \left(\frac{c_i}{c_i^0} \right)$$

<< Counting Configurations

* Consider simple system with particles with only 2 energy levels

Ex1 $U = \sum_{i=1}^N E_i = 0 \quad \Omega_2 = 1$

$$E_i = E^* \quad - - - - - \dots - \quad S = 0$$

$$E_i = 0 \quad \uparrow \uparrow \uparrow \uparrow \uparrow \dots \uparrow$$

Ex2 $U = E_0$

$$E_i = E^* \quad - - - \downarrow - \dots - \quad \Omega_2 = N$$

$$E_i = 0 \quad \uparrow \uparrow \uparrow \uparrow \uparrow \dots \uparrow \quad S = k_B \ln(N)$$

Ex3 $U = 3E_0$

$$E_i = E_0 \quad - \downarrow - \uparrow + \dots - \quad \Omega_2 = N(N-1)(N-2) \quad \text{distinguishable}$$

$$E_i = 0 \quad \uparrow - \downarrow - - \dots \uparrow \quad = \frac{N!}{(N-3)!}$$

→ Permutations

> Permutability Π - number of ways N_A

distinguishable particles can be placed on N sites.

$$\Pi = \frac{N!}{(N-N_A)!}$$

> Multiplicity Ω_2 - number of ways N_A indistinguishable particles can be placed on N sites.

$$\Omega_2 = \frac{N!}{N_A!(N-N_A)!}$$

* Multiplicity for N sites filled with A, B, C ...

$$\Omega = \frac{N!}{N_A! N_B! N_C! \dots} \quad \text{e.g. AABBBBC}$$

\leftrightarrow Counting Configurations

\rightarrow Generalization with Stirling Approximation

Ex4 Consider N sites with fraction x activated.

$$U = xNE_0$$

$$E_i = E_0 \quad \underbrace{+ + + +}_{xN} - \dots -$$

$$E_i = 0 \quad - - - + \dots +$$

$$\Omega = \frac{N!}{(xE_0)!(N-xE_0)!}$$

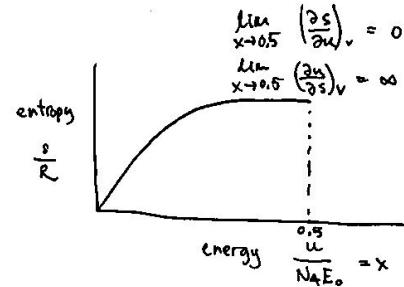
$$S = k_B \ln(\Omega)$$

\rightarrow Stirling approximation -

$$\lim_{a \rightarrow \infty} [\ln(a!)] = a \ln a - a$$

With approx. $S = k_B N \left[-x \ln x - (1-x) \ln(1-x) \right]$

- $u \uparrow, s \uparrow$
- increase in internal energy allows occupation of higher energy state not accessible at lower energy, leading to more ways energy can be rearranged
- At $x=0.5$, so much energy in the system that all states can flip up or down randomly, which maximizes the entropy.



*** Definition of T and P.

Find entropy S for particle in a 3D box (ideal gas)



- From Schrödinger equation,

$$E_x = \frac{\hbar^2 \pi^2 L_x^2}{2ma^2}$$

L_x = quantum # in x direction

a = length of box

$$U = \sum_{i=1}^N \frac{\hbar^2 \pi^2}{2ma^2} (L_{x_i}^2 + L_{y_i}^2 + L_{z_i}^2)$$

① Ground state, 1 particle

- $L_x = L_y = L_z = 1$

- $\Omega = 1, S = 0$

② N particles with total energy U

- $\Omega = \frac{3N\pi^{3N/2}}{(3N/2)!} \left(\frac{a\sqrt{2mU}}{\pi\hbar} \right)^{3N-1} \frac{1}{N!}$

- Plug into entropy equation, apply Sterling approximation, retain terms larger than $N \ln N$.

- $\frac{S}{N} = k_B \ln \left(\frac{a^3 (2mU)^{3/2}}{N (\pi \hbar)^3} \right)$

- $S = (\text{const}) + R \ln (V u^{3/2})$

- $u = (\text{const}) V^{-2/3} \exp \left(\frac{2}{3} \frac{S}{R} \right)$

- $\left(\frac{\partial u}{\partial S} \right)_V = \frac{2}{3} \frac{u}{R}, \quad \left(\frac{\partial u}{\partial V} \right)_S = -\frac{2}{3} \frac{u}{V}$

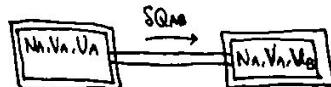
- Define thermodynamic temperature & pressure

- $T = \left(\frac{\partial u}{\partial S} \right)_V \Rightarrow u = \frac{3}{2} RT$

- $P = - \left(\frac{\partial u}{\partial V} \right)_S \Rightarrow P = \frac{RT}{V}$

<< Understanding temperature

- heat flows to maximize entropy



$$dU_A = -\delta Q_{AB} \quad dU_B = +\delta Q_{AB}$$

$$dS_A = \frac{dU_A}{(\partial U_A)_{N_A, V_A}} \quad dS_B = \frac{dU_B}{(\partial U_B)_{N_B, V_B}}$$

- entropy of the system changes:

$$dS_{AB} = dS_A + dS_B \\ = \frac{\delta Q_{AB}}{(\partial S_A)_{N_A, V_A} (\partial S_B)_{N_B, V_B}} \left[\left(\frac{\partial U_A}{\partial S_A} \right)_{N_A, V_A} - \left(\frac{\partial U_B}{\partial S_B} \right)_{N_B, V_B} \right]$$

- From 2nd law,

$$dS_{AB} \geq 0 \quad (\text{isolated sys})$$

and note

$$\frac{\partial U}{\partial S} > 0$$

so

$$\frac{\partial U_A}{\partial S_A} - \frac{\partial U_B}{\partial S_B} \geq 0 \Rightarrow \frac{\partial U_A}{\partial S_A} \geq \frac{\partial U_B}{\partial S_B} \Rightarrow T_A \geq T_B$$

$\xrightarrow{\delta Q_{AB}}$

> Temperature - propensity of thermal energy to move to maximize entropy of a system

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N}$$

> Pressure - propensity of a fluid to expand to maximize entropy of a system

$$P = - \left(\frac{\partial U}{\partial V} \right)_{S, N}$$

<< Fundamental Property Relation

- Known $U = U(S, V)$

- total derivative $dU = \left(\frac{\partial U}{\partial S} \right)_{V, N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N} dV$

$$dU = T dS - P dV$$

- For constant volume closed system, $dV = 0$,

$$dU = T dS \Rightarrow dS = \frac{dU}{T}$$

- 1st law : $dU = \delta Q + \delta W^{\text{ext}} = \delta Q$

$$dS = \frac{\delta Q}{T}$$

<< Entropy

- entropy is not conserved; it can be generated.

- open vs. closed system

- reversible vs. irreversible

<< Reversible Process

> reversible process - process which direction can be reversed to return system to original state.

Ex1 Consider particle in a 3D box at constant volume and constant entropy.

Determine heat and work from internal energy using $dU = TdS - PdV$

A Change U at constant V ($dv=0$)

$$du = Tds - PdV^0 \quad (\text{fundamental property relation})$$

$$du = Tds$$

and

$$du = \delta q + \delta r^0 \quad (\text{1st law})$$

$$du = \delta q$$

so

$$\delta q = Tds \rightarrow \boxed{\delta q = \int T ds} \quad \text{at eqm (reversible)}$$

B Change u at constant S ($ds=0$)

$$du = TdS^0 - PdV \quad (\text{fundamental property relation})$$

$$du = -PdV$$

and to ↑ u without ↑ S (TS), we can decrease system size ↓ V
the raise in energy levels does not require heat q.

$$du = \delta q^0 + \delta w \quad (\text{1st law})$$

$$du = \delta w$$

so

$$\delta w = -PdV \rightarrow \boxed{w = \int -P dV} \quad \text{at eqm (reversible)}$$

* Note: the system must be in continuous state of eqm during transformation.

<< Irreversible Process

> irreversible process - direction cannot be reversed to its original state.

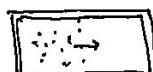
Ex2 Isolated system with membrane rupture.

$$\Delta U = 0, W = 0, q = 0 \quad (\text{isolated})$$

$$\therefore \Delta V > 0, \Delta S > 0, \Delta S > 0.$$

$$\Rightarrow q \neq \int T ds \\ w \neq \int -P dV \quad \left. \begin{array}{l} \text{Irreversible} \\ \text{process} \end{array} \right\}$$

• irreversible transformation $\left\{ \begin{array}{l} \text{- depart from eqm} \\ \text{- entropy generated} \end{array} \right.$



• cannot reverse process spontaneously

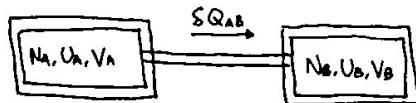
• need w to ↓ V (will change u)

• need q to get back to original u

$\left. \begin{array}{l} \Delta V, \Delta E, du, \Delta T \\ \Delta V, \Delta S \\ \Delta T, \Delta S \end{array} \right\}$ cancel
 ΔS no change

1. Entropy Generation

Ex1 Consider isolated system connected by bridge.



$$dV_A = -SQ_{AB}$$

$$dV_B = SQ_{AB}$$

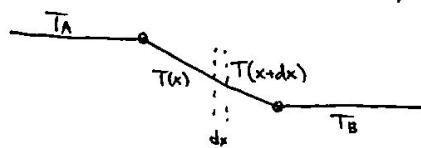
A if $T_A = T_B = T$, $dS_A = -\frac{SQ_{AB}}{T}$ $dS_B = \frac{SQ_{AB}}{T}$ ($dS_A = dS_B$)

$$dS_{A+B} = dS_A + dS_B = 0$$

$$dS_{gen} = 0$$

B if $T_A > T_B$, $dS_{A+B} = dS_A + dS_B = SQ_{AB} \left(\frac{1}{T_B} - \frac{1}{T_A} \right)$

The temperature profile at quasi-steady state is



The systems each only sees the end of conduit that share the same temperature, so entropy change in each system is only caused by heat flow in & out, not by entropy generated within the system.

⇒ entropy is generated in the conduit

• gradient → entropy generation

$$d(SS_{gen}) = SQ_{AB} \left(\frac{1}{T(x+dx)} - \frac{1}{T(x)} \right) = -SQ_{AB} \frac{dT}{T^2}$$

$$dS_{gen} = SQ_{AB} \left(\frac{1}{T_B} - \frac{1}{T_A} \right) = dS_{A+B} = dS_A + dS_B$$

Since entropy of conduit cannot increase with time at steady state, the generated entropy is transferred into system B:

$$dS_B = dS_A + SS_{gen}$$

→ Summary

• reversible $S_{gen} = 0$

• irreversible $S_{gen} > 0$

• gradient = entropy generation

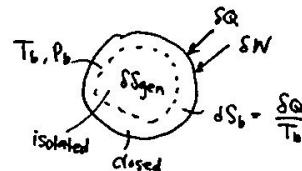
<< Second Law for Closed System

EY: Closed system boundary @ continuous state of equilibrium (reversible)

$$\cdot dS = \frac{\delta Q}{T_b} + \delta S_{gen}, \quad \underbrace{\delta S_{gen} \geq 0}_{\text{only way for isolated system}}$$

$$\cdot \Delta S = \int \frac{\delta Q}{T_b} + S_{gen}$$

isolated
closed



$$dS_b = \frac{\delta Q}{T_b}$$

closed system is continuous with the isolated system.

<< A Summary of Second Law

→ Isolated system

$$\Delta S = S_{gen}, \quad S_{gen} \geq 0$$



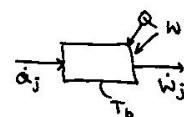
→ Closed System

$$\Delta S = \int \frac{\delta Q}{T_b} + S_{gen}, \quad S_{gen} \geq 0$$

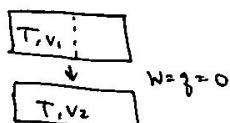


→ Open System @ steady state

$$0 = \sum_i^{\text{in}} n_i s_i - \sum_i^{\text{out}} n_i s_i + \sum_j \frac{\dot{Q}_j}{T_b, j} + \dot{S}_{gen}, \quad \dot{S}_{gen} \geq 0$$

<< Measurement of ΔS

Irreversible



$$ds = \frac{\delta Q}{T} + \delta S_{gen}$$

$$ds = \delta S_{gen}$$

not measurable

- involve internal gradient of T/P, composition
- generates entropy inside system
- cannot be performed backward by an equal & opposite flow of work across system boundary

• ΔS is not S_{gen} ! : $\Delta S = \int \frac{\delta Q}{T_b} + S_{gen}$

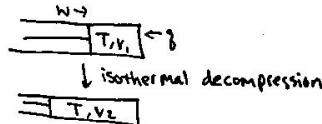
• reversible process with $S_{gen} = 0$ within the system usually involve S_{gen} outside the system

ideal gas

$$\Delta U = 0$$

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right)$$

Reversible



$$ds = \frac{\delta Q}{T} + \delta S_{gen}$$

$$\Delta S = \int \frac{\delta Q}{T} = \int -\frac{\delta W}{T} = \int_{V_1}^{V_2} \frac{P \, dv}{T}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{R}{v} \, dv = R \ln\left(\frac{V_2}{V_1}\right)$$

- internal equilibrated at all times
- no entropy generated inside system
- can be performed backward ...

<< Fundamental Property Relations

$$\cdot dU = TdS - pdV$$

Ex1 Derive dH from dU .

$$\cdot dH = TdS + Vdp$$

$$H = U + pV$$

$$\cdot dA = -pdV - SdT$$

$$dH = dU + \cancel{d(pV)}$$

$$\cdot dG = Vdp - SdT$$

$$= dU + pdV + Vdp$$

$$= TdS - pdV + pdV + Vdp$$

$$= TdS + Vdp \quad \checkmark$$

<< Maxwell Relations

→ **Clairaut's Theorem**

For $z = z(x, y)$, the total derivative is

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

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

If $z(x, y)$ is continuous and x, y, z are point (state) function,

$$\text{then } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

→ Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$$

Ex2 Derive Maxwell relation of dU .

$$dU = TdS - pdV$$

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

$$\begin{cases} M = T \\ N = -p \end{cases} \quad \begin{cases} x = S \\ y = V \end{cases}$$

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

$$\text{so } \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$$

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

Ex3 Derive Maxwell relation of dH

$$dH = TdS + Vdp$$

$$\begin{cases} M = T \\ N = V \end{cases} \quad \begin{cases} x = S \\ y = P \end{cases}$$

Ex4 If $S = S(T, V)$, simplify

dS using $dQ = TdS$

$$\text{and } C_V = \left(\frac{\partial V}{\partial T}\right)_S.$$

$$C_V = \left(\frac{\partial V}{\partial T}\right)_S = \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial(TdS)}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\text{and } \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{so } dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\text{If } dV = 0, dS = \frac{C_V}{T} dT$$

Ex5 If $S = S(T, P)$, simplify dS using $dQ = TdS$, $C_p = \left(\frac{\partial Q}{\partial T}\right)_p$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial (T dS)}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

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

$$\text{so } dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\boxed{dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP} \quad \text{if } d_P = 0, \boxed{dS = \frac{C_p}{T} dT}$$

~~cc~~ Second Law Analysis

[EX] Closed system gas compression

$$T_0, P_0 \quad \text{[Diagram: horizontal cylinder]}$$

$$T_i, P_i \quad \text{[Diagram: horizontal cylinder with compressed gas]}$$

► Calculate change in entropy.

[I] Ideal, reversible, isobaric

$$dS = \frac{\delta q}{T} + \delta S_{\text{gen}}^{\circ} \quad \text{second law}$$

$$\delta q = du - \delta w \quad \text{first law}$$

$$= du - (-Pdv)$$

$$= du + Pdv$$

$$= dh$$

$$= C_p(T) dT$$

$$dS = \frac{C_p}{T} dT$$

$$\Delta S_I = \int \frac{C_p}{T} dT$$

[II] Ideal, reversible, isothermal

$$\Delta T = 0 \Rightarrow \Delta U = \Delta h = 0$$

$$\delta q = -\delta w = PdV = -\frac{RT}{P} dP$$

$$dS = \frac{\delta q}{T} + \delta S_{\text{gen}}^{\circ}$$

$$= -\frac{R}{P} dP$$

$$\Delta S_{II} = \int_{P_i}^{P_f} -\frac{R}{P} dP = -R \ln\left(\frac{P_f}{P_i}\right)$$

[III] Ideal \rightarrow Real

$$\Delta S_{III} = R \left(\frac{s_{\text{real}} - s_{\text{ideal}}}{R} \right)$$

departure
function
of L-K EOS {Figure 5.7, 5.8
Table C.5, C.6}

→ Isochoric process

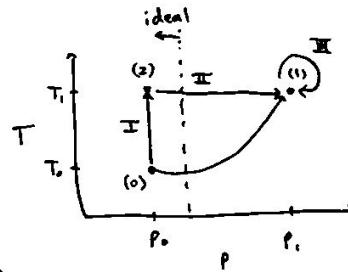
$$\Delta V = 0 \Rightarrow \delta w = 0$$

$$\delta q = du = C_v dT \quad \text{1st law}$$

$$ds = \frac{\delta q}{T} + \delta S_{\text{gen}}^{\circ} \quad \text{second law}$$

$$= \frac{C_v}{T} dT$$

$$\Delta S = \int \frac{C_v}{T} dT$$



$$\Delta S = \Delta S_I + \Delta S_{II} + \Delta S_{III}$$

<< Ideal Gas Entropy Change

$$\Delta S = \underbrace{\int_{T_0}^{T_1} \frac{C_p(T)}{T} dT}_{\text{energy content}} - \underbrace{R \ln\left(\frac{P}{P_0}\right)}_{\text{volume}} \Rightarrow \Delta S(T, P) \text{ for ideal gas}$$

$\Delta u(T), \Delta h(T)$

<< Incompressible liquid & Solid

$$u = e_p(v(T)) + e_k(T)$$

$$u = u(T)$$

$$s = s(T)$$

volume does not change much with P, so s_2 and s does not depend on P.

$$\Delta s = \int_{T_0}^{T_1} \frac{C_p}{T} dT = C_p \ln\left(\frac{T_1}{T_0}\right)$$

<< Phase Change

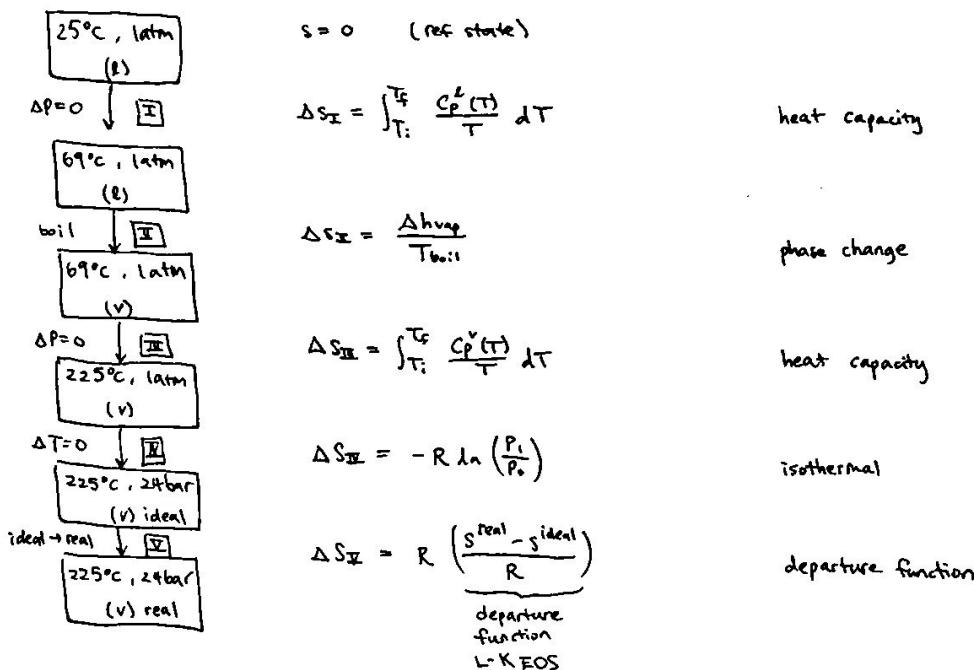
T, P fixed

$$q = \Delta h$$

$$\Delta s^\circ = \int \frac{\delta q}{T} = \frac{q}{T} = \frac{\Delta h^\circ}{T}$$

--> Second Law Analysis Example

[Ex] Find molar entropy s of gaseous n-hexane at 225°C and 23.7 bar. $\Delta h_{\text{vap}}^{\circ}(68.7^\circ\text{C}, 1\text{ atm}) = 28.86 \text{ kJ/mol}$



$$\boxed{\text{II}} \quad \Delta S_{II} = \frac{\Delta h_{\text{vap}}}{T_{\text{boil}}} = \frac{28.86 \text{ kJ/mol}}{341.85 \text{ K}} = 84.42 \text{ J/mol.K}$$

$$\boxed{\text{III}} \quad \Delta S_{III} = \int_{T_i}^{T_f} \frac{C_p^v(T)}{T} dT = \int_{T_i}^{T_f} \frac{B}{T} [A + BT + CT^2] dT = 70.11 \text{ J/mol.K} \quad A = 3.025 \\ B = 53.12 \times 10^{-3} \\ C = -16.79 \times 10^{-6}$$

$$\boxed{\text{IV}} \quad \Delta S_{IV} = -R \ln\left(\frac{P_f}{P_i}\right) = -(8.314 \text{ J/mol.K}) \ln\left(\frac{24 \text{ bar}}{1 \text{ atm}} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}}\right) = -26.31 \text{ J/mol.K}$$

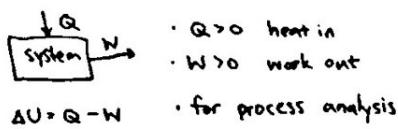
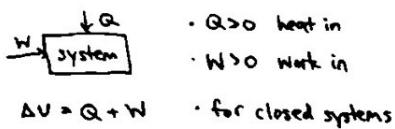
$$\boxed{\text{V}} \quad \Delta S_{IV} = R \left(\frac{s^{real} - s^{ideal}}{R} \right) = -(8.314 \text{ J/mol.K}) (-1.35) = -11.22 \text{ J/mol.K}$$

$$T_c = 507.4 \text{ K} \quad T_r = \frac{T_f}{T_c} = \frac{498.15 \text{ K}}{507.4 \text{ K}} = 0.98 \quad \left(\frac{s^r - s^e}{R} \right)^{(b)} = -0.97 \quad \left(\frac{s^r - s^e}{R} \right)^{(c)} = -1.3 \\ P_c = 29.7 \text{ bar} \quad P_r = \frac{P_f}{P_c} = \frac{23.7 \text{ bar}}{29.7 \text{ bar}} = 0.8 \quad \frac{s^r - s^e}{R} = ()^{(b)} + \omega ()^{(c)} = -1.35 \\ \omega = 0.296$$

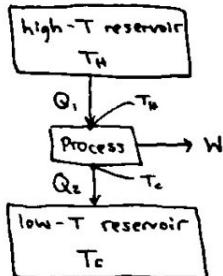
$$\Delta S_{\text{total}} = \sum_i \Delta S_i = 144 \text{ J/mol.K}$$

$$\text{NIST value: } \Delta S = 146.5 \text{ J/mol.K}$$

↔ Local Sign Convention

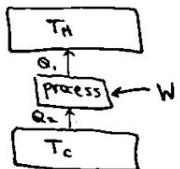


↔ Closed System Heat Engine



- 1st law: $\Delta U = Q - W$
- $0 = Q_1 - W - Q_2$ @ steady state
- 2nd law: $\Delta S = \frac{Q_1}{T_H} + S_{gen}$
- $0 = \frac{Q_1}{T_H} - \frac{Q_2}{T_C} + S_{gen}$ @ steady state, ΔT within process
- Work output: $W = Q_1 \left(1 - \frac{T_C}{T_H}\right) - T_C S_{gen}$
- max work: $(S_{gen} = 0)$ $W_{max} = Q_1 \left(1 - \frac{T_C}{T_H}\right)$

↔ Closed System Heat Pump



- 1st law: $0 = -Q_1 + W + Q_2$
- 2nd law: $0 = -\frac{Q_1}{T_H} + \frac{Q_2}{T_C} + S_{gen}$
- Work: $W = Q_1 \left(1 - \frac{T_C}{T_H}\right) + T_C S_{gen}$
- min work: $(S_{gen} = 0)$ $W_{min} = Q_1 \left(1 - \frac{T_C}{T_H}\right)$

↔ Carnot Efficiency

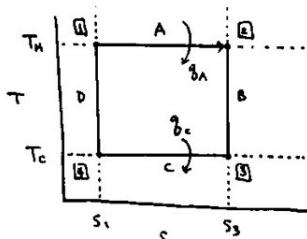
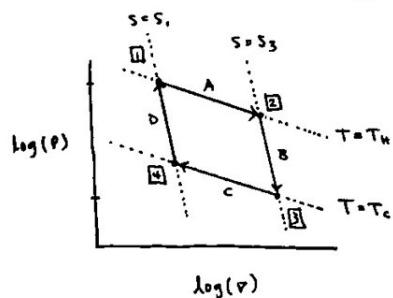
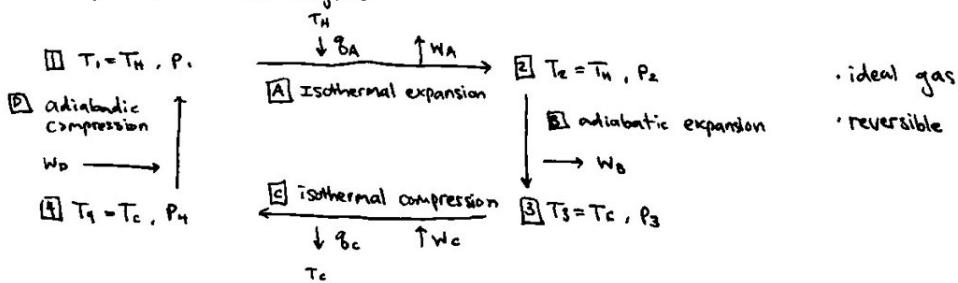
• reversible work

$$W_{rev} = Q_1 \left(1 - \frac{T_C}{T_H}\right)$$

> Carnot Efficiency

$$\eta_C = \frac{W_{rev}}{Q_1} = 1 - \frac{T_C}{T_H}$$

↔ Carnot Cycle (Ideal Heat Engine)



<< Ideal Gas Energy & Entropy

Constant V

$$\Delta U = \int C_V dT$$

$$\Delta S = \int \frac{C_V}{T} dT + R \ln\left(\frac{V}{V_0}\right)$$

$$\Delta S = \int \frac{C_V}{T} dT + R \ln\left(\frac{RT}{P} \frac{P_0}{RT_0}\right)$$

$$\Delta S = \int \frac{C_V}{T} dT + R \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{P}{P_0}\right)$$

constant P

$$\Delta H = \int C_P dT$$

$$\Delta S = \int \frac{C_P}{T} dT - R \ln\left(\frac{P}{P_0}\right)$$

$$\Delta S = \int \frac{C_V + R}{T} dT - R \ln\left(\frac{P}{P_0}\right)$$

<< Carnot Cycle Paths

A Isothermal Expansion

• $\Delta T = 0 \rightarrow \Delta U_A = 0$

• 1st law: $\Delta U_A = q_A - w_A = 0 \Rightarrow q_A = w_A$

• 2nd law: $\Delta S_A = \int \frac{dq_A}{T} + \cancel{s_{gen}^{\neq 0}} \Rightarrow \Delta S_A = \int \frac{dq_A}{T} = \frac{q_A}{T_H}$

$$\Delta S_A = -R \ln\left(\frac{P_2}{P_1}\right)$$

• so $q_A = T_H \Delta S_A = RT_H \ln\left(\frac{P_1}{P_2}\right)$

$$w_A = RT_H \ln\left(\frac{P_1}{P_2}\right)$$

* ideal gas

* reversible

* constant C_V, C_P

B Adiabatic Expansion, Isentropic

• $q_B = 0, \Delta S = 0$

• 1st law: $\Delta U_B = -w_B$

$$w_B = -\Delta U_B = -C_V(T_C - T_H) = C_V(T_H - T_C)$$

• 2nd law: $\Delta S_B = \int \frac{C_P}{T} dT - R \ln\left(\frac{P_2}{P_C}\right)$

$$0 = C_P \ln\left(\frac{T_2}{T_C}\right) - R \ln\left(\frac{P_2}{P_C}\right)$$

$$P_2 = P_C \left(\frac{T_C}{T_H}\right)^{-C_P/R}$$

C Isothermal Compression

$$w_C = q_C = RT_C \ln\left(\frac{P_2}{P_1}\right)$$

D Adiabatic Compression, Isoentropic

$$w_D = \Delta U_D = C_V(T_H - T_C)$$

$$P_H = \left(\frac{T_C}{T_H}\right)^{C_P/R}$$

\leftrightarrow Carnot Cycle Efficiency

- Net work output

$$W_{\text{tot}}^{\text{out}} = W_A + W_B - W_C - W_D$$

$$= R T_H \ln \left(\frac{P_1}{P_2} \right) + C_p (T_H - T_C) - R T_C \ln \left(\frac{P_3}{P_4} \right) - C_p (T_H - T_C)$$

Plug in P_2, P_4

$$= R (T_H - T_C) \ln \left(\frac{P_1}{P_3} \right) - C_p (T_H - T_C) \ln \left(\frac{T_C}{T_H} \right)$$

- Heat input is q_A

$$\dot{q}_{\text{in}}^{\text{in}} = q_A = R T_H \ln \left(\frac{P_1}{P_2} \right) + C_p T_H \ln \left(\frac{T_C}{T_H} \right)$$

- Process efficiency

$$\eta = \frac{W_{\text{tot}}^{\text{out}}}{\dot{q}_{\text{in}}^{\text{in}}} = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} \quad \rightarrow \text{Carnot efficiency}$$

- If individual steps are reversible, the overall process is reversible.

\leftrightarrow Heat and Work on Graph

- Heat is area under the T - s curve.

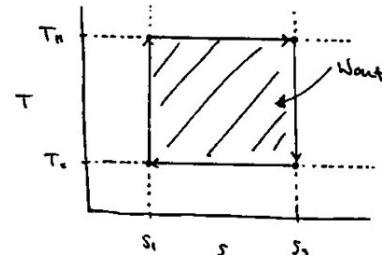
$$\dot{q}_{\text{in}} = T_H \Delta S_A = T_H (S_3 - S_1)$$

$$\dot{q}_{\text{out}} = T_C \Delta S_C = T_C (S_2 - S_1)$$

- Net work is area enclosed by process paths.

$$W_{\text{out}} = \dot{q}_{\text{in}} - \dot{q}_{\text{out}}$$

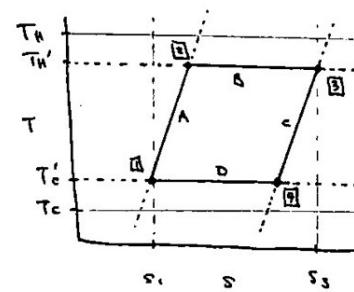
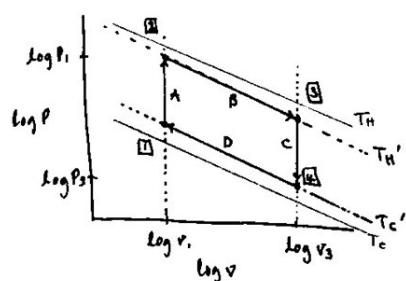
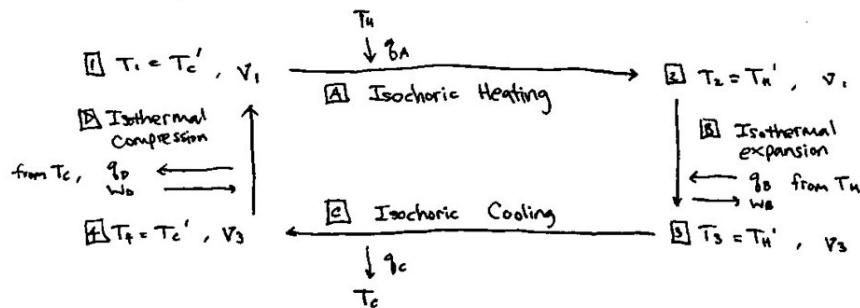
$$= (T_H - T_C) (S_3 - S_1)$$



\leftrightarrow Sterling Cycle

- Less efficient

- Incomplete transition to ambient conditions : $T_H' < T_H, T_C' > T_C$



«« Sterling Cycle Paths

■ Isochoric Heating : $\Delta V = 0 \Rightarrow W = 0$

$$\cdot 1st\ law: \Delta u_A = q_A = \int C_V dT = C_V (T_H' - T_C')$$

$$\cdot 2nd\ law: \Delta S_A = \int \frac{dq}{T} + S_{gen}$$

$$C_V \ln\left(\frac{T_H'}{T_C'}\right) = \frac{q_A}{T} + S_{gen,A}$$

$$S_{gen,A} = C_V \left[\ln\left(\frac{T_H'}{T_C'}\right) - \frac{T_H' - T_C'}{T_H} \right]$$

• Even as $T_H' \rightarrow T_H$ and $T_C' \rightarrow T_C$, $S_{gen} > 0$.

• Entropy generation is inherent to the path.

■ Isothermal Expansion : $\Delta T = 0 \Rightarrow \Delta u = 0$

$$\cdot 1st\ law: \Delta u_B = q_B - w_B = 0 \Rightarrow q_B = w_B$$

$$w_B = \int P dV = R T_H \ln\left(\frac{V_2}{V_1}\right)$$

$$\cdot 2nd\ law: \Delta S_B = \int \frac{dq}{T} + S_{gen}$$

$$R \ln\left(\frac{V_2}{V_1}\right) = \frac{q_B}{T_H} + S_{gen}$$

$$S_{gen} = \left(1 - \frac{T_H'}{T_H}\right) R \ln\left(\frac{V_2}{V_1}\right)$$

• Entropy is generated only if $T_H' \neq T_H$.

■ Isochoric Cooling

$$\cdot q_C = C_V (T_C' - T_C)$$

$$\cdot \Delta S_C = -C_V \ln\left(\frac{T_C'}{T_C}\right)$$

$$\cdot S_{gen,C} = C_V \left[-\ln\left(\frac{T_C'}{T_C}\right) + \frac{T_C' - T_C}{T_C} \right]$$

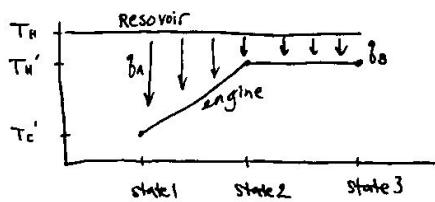
■ Isothermal Compression

$$\cdot q_D = w_D = R T_C' \left(\frac{V_2}{V_1}\right)$$

$$\cdot \Delta S_D = -R \ln\left(\frac{V_2}{V_1}\right)$$

$$\cdot S_{gen,D} = \left(-1 + \frac{T_C'}{T_C}\right) R \ln\left(\frac{V_2}{V_1}\right)$$

«« Entropy Generation



• $T_H' \neq T_H$ creates a temperature gradient that generates entropy during heat transfer when relaxing to eqm.

• T gradient in step A drives heat flow.

• $T_C' \rightarrow T_H$ { step A still has S_{gen} : T gradient
step B $S_{gen} \rightarrow 0$: lack of T gradient

• In Carnot cycle, the temp gradient is not realized since it's an adiabatic ($q_{geo} = 0$) step, so $S_{gen} = 0$

• In Sterling cycle, the temp gradient is used to drive heat transfer ($q > 0$), so $S_{gen} > 0$

↳ Loss Work Analysis

→ Work perspective

- $W_{\text{tot}}^{\text{out}} = W_B - W_D = R(T_H' - T_C') \ln\left(\frac{V_2}{V_1}\right)$

- $W_{\text{max}}^{\text{out}} = \eta q_{\text{in}}^{\text{in}} = \left(1 - \frac{T_C}{T_H}\right)(q_A + q_B) = \left(1 - \frac{T_C}{T_H}\right)\left(C_V(T_H' - T_C') + RT_H' \ln\left(\frac{V_2}{V_1}\right)\right)$

- $W_{\text{lost}} = W_{\text{max}}^{\text{out}} - W_{\text{tot}}^{\text{out}} = \left(1 - \frac{T_C}{T_H}\right)C_V(T_H' - T_C') + \left(\frac{T_C'}{T_C} - \frac{T_H'}{T_H}\right)RT_C \ln\left(\frac{V_2}{V_1}\right)$

→ entropy generation perspective

- From closed system heat engine analysis,

$$W_{\text{total}}^{\text{out}} = Q\eta - T_C S_{\text{gen}} = \underbrace{Q\left(1 - \frac{T_C}{T_H}\right)}_{W_{\text{tot}}^{\text{out}}} - \underbrace{T_C S_{\text{gen}}}_{W_{\text{lost}}}$$

- $S_{\text{gen}} = \sum_i S_{\text{gen},i} = \left(-\frac{T_C}{T_H}\right)C_V\left(\frac{T_H' - T_C'}{T_C}\right) + \left(\frac{T_C'}{T_C} - \frac{T_H'}{T_H}\right)R \ln\left(\frac{V_2}{V_1}\right)$

- $W_{\text{lost}} = T_C S_{\text{gen}} = \left(1 - \frac{T_C}{T_H}\right)C_V(T_H' - T_C') + \left(\frac{T_C'}{T_C} - \frac{T_H'}{T_H}\right)R T_C \ln\left(\frac{V_2}{V_1}\right)$

- The generated entropy leaves as heat to the cold reservoir.

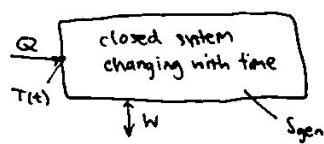
- Since $\Delta S = 0$ for whole process cycle (returns to original state), the entropy generated must flow as heat.

agreement

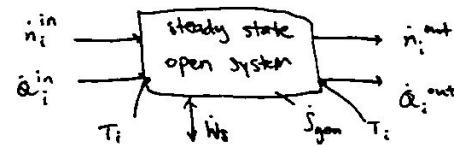
<< Second Law Review

→ Closed system

→ Open System

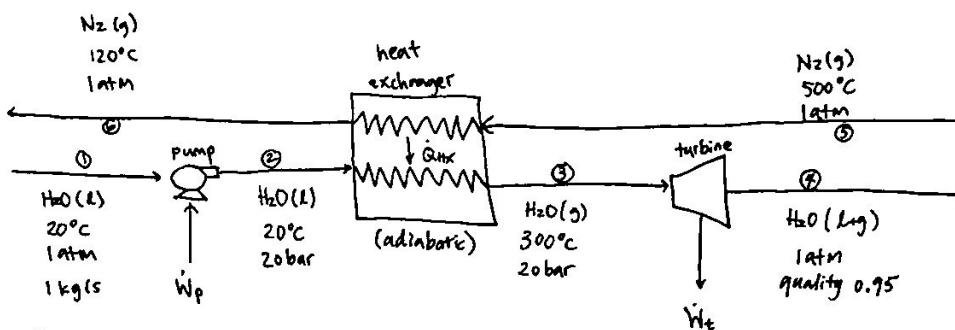


$$\Delta S = \int \frac{dQ}{T(t)} + S_{\text{gen}}, \quad S_{\text{gen}} > 0$$



$$0 = \sum_i n_i s_i - \sum_i n_i s_i + \sum_i \frac{Q_i}{T_i} - \sum_i \frac{Q_i}{T_i} + S_{\text{gen}}$$

<< Steam Engine Analysis



- How much net work is produced?
- How much work is lost? Where?
- How much work is theoretically producible?

- No obvious hot/cold reservoir
- Carnot efficiency does not apply to open system
- Each unit is adiabatic
- No heat exchange with environment here.

→ Thermodynamic Data

- Environmental condition : $P_0 = 1 \text{ atm}$, $T_0 = 20^\circ\text{C}$

- H_2O : from steam table (h, s)

- $\text{N}_2(\text{g})$: 1 atm, assume ideal gas

$$h = \int_{T_0}^T C_p^{\text{IG}} dT, \quad s = \int_{T_0}^T \frac{C_p^{\text{IG}}}{T} dT$$

$$C_p^{\text{IG}} = R \left[A + BT + \frac{D}{T^2} \right] \quad \begin{cases} A = 3.280 \\ B = 0.593 \times 10^{-3} \text{ K}^{-1} \\ C = 0.04 \times 10^{-5} \text{ K}^{-2} \end{cases}$$

T(K)	h (kJ/mol)	s (J/mol.K)
293	0	0
393	2.93	8.59
773	14.42	28.99

↔ Steam Engine Analysis (cont.)

→ Pump

• 1st law: $0 = \dot{m}_1 \hat{h}_1 - \dot{m}_2 \hat{h}_2 + \dot{W}_p + \dot{Q}^P$

$$\dot{W}_p = \dot{m}_{H2O} (\hat{h}_2 - \hat{h}_1) \quad (\dot{m}_1 = \dot{m}_2 = \dot{m}_{H2O})$$

$$\hat{h}_1 = 83.9 \text{ kJ/kg} \quad (\text{steam table})$$

$$\hat{h}_2 = \hat{h}_1 + \hat{v} (P_2 - P_1) = 85.8 \text{ kJ/kg} \quad (\text{not in table.})$$

$$\dot{W}_p = 1.9 \text{ kW}$$

• 2nd law: $0 = \dot{m}_1 \hat{s}_1 - \dot{m}_2 \hat{s}_2 - \frac{\dot{Q}^P}{T} + \dot{S}_{gen}$

$$\dot{S}_{gen} = \dot{m}_{H2O} (\hat{s}_2 - \hat{s}_1)$$

$$\hat{s}_1 = \hat{s}_2 = 0.297 \text{ kJ/kg·K}$$

$$\dot{S}_{gen} = 0 \quad (\text{incompressible, } S \text{ does not change with } P)$$

$$\dot{W}_{loss} = T_0 \dot{S}_{gen} = 0$$

→ Turbine

• 1st law: $0 = \dot{m}_3 \hat{h}_3 - \dot{m}_4 \hat{h}_4 - \dot{W}_t + \dot{Q}^T$

$$\dot{W}_t = \dot{m}_{H2O} (\hat{h}_3 - \hat{h}_4) \quad (\dot{m}_3 = \dot{m}_4 = \dot{m}_{H2O})$$

$$\hat{h}_3 = 3023.5 \text{ kJ/kg} \quad (\text{steam table})$$

$$\hat{h}_4 = g \hat{h}^0 + (1-g) \hat{h}^l = 2563.2 \text{ kJ/kg}$$

$$\dot{W}_t = 460.3 \text{ kW}$$

• 2nd law: $0 = \dot{m}_3 \hat{s}_3 - \dot{m}_4 \hat{s}_4 - \frac{\dot{Q}^T}{T} + \dot{S}_{gen}$

$$\dot{S}_{gen} = \dot{m}_{H2O} (\hat{s}_4 - \hat{s}_3)$$

$$\hat{s}_3 = 6.766 \text{ kJ/kg·K}$$

$$\hat{s}_4 = g \hat{s}^0 + (1-g) \hat{s}^l = 7.053 \text{ kJ/kg·K}$$

$$\dot{S}_{gen} = 0.287 \text{ kJ/K·s}$$

$$\dot{W}_{lost} = T_0 \dot{S}_{gen} = 84 \text{ kW}$$

→ Heat Exchanger

• 1st law: $0 = \dot{m}_1 \hat{h}_1 - \dot{m}_2 \hat{h}_2 + \dot{m}_3 \hat{h}_3 - \dot{m}_4 \hat{h}_4$

$$\dot{n}_{N2} = \frac{\dot{m}_{H2O} (\hat{h}_3 - \hat{h}_2)}{\hat{h}_3 - \hat{h}_4} = 255.5 \text{ mol/s}$$

• 2nd law: $0 = \dot{m}_1 \hat{s}_1 - \dot{m}_2 \hat{s}_2 - \dot{m}_3 \hat{s}_3 + \dot{m}_4 \hat{s}_4 - \frac{\dot{Q}^H}{T} + \dot{S}_{gen}$

$$\dot{S}_{gen} = \dot{m}_{H2O} (\hat{s}_3 - \hat{s}_1) + \dot{n}_{N2} (s_4 - s_3) = 1.257 \text{ kJ/K·s}$$

$$\dot{W}_{loss} = T_0 \dot{S}_{gen} = 368 \text{ kW}$$

↳ Steam Engine Analysis (cont.)

→ Summary of Work

$$\cdot \dot{W}_{\text{net}} = \dot{W}_t - \dot{W}_p = (460.3 - 1.9) \text{ kW} = 458 \text{ kW}$$

$$\cdot \dot{W}_{\text{loss}} = \begin{cases} \text{pump: } & 0 \text{ kW} \\ \text{HX: } & 368 \text{ kW} \\ \text{turbine: } & 84 \text{ kW} \end{cases}$$

→ Exthalpy Analysis (Theory)

$$\cdot \text{1st law: } \dot{Q} = \sum_i^{\text{source}} \dot{n}_i h_i - \sum_i^{\text{ground}} \dot{n}_i h_i - \dot{Q}_{\text{rev}} - \dot{W}_{\text{rev}}$$

$$\cdot \text{2nd law: } \dot{Q} = \sum_i^{\text{source}} \dot{n}_i s_i - \sum_i^{\text{ground}} \dot{n}_i s_i - \frac{\dot{Q}_{\text{rev}}}{T_0}$$

$$\cdot \dot{E} = \dot{W}_{\text{rev}} = \sum_i^{\text{source}} \dot{n}_i (h_i - T_0 s_i) - \sum_i^{\text{ground}} \dot{n}_i (h_i^\circ - T_0 s_i^\circ)$$

> Exthalpy - $\dot{E} = \dot{W}_{\text{rev}}$, maximum amount of reversible work we can get from a fluid crossing a system boundary. (aka. flow exergy, availability)

→ Exthalpy Analysis (Application)

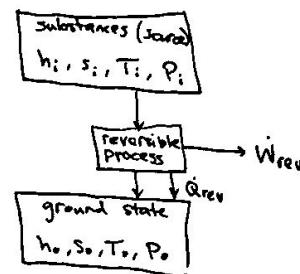
$$\begin{aligned} \cdot \dot{E}_{\text{in}} &= \sum_i^{\text{source}} \dot{n}_i (h_i - T_0 s_i) - \sum_i^{\text{ground}} \dot{n}_i (h_i^\circ - T_0 s_i^\circ) \\ &= \dot{m}_{\text{H}_2\text{O}} (h_1 - T_0 s_1) + \dot{m}_{\text{N}_2} (h_2 - T_0 s_2) - \dot{m}_{\text{H}_2\text{O}} (\overset{\circ}{h}_{\text{H}_2\text{O}} - T_0 \overset{\circ}{s}_{\text{H}_2\text{O}}) - \dot{m}_{\text{N}_2} (\overset{\circ}{h}_{\text{N}_2} - T_0 \overset{\circ}{s}_{\text{N}_2}) \\ &= \dot{m}_{\text{H}_2\text{O}} (h_1 - \underset{\substack{\text{at ground state} \\ \text{ref state def. as 0.}}}{T_0 \overset{\circ}{s}_{\text{H}_2\text{O}}}) + \dot{m}_{\text{N}_2} (h_2 - \underset{\substack{\text{ref state def. as 0.}}}{T_0 (s_2 - \overset{\circ}{s}_{\text{N}_2})}) \\ &= \dot{m}_{\text{N}_2} (h_2 - T_0 s_2) \\ &= 1514 \text{ kW} \end{aligned}$$

$$\cdot \dot{W}_{\text{rev}} = \dot{E}_{\text{in}} = 1514 \text{ kW}$$

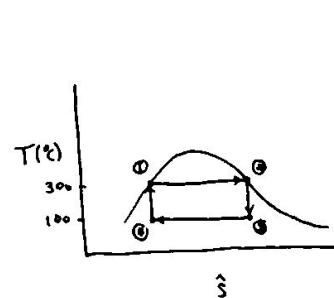
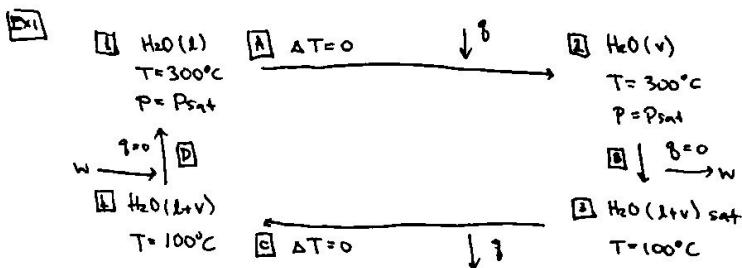
$$\begin{aligned} \cdot \dot{E}_{\text{out}} &= \sum_i^{\text{source}} \dot{n}_i (h_i - T_0 s_i) - \sum_i^{\text{ground}} \dot{n}_i (h_i^\circ - T_0 s_i^\circ) \\ &= \dot{m}_{\text{H}_2\text{O}} (\overset{\circ}{h}_1 - T_0 \overset{\circ}{s}_1) + \dot{m}_{\text{N}_2} (\overset{\circ}{h}_2 - T_0 \overset{\circ}{s}_2) - \dot{m}_{\text{H}_2\text{O}} (\overset{\circ}{h}_{\text{H}_2\text{O}} - T_0 \overset{\circ}{s}_{\text{H}_2\text{O}}) - \dot{m}_{\text{N}_2} (\overset{\circ}{h}_{\text{N}_2} - T_0 \overset{\circ}{s}_{\text{N}_2}) \\ &= 604 \text{ kW} \end{aligned}$$

→ Summary

$\dot{W}_{\text{net}} = \dot{W}_t - \dot{W}_p$	=	458 kW	(30.2%)
$\dot{W}_{\text{HX, lost}}$	=	368 kW	(24.3%)
$\dot{W}_{\text{turbine, lost}}$	=	84 kW	(5.5%)
$\dot{W}_{\text{pump, lost}}$	=	0 kW	(0%)
$+ \dot{E}_{\text{out}}$	=	604 kW	(39.9%)
$\dot{W}_{\text{max}} = \dot{E}_{\text{in}}$	=	1514 kW	



<< Open System Cycle



► What are the specific entropy of each state?

- From NIST, $\hat{s}_1 = \hat{s}_4 = \hat{s}_{\text{sat}}^L(300^\circ\text{C}) = 3.253 \text{ kJ/(kg K)}$
- $\hat{s}_2 = \hat{s}_3 = \hat{s}_{\text{sat}}^V(300^\circ\text{C}) = 5.104 \text{ kJ/(kg K)}$

} B & D are adiabatic & reversible,
so it's also isentropic $\Delta S = 0$

► What is the quality of states 3 and 4?

- State 3: $\hat{s}_3 = 5.104 \text{ kJ/(kg K)}, \hat{s}_v(100^\circ\text{C}) = 1.307 \text{ kJ/(kg K)}, \hat{s}_v(100^\circ\text{C}) = 7.355 \text{ kJ/(kg K)}$

$$\eta_3 = \frac{\hat{s}_3 - \hat{s}_1}{\hat{s}_v - \hat{s}_1} = 0.73$$

$$\text{State 4: } \eta_4 = \frac{\hat{s}_4 - \hat{s}_2}{\hat{s}_v - \hat{s}_2} = 0.32$$

► What are the specific enthalpy of states 3 and 4?

- From NIST, $\hat{h}_1 = \hat{h}_{\text{sat}}^L(300^\circ\text{C}) = 1344 \text{ kJ/kg}$

$$\hat{h}_2 = \hat{h}_{\text{sat}}^V(300^\circ\text{C}) = 2749 \text{ kJ/kg}$$

$$\hat{h}_{\text{sat}}^L(100^\circ\text{C}) = 419.02 \text{ kJ/kg}$$

$$\hat{h}_{\text{sat}}^V(100^\circ\text{C}) = 2676.0 \text{ kJ/kg}$$

$$\cdot \hat{h}_3 = \eta_3 \hat{h}_v + (1-\eta_3) \hat{h}_L = 2060 \text{ kJ/kg}$$

$$\cdot \hat{h}_4 = \eta_4 \hat{h}_v + (1-\eta_4) \hat{h}_L = 1145 \text{ kJ/kg}$$

► What are the heat and shaft work at each process?

$$\cdot \boxed{1} \quad q_A = 0, \quad \dot{q}_A = \hat{h}_2 - \hat{h}_1 = 1405 \text{ kJ/kg}$$

$$\cdot \boxed{2} \quad \dot{q}_B = 0, \quad \dot{w}_B = -(\hat{h}_3 - \hat{h}_2) = 689 \text{ kJ/kg}$$

$$\cdot \boxed{3} \quad \dot{q}_C = 0, \quad \dot{q}_C = \hat{h}_4 - \hat{h}_3 = -915 \text{ kJ/kg}$$

$$\cdot \boxed{4} \quad \dot{q}_D = 0, \quad \dot{w}_D = -(\hat{h}_1 - \hat{h}_4) = -199 \text{ kJ/kg}$$

► What is the net work and efficiency?

$$\cdot W_{\text{net}} = \sum \dot{w} = \dot{w}_B + \dot{w}_D = 490 \text{ kJ/kg}$$

$$\cdot \eta = \frac{W_{\text{net}}}{\dot{q}_A} = 0.349$$

► What's power produced if $m = 1 \text{ kg/h}$?

$$\cdot \dot{W}_{\text{net}} = W_{\text{net}} m = 136 \text{ W}$$

<< Carnot Efficiency

EX2 $T_H = 1500\text{K}$ $\dot{q} = 91.7 \text{ kJ/s}$
 $T_C = 25^\circ\text{C} = 298\text{K}$

Find the ideal efficiency.

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{1500\text{K}}{298\text{K}} = 0.80$$

<< Enthalpy

EX3 Find enthalpy that change liquid H₂O at 298K to ice at 273K under 0.1013 MPa = 1 atm with environmental temperatures 298K and 248K. Given data:

Water state	T [K]	\hat{h} [kJ/kg]	\hat{s} [kJ/kgK]
liquid	298	104.8	0.3666
Solid	273	-334.9	-1.2265

(a) At $T_{env} = 298\text{K}$,

$$\begin{aligned} E_x &= \hat{W}_{ideal} = \Delta\hat{h} - T_0\Delta\hat{s} = (\hat{h}_s - \hat{h}_e) - T_{env}(\hat{s}_s - \hat{s}_e) \\ &= (-334.9 - 104.8) \text{ kJ/kg} - (298\text{K})(-1.2265 - 0.3666) \\ &= 35.04 \text{ kJ/kg} \end{aligned}$$

(b) At $T_{env} = 248\text{K}$

$$E_x = \hat{W}_{ideal} = \Delta\hat{h} - T_0\Delta\hat{s} = (\hat{h}_s - \hat{h}_e) - T_{env}(\hat{s}_s - \hat{s}_e) = -44.61 \text{ kJ/kg}$$

- $T_{env} > T_{ice}$, need outside work, not reversible
- $T_{env} < T_{ice}$, doesn't need outside work, reversible
- Enthalpy, the ideal work, is a path function

EX4 Overheated water vapor (119.6°C , 0.197 MPa) is used to heat liquid hydrocarbons (45°C) to gas (45°C). Water vapor condenses to liquid (40°C) after heat exchange. The environmental temp is 20°C . Given data below: $\Delta\hat{h}_{vap}^{\text{hydrocarb}} = 293 \text{ kJ/kg}$, $\Delta\hat{s}_{vap}^{\text{hydrocarb}} = 0.921 \text{ kJ/(kgK)}$

water state	T [$^\circ\text{C}$]	\hat{h} [kJ/kg]	\hat{s} [kJ/kgK]
sat vapor	119.6	2706	7.133
sat liquid	40	167.4	0.572

$$m_{\text{H}_2\text{O}} = 1 \text{ kg}$$

$$m_{\text{HC}} = -\frac{\Delta\hat{h}_{\text{H}_2\text{O}}}{\Delta\hat{h}_{\text{HC}}} = -\frac{\hat{h}_e - \hat{h}_v}{\Delta\hat{h}_{\text{vap}}} = -\frac{167.4 - 2706}{293} = 8.66 \text{ kg}$$

$$E_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}}(\Delta\hat{h} - T_0\Delta\hat{s}) = (1 \text{ kg})((167.4 - 2706) \text{ kJ/kg} - (293\text{K})(0.572 - 7.133) \text{ kJ/kgK}) = -616 \text{ kJ}$$

$$E_{\text{HC}} = m_{\text{HC}}(\Delta\hat{h}_{\text{vap}} - T_0\Delta\hat{s}_{\text{vap}}) = (8.66 \text{ kg})((293 \text{ kJ/kg} - (293\text{K})(0.921 \text{ kJ/kgK})) = 200 \text{ kJ}$$

$$W_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}}\Delta\hat{s} = (1 \text{ kg})(293\text{K})(0.572 - 7.133) \text{ kJ/kgK} = -1922 \text{ kJ}$$

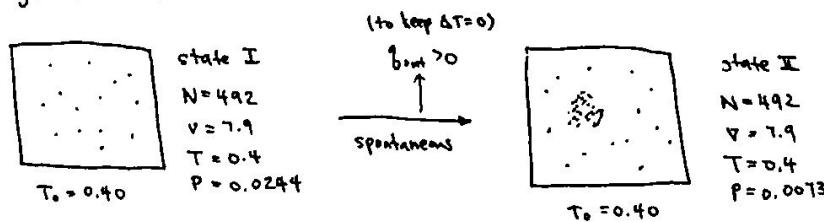
$$W_{\text{loss}} = m_{\text{HC}}\Delta\hat{s}_{\text{vap}} = (8.66 \text{ kg})(0.921 \text{ kJ/kgK}) = 2337 \text{ kJ}$$

Find enthalpy and work loss of water and hydrocarbon for heating 1kg water.

$$\left. \begin{array}{l} W_{\text{loss}}^{\text{tot}} = -\sum E_x = 415 \text{ kJ} \\ W_{\text{loss}} = +415 \text{ kJ} \end{array} \right\} \text{consistent!}$$

Single Component Phase Formation

- Ex1** Find the u and s of each state. Explain phase formation in terms of entropy of system, surrounding, and universe.



→ Qualitative argument

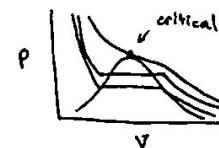
- $S_I > S_{II}$ because state II clump together has less configurations
- $\Delta S_{syst} < 0$
- $u_I > u_{II}$ because both states has same T , thus same e_k , but state II has closer distance, thus lower e_p .
- $b_{out} > 0$ is needed to maintain constant T .
- $\Delta S_{surr} > 0$ because $b_{out} > 0$

→ Reference States

$$\begin{aligned} \cdot u = 0 & \quad \left\{ \begin{array}{l} V \rightarrow \infty \\ T \rightarrow 0 \end{array} \right. \quad (e_p = 0) \\ \cdot s = 0 & \quad \left\{ \begin{array}{l} V_0 = 10^3 \\ T = 0.4 \end{array} \right. \quad (\text{avoid zero division}) \end{aligned}$$

→ State I (single phase fluid)

$$\begin{aligned} \cdot u_I &= e_k + e_p \\ &= T - \frac{a}{V} \\ &= 0.4 - \frac{2}{7.9} \\ &= 0.15 \end{aligned} \quad \begin{aligned} T_c &= 0.5 \\ P_c &= 0.052 \end{aligned} \quad \begin{aligned} &\text{from vdW EOS chart} \\ R &= 1 \quad (\text{unitless in simulation}) \\ a &= \frac{RT_c}{64} \frac{(RT_c)^2}{P_c} = 2 \end{aligned}$$



$$\begin{aligned} \cdot S_I &= \int_{T_0}^T \frac{C_V}{T} dT + R \ln\left(\frac{V}{V_0}\right) + R \left(\frac{s - s^{ref}}{R} \right) \\ &= \ln\left(\frac{T}{T_0}\right) + \ln\left(\frac{V}{V_0}\right) + \ln\left(\frac{V-b}{V}\right) \\ &= \ln\left(\frac{0.4}{0.4}\right) + \ln\left(\frac{7.9}{10^3}\right) + \ln\left(\frac{7.9 - 1.05}{7.9}\right) \\ &= -4.98 \end{aligned}$$

$$C_V = 1 \quad (\text{unitless in simulation}) \\ R = 1$$

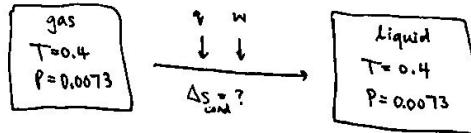
$$b = \frac{RT_c}{8P_c} = 1.05$$

<< Single Component Phase Formation

Ex1 → state? (two phases)
(cont.)

- From simulation, known $u_{\text{II}} = -1.39$, $v_{\text{II}} = 7.9$
 - Find u_v , u_L , v_v , v_L from vdW EOS
 - Calculate quality
 - Find S_v , S_L and calculate S_{II} .
 - Read vdW EOS chart using $T=0.4$, $P=0.0073$ using tie line, we have
 - $v_v = 40$, $v_L = 1.5 \Rightarrow q = \frac{v_v - v_L}{v_v - v_c} = 0.17$
 - $u_v = 0.1$, $u_L = -1.7 \Rightarrow q = \frac{u_v - u_L}{u_v - u_c} = 0.17$ agree
 - Estimate S_v using equation used for state I
- $$\begin{aligned} S_v &= \ln\left(\frac{T}{T_c}\right) + \ln\left(\frac{v_v}{v_c}\right) + \lambda \ln\left(\frac{v_v - b}{v_v}\right) \\ &= \ln\left(\frac{T}{T_c}\right) + \ln\left(\frac{v_v - b}{v_c}\right) \quad b = \frac{RT_c}{8P_c} = 1.05 \\ &= \ln\left(\frac{0.4}{0.4}\right) + \ln\left(\frac{40 - 1.05}{10^3}\right) \\ &= -3.25 \end{aligned}$$

- Estimate S_L using hypothetical condensation path



- $q = \Delta u - w$
- $= \Delta u - P \Delta v$
- $= (-1.7 - 0.1) - (0.0073)(1.5 - 40)$
- $= -1.52$
- $\Delta S = \frac{q}{T} = \frac{-1.52}{0.4} = -3.80$
- $S_L = S_v + \Delta S = -3.25 - 3.80 = -7.05$
- Find S_{II} using quality weighted average

$$\begin{aligned} S_{\text{II}} &= q S_v + (1-q) S_L \\ &= (0.17)(-3.25) + (1-0.17)(-7.05) \\ &= -6.41 \end{aligned}$$

→ Entropy change of universe

- $\Delta u = u_{\text{II}} - u_{\text{I}} = -1.32 - (-0.15) = -1.17 \Rightarrow q_{\text{univ}} = -\Delta u = 1.17$
- $\Delta S_{\text{sys}} = S_{\text{II}} - S_{\text{I}} = -6.41 - (-4.98) = -1.43$
- $\Delta S_{\text{surv}} = \frac{q_{\text{univ}}}{T} = \frac{1.17}{0.4} = 3.85$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surv}} = -1.43 + 3.85 = 2.4 > 0$

<< Gibbs Free Energy (Constant T, P)

- closed system
- constant T, P (e.g. phase change)

 \rightarrow System

$$\Delta U_{\text{sys}} = Q + W$$

$$Q = \Delta U_{\text{sys}} - W$$

$$= \Delta U_{\text{sys}} - (-P\Delta V_{\text{sys}})$$

$$= \Delta H_{\text{sys}}$$

 \rightarrow Surrounding

$$\Delta S_{\text{surr}} = -\frac{Q}{T}$$

$$= -\frac{\Delta H_{\text{sys}}}{T}$$

 \rightarrow Universe

$$\cdot \text{2nd law: } \Delta S_{\text{univ}} \geq 0$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0$$

$$\Delta(H_{\text{sys}} - TS_{\text{sys}}) \leq 0$$

$$\Delta(H - TS) \leq 0$$

$$\boxed{\Delta G \leq 0}$$

 \rightarrow Gibbs Free Energy

$$\boxed{G \equiv H - TS}$$

\cdot All state properties of system, no need of surrounding

\cdot At fixed T, P, system will spontaneously evolve to minimize G.

 \rightarrow Phase Change

$$\cdot g = g_v + (1-g)g_e$$

$\cdot g_v < g_e$, evolve to entirely vapor

$\cdot g_v > g_e$, evolve to entirely liquid

$\cdot g_v = g_e$, vapor-liquid equilibrium

$\left. \right\} \text{to minimize } g.$

<< Helmholtz Free Energy (Constant V, T)

- closed system

- constant V, T

 \rightarrow System

$$\Delta U_{\text{sys}} = Q + \cancel{V^0} = Q$$

 \rightarrow Universe

$$\Delta S_{\text{univ}} \geq 0$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\Delta S_{\text{sys}} - \frac{\Delta U_{\text{sys}}}{T} \geq 0$$

$$\Delta(U - TS) \leq 0$$

$$\boxed{\Delta F \leq 0}$$

 \rightarrow Surrounding

$$\Delta S_{\text{surr}} = -\frac{Q}{T} = -\frac{\Delta U_{\text{sys}}}{T}$$

 \rightarrow Helmholtz Free Energy

$$\boxed{F \equiv U - TS}$$

<< Solving Single Component Equilibrium

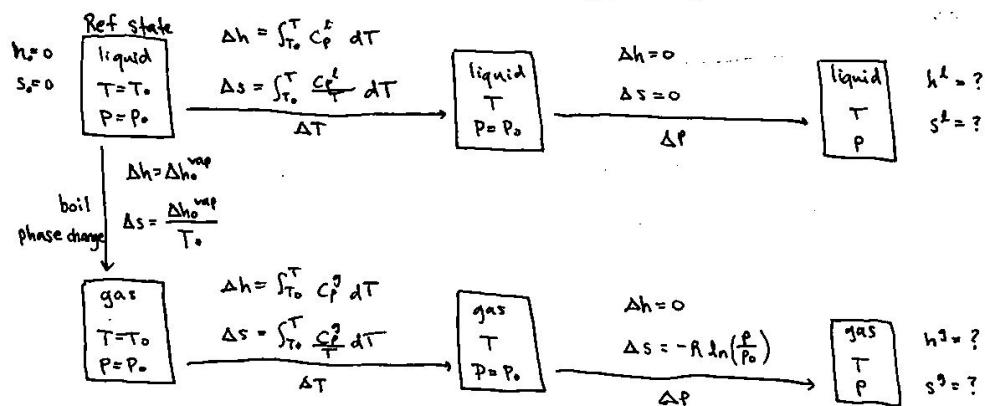
1. Pick convenient reference state for u, h, s.
2. Pick a model and make assumptions (e.g. vdW EOS, ideal gas, incompressible)
3. Construct hypothetical path from reference state to each phase
 - Calculate $h(T, P)$, $s(T, P) \rightarrow g(T, P)$
4. Impose equilibrium relationships
 - $T^{\alpha} = T^{\beta}$
 - $P^{\alpha} = P^{\beta}$
 - $g^{\alpha} = g^{\beta}$

5. Solve for unknown variables

<< Saturation Pressure

→ Calculate the saturation pressure of vapor in eqm with liquid

- Assume modest pressure, incompressible liquid, ideal gas
- Ref state : $P_0 = 1\text{ atm}$, $T_0 = T_b = \text{boiling pt of liquid}$



→ Liquid

$$h^L = h_0 + \sum \Delta h$$

$$= \int_{T_0}^T C_p^f dT$$

$$s^L = s_0 + \sum \Delta s$$

$$= \int_{T_0}^T \frac{C_p^f}{T} dT$$

$$g^L = h^L - T s^L$$

→ Gas

$$h^g = h_0 + \sum \Delta h$$

$$= \Delta h_vap + \int_{T_0}^T C_p^g dT$$

$$s^g = s_0 + \sum \Delta s$$

$$= \frac{\Delta h_vap}{T_0} + \int_{T_0}^T \frac{C_p^g}{T} dT - R \ln(\frac{P}{P_0})$$

$$g^g = h^g - T s^g$$

- At equilibrium, $g^L = g^g$

<< Saturation Pressure (cont.)

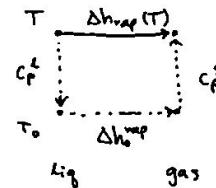
- Impose eqn condition $g^l = g^g$, and rearrange

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta h_{vap}^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{1}{RT} \int_{T_0}^T (C_p^g - C_p^l) dT + \frac{1}{R} \int_{T_0}^T \frac{C_p^g - C_p^l}{T} dT$$

$$\frac{d \ln(P_{sat})}{d(1/T)} = -\frac{1}{R} (\Delta h_{vap}^0 + \int_{T_0}^T C_p^g - C_p^l dT)$$

$$\boxed{\frac{d \ln(P_{sat})}{d(1/T)} = -\frac{1}{R} \Delta h_{vap}^0(T)}$$

Clausius-Clapeyron eqn

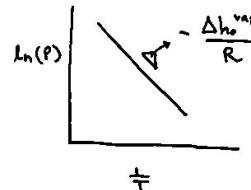


- If $\Delta h_{vap}(T)$ is constant (independent of T):

$$\frac{d \ln(P_{sat})}{d(1/T)} = -\frac{\Delta h_{vap}^0}{R}$$

$$\boxed{\ln\left(\frac{P_{sat}}{P_0}\right) = -\frac{\Delta h_{vap}^0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

- modest pressure
- incompressible liquid
- ideal gas
- $\Delta h_{vap}(T) = \text{const}$



- $\frac{E}{AT}$ is Arrhenius dependence related to kinetics and overcoming energy barriers.

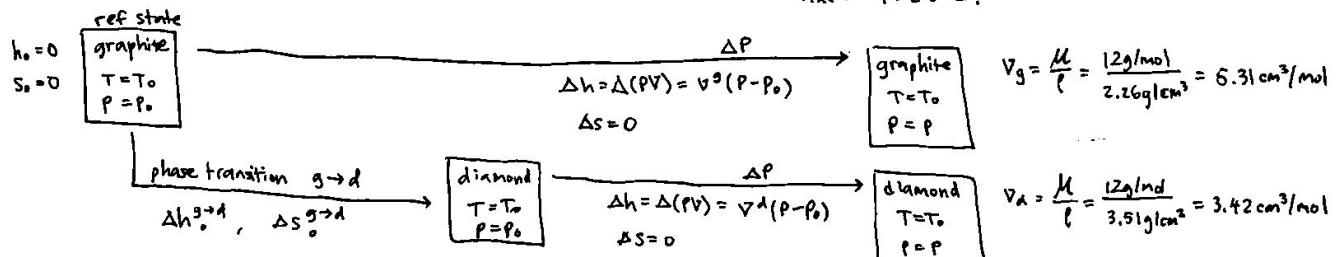
- Saturation pressure is tabulated as Antoine Equation

→ Antoine Equation

$$\ln(P_{sat}) = A - \frac{B}{C+T}$$

<< Solid Phase Transitions

- Calculate pressure required to transform graphite to diamond. Given $\rho_A = 3.51 \text{ g/cm}^3$, $\rho_g = 2.26 \text{ g/cm}^3$, $\Delta g_{9 \rightarrow d}^0(25^\circ\text{C}) = 2866 \text{ J/mol}$. Assume incompressible solids and fixed $T=25^\circ\text{C}$.



→ Graphite

$$h^g = V^g(P-P_0)$$

$$S^g = 0$$

$$g^g = V^g(P-P_0)$$

→ Equilibrium Condition

$$g^d = g^g$$

$$\Delta g_{9 \rightarrow d}^0 + V^d(P-P_0) = V^g(P-P_0)$$

$$P-P_0 = \frac{\Delta g_{9 \rightarrow d}^0}{V^g - V^d}$$

$$P-P_0 = \frac{2866 \text{ J/mol}}{(5.31 - 3.42) \text{ cm}^3/\text{mol}} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3$$

$$= 1.52 \times 10^9 \text{ Pa} \times \frac{1 \text{ bar}}{10^5 \text{ Pa}}$$

$$= 15200 \text{ bar}$$

→ Diamond

$$h^d = \Delta h_{9 \rightarrow d}^0 + V^d(P-P_0)$$

$$S^d = \Delta S_{9 \rightarrow d}^0$$

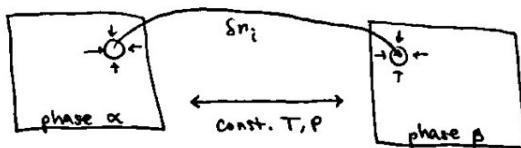
$$g^d = \underbrace{(\Delta h_{9 \rightarrow d}^0 - T \Delta S_{9 \rightarrow d}^0)}_{\Delta g_{9 \rightarrow d}^0} + V^d(P-P_0)$$

$$= \Delta g_{9 \rightarrow d}^0 + V^d(P-P_0)$$

<< Multicomponent Equilibrium

→ Determine equilibrium condition of multicomponent two-phase equilibrium at constant T, P.

$$\begin{aligned} dn_i^\alpha &= -\delta n_i \\ dn_{j \neq i}^\alpha &= 0 \end{aligned}$$



$$\begin{aligned} dn_i^\beta &= +\delta n_i \\ dn_{j \neq i}^\beta &= 0 \end{aligned}$$

- Components i, j, ... (species)
- phase α, β

• 2nd law

$$\Delta G \leq 0$$

$$\Delta G^\alpha + \Delta G^\beta \leq 0$$

• at eqm

$$\Delta G^\alpha + \Delta G^\beta = 0$$

$$\Delta G^\alpha = -\Delta G^\beta$$

• Since G depends on T, P, n_j: $G = G(T, P, n_1, n_2, \dots, n_j)$,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_j} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i} dn_i$$

• At constant T, P, it reduces to

$$dG = \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i} dn_i$$

$$dG = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i} dn_i$$

(only species i changes by δn_i)

> partial molar gibbs free energy -

$$\bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$dG = \bar{g}_i dn_i$$

• at eqm,

$$\Delta G^\alpha = -\Delta G^\beta$$

$$\bar{g}_i^\alpha dn_i^\alpha = -\bar{g}_i^\beta dn_i^\beta$$

$$\bar{g}_i^\alpha (-\delta n_i) = -\bar{g}_i^\beta \delta n_i$$

$$\bar{g}_i^\alpha = \bar{g}_i^\beta$$

Applicable to all species

→ Partial Molar Properties

> partial molar enthalpy -

$$\bar{h}_i = \left(\frac{\partial h}{\partial n_i}\right)_{T, P, n_j \neq i}$$

> partial molar entropy -

$$\bar{s}_i = \left(\frac{\partial s}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$G = H - TS$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i} = \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_j \neq i} - T \left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$\bar{g}_i = \bar{h}_i - T \bar{s}_i$$

• For single component, partial molar properties reduce to pure species property.

$$\bar{g}_i = g_i$$

$$\bar{h}_i = h_i$$

$$\bar{s}_i = s_i$$

Thermodynamic Web

Investigate the first two terms of dG :

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j+1}} dN_i$$

First term

Calculate $\left(\frac{\partial G}{\partial T}\right)_{P,n_j}$

$G = H - TS$

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_j} = \left(\frac{\partial H}{\partial T}\right)_{P,n_j} - T \left(\frac{\partial S}{\partial T}\right)_{P,n_j} - S \left(\frac{\partial T}{\partial T}\right)_{P,n_j}^1$$

$H = U + PV$

$$\left(\frac{\partial H}{\partial T}\right)_{P,n_j} = \left(\frac{\partial U}{\partial T}\right)_{P,n_j} + V \left(\frac{\partial P}{\partial T}\right)_{P,n_j}^0 + P \left(\frac{\partial V}{\partial T}\right)_{P,n_j}$$

$dU = TdS - PdV$

$$\frac{\partial U}{\partial T} = T \frac{\partial S}{\partial T} - P \frac{\partial V}{\partial T}$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,n_j} = T \frac{\partial S}{\partial T} - P \cancel{\frac{\partial V}{\partial T}} + V$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,n_j} = T \frac{\partial S}{\partial T}$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_j} = T \frac{\partial S}{\partial T} - T \frac{\partial S}{\partial T} - S$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_{P,n_j} = -S}$$

Second term

Calculate $\left(\frac{\partial G}{\partial P}\right)_{T,n_j}$

$G = H - TS$

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_j} = \left(\frac{\partial H}{\partial P}\right)_{T,n_j} - T \left(\frac{\partial S}{\partial P}\right)_{T,n_j} - S \left(\frac{\partial T}{\partial P}\right)_{T,n_j}^0$$

$H = U + PV$

$$\left(\frac{\partial H}{\partial P}\right)_{T,n_j} = \left(\frac{\partial U}{\partial P}\right)_{T,n_j} + P \left(\frac{\partial V}{\partial P}\right)_{T,n_j} + V \left(\frac{\partial P}{\partial P}\right)_{T,n_j}^1$$

$dU = TdS - PdV$

$$\frac{\partial U}{\partial P} = T \frac{\partial S}{\partial P} - P \frac{\partial V}{\partial P}$$

$$\left(\frac{\partial H}{\partial P}\right)_{T,n_j} = T \frac{\partial S}{\partial P} - P \cancel{\frac{\partial V}{\partial P}} + P \frac{\partial V}{\partial P} + V$$

$$\left(\frac{\partial H}{\partial P}\right)_{T,n_j} = T \frac{\partial S}{\partial P} + V$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_j} = T \frac{\partial S}{\partial P} + V - T \frac{\partial S}{\partial P}$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_{T,n_j} = V}$$

Together

$$\boxed{dG = -SdT + VdP + \sum_i \bar{\beta}_i dN_i}$$

<< Chemical Potential

- Isolated system, V,S constrained, $U(V,S)$
- Closed system, V,T constrained, $A(V,S) = U - TS$
- Open system, P,T constrained, $G(P,T) = H - TS$
- > chemical potential μ_i - reversible work to add species i to system.

$$\boxed{\mu_i = \bar{g}_i} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i} = \left(\frac{\partial A}{\partial n_i} \right)_{V,S,n_j \neq i} = \left(\frac{\partial U}{\partial n_i} \right)_{V,S,n_j \neq i}$$

At eqm, $\mu_i^a = \mu_i^b$

<< Equations for equilibrium of two phases

- consider α, β phase and multiple species.

- thermal eqm $\boxed{T^\alpha = T^\beta}$
- mechanical eqm $\boxed{P^\alpha = P^\beta}$
- chemical eqm $\boxed{\mu_i^\alpha = \mu_i^\beta}$

- One component : $\mu_i = \left(\frac{\partial g_i(n_i)}{\partial n_i} \right)_{T,P} = \bar{g}_i = h_i - TS_i$ ← molar Gibbs free energy

- multicomponent : $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i} = \bar{g}_i = \bar{h}_i - TS_i$ ← partial molar Gibbs free energy

<< Raoult's Law

- Consider binary ideal mixture of A and B

- assumptions
 - A-B interactions similar to A-A, B-B interactions
 - random mixing of A and B
 - ideal gas for vapor

- $H = n_A h_A + n_B h_B$
- $S = n_A S_A + n_B S_B - \underbrace{nR(x_A \ln x_A + x_B \ln x_B)}_{\text{config entropy from mixing}}$

} works for ideal gas and liquid

- $\bar{h}_A = \left(\frac{\partial H}{\partial n_A} \right)_{T,P,n_B} = \left(\frac{\partial}{\partial n_A} \right)_{T,P,n_B} (n_A h_A + n_B h_B) = h_A$

- liquid $\bar{h}_A^L = h_A^L(T)$

- gas $\bar{h}_A^G = h_A^G(T)$

- $\bar{S}_A = \left(\frac{\partial S}{\partial n_A} \right)_{T,P,n_B} = \left(\frac{\partial}{\partial n_A} \right)_{T,P,n_B} [n_A S_A + n_B S_B - nR(x_A \ln x_A + x_B \ln x_B)] = S_A - R \ln x_A$

- liquid $\bar{S}_A^L = S_A^L(T) - R \ln x_A^L$

- gas $\bar{S}_A^G = S_A^G(T, P_0) - R \ln \left(\frac{P}{P_0} \right) - R \ln x_A^G$

<< Raoult's Law

- At vapor-liquid eqm,

$$\mu_A^{\text{v}} = \mu_A^{\text{l}}$$

$$\bar{g}_A^{\text{v}} = \bar{g}_A^{\text{l}}$$

$$\bar{h}_A^{\text{v}} - T \bar{s}_A^{\text{v}} = \bar{h}_A^{\text{l}} - T \bar{s}_A^{\text{l}}$$

$$h_A^{\text{v}}(T) - T s_A^{\text{v}}(T, P_0) + RT \ln\left(\frac{x_A^{\text{v}} P}{x_A^{\text{l}} P_0}\right) = h_A^{\text{l}}(T) - T s_A^{\text{l}}(T) + RT \ln(x_A^{\text{l}})$$

$$RT \ln\left(\frac{x_A^{\text{v}} P}{x_A^{\text{l}} P_0}\right) = -(g_A^{\text{v}}(T, P_0) - g_A^{\text{l}}(T))$$

$$RT \ln\left(\frac{x_A^{\text{v}} P}{x_A^{\text{l}} P_0}\right) = -\Delta g_A^{\text{(vap)}}(T, P_0)$$

$$\left. \begin{array}{l} \text{liquid} \\ \mu_i = \mu_i^{\circ} + RT \ln(x_A^i) \\ \bar{g}_i = \bar{g}_i^{\circ} + RT \ln(x_A^i) \end{array} \right\} \text{since } \mu_i = \bar{g}_i$$

$$\left. \begin{array}{l} g^{\text{o}} \\ \mu_i = \mu_i^{\circ} + RT \ln\left(\frac{x_A^{\text{v}} P}{P_0}\right) \\ \bar{g}_i = \bar{g}_i^{\circ} + RT \ln\left(\frac{x_A^{\text{v}} P}{P_0}\right) \end{array} \right\}$$

equate

- At $x_A=1, P=P_A^{\text{sat}}$

$$RT \ln\left(\frac{P_A^{\text{sat}}}{P_0}\right) = -\Delta g_A^{\text{(vap)}}(T, P_0)$$

- Equate above,

$$RT \ln\left(\frac{P_A^{\text{sat}}}{P_0}\right) = RT \ln\left(\frac{x_A^{\text{v}} P}{x_A^{\text{l}} P_0}\right)$$

> Raoult's law

$$P_A = \boxed{x_A^{\text{v}} P = x_A^{\text{l}} P_A^{\text{sat}}}$$

- partial pressure of gaseous A = (mol frac of liquid A)(sat. pressure of A)

<< Pxy Diagram

$$P = P_A + P_B$$

$$= x_A^{\text{v}} P + x_B^{\text{v}} P$$

$$= x_A^{\text{l}} P_A^{\text{sat}} + (1-x_A^{\text{l}}) P_B^{\text{sat}}$$

Raoult's law

$$\boxed{P = (P_A^{\text{sat}} - P_B^{\text{sat}}) x_A^{\text{l}} + P_B^{\text{sat}}}$$

for liquid condensation curve

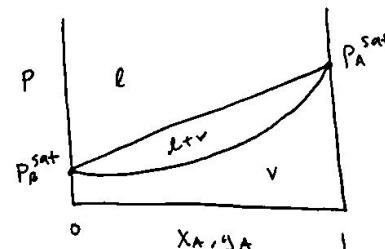
- System pressure is a weighted average of the saturation pressure of each species

$$\text{Substitute } x_A^{\text{l}} = x_A^{\text{v}} \frac{P}{P_A^{\text{sat}}}$$

$$P = (P_A^{\text{sat}} - P_B^{\text{sat}}) x_A^{\text{v}} \frac{P}{P_A^{\text{sat}}} + P_B^{\text{sat}}$$

$$\boxed{P = \frac{P_A^{\text{sat}} P_B^{\text{sat}}}{P_A^{\text{sat}} - (P_A^{\text{sat}} - P_B^{\text{sat}}) x_A^{\text{v}}}}$$

for gas boiling curve



<< Chemical Potential of Dilute Species

- Consider solvent-species i binary mixture

assumptions { solvent behave as ideal liquid
species i , the solute, interact only with solvent since dilute

$$\cdot H(T, P) = H_{\text{solvent}}(T, P) + n_i h_i^\circ(T, P)$$

$$\cdot S(T, P) = S_{\text{solvent}}(T, P) + n_i s_i^\circ(T, P) - \underbrace{n_i R \ln\left(\frac{c_i}{c_i^\circ}\right)}_{\text{dilute mixing}}$$

$$\cdot \bar{h}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, P} = h_i^\circ$$

$$\cdot \bar{s}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T, P} = s_i^\circ - R \ln\left(\frac{c_i}{c_i^\circ}\right)$$

$$\begin{aligned} \cdot \bar{\mu}_i &= \bar{g}_i = \bar{h}_i - T \bar{s}_i \\ &= h_i^\circ - T s_i^\circ + RT \ln\left(\frac{c_i}{c_i^\circ}\right) \\ &= g_i^\circ + RT \ln\left(\frac{c_i}{c_i^\circ}\right) \end{aligned}$$

$$\cdot \mu_i = \mu_i^\circ + RT \ln\left(\frac{c_i}{c_i^\circ}\right)$$

→ Secondary reference state

$$\cdot \text{ideal liquid} \quad \mu_i = \mu_i^\circ + RT \ln(x_i^2) \quad , \quad x_i^\circ = 1$$

$$\cdot \text{ideal gas} \quad \mu_i = \mu_i^\circ + RT \ln\left(x_i^g \frac{P}{P_0}\right) \quad , \quad P_0 \text{ is ref standard pressure}$$

$$\cdot \text{dilute mix} \quad \mu_i = \mu_i^\circ + RT \ln\left(\frac{c_i}{c_i^\circ}\right) \quad , \quad c_i^\circ \text{ is ref standard concentration}$$

<< Henry's Law

- Consider O₂ dissolution in water $O_{2,g} \rightleftharpoons O_{2,aq}$

$$\cdot \mu_{O_2}^\circ = \mu_{O_2}^{0,g} + RT \ln\left(\frac{P_{O_2}}{P}\right) \quad \text{ideal gas, } P_0 = 1 \text{ atm}$$

$$\cdot \mu_{O_2}^\circ = \mu_{O_2}^{0,g} + RT \ln\left(\frac{C_{O_2}}{C_0}\right) \quad \text{dilute O}_2 \text{ in ag, } C_0 = 1 \text{ mol/kg}$$

$$\cdot \text{At eqm.} \quad \mu_{O_2}^\circ = \mu_{O_2}^{0,g}$$

$$\mu_{O_2}^{0,g} + RT \ln\left(\frac{P_{O_2}}{P}\right) = \mu_{O_2}^{0,g} + RT \ln\left(\frac{C_{O_2}}{C_0}\right)$$

$$C_{O_2} = C_0 \frac{P_{O_2}}{P_0} \exp\left[\frac{\mu_{O_2}^{0,g} - \mu_{O_2}^{0,g}}{RT}\right] \quad (\Delta g_{\text{dissolution}}^\circ = \mu_{O_2}^{0,g} - \mu_{O_2}^{0,g})$$

$$C_{O_2} = C_0 \frac{P_{O_2}}{P_0} \exp\left[\frac{-\Delta g_{\text{dissolution}}^\circ}{RT}\right] P_{O_2}$$

Henry's constant $K_H(T) = H(T)$

> Henry's Law

$$C_{O_2} = K_H(T) P_{O_2}$$

linear relationship between solute concentration
& gas phase partial pressure

<< Accuracy of Henry's Law

- Consider O_2 dissolve in water $O_{2,g} \rightleftharpoons O_{2,aq}$, calculate Henry's constant $K_H(T)$ at $T = 298K$.

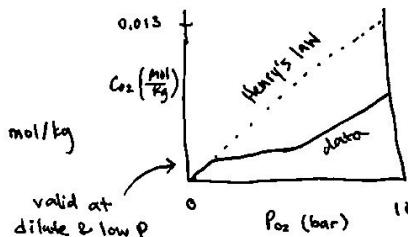
$$\left. \begin{array}{l} \cdot T = 298K \\ \cdot \Delta g_{O_2}^{sol}(298K) = 16.5 \text{ kJ/mol} \\ \cdot C_0 = 1 \text{ mol/kg} \\ \cdot P_0 = 1 \text{ bar} \\ \cdot R = 8.314 \text{ J/mol K} \end{array} \right\} \rightarrow K_H = \frac{C_0}{P_0} \exp\left(\frac{-\Delta g_{O_2}^{sol}}{RT}\right) = \frac{1 \text{ mol/kg}}{1 \text{ bar}} \exp\left(\frac{-16.5 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/mol K})(298 \text{ K})}\right) = 0.0013 \text{ mol/kg bar}$$

Note that $\Delta g_{O_2}^{sol} > 0$, which is unfavorable for solvation, but dilute concentration allows O_2 to be spread out, counterbalance the unfavorability.

At $P = 1 \text{ atm}$, $P_{O_2} = (1 \text{ atm})(0.21) = 0.21 \text{ atm} \approx 0.21 \text{ bar}$, so

$$C_{O_2} = K_H(T)P_{O_2} = (0.0013 \text{ mol/kg bar})(0.21 \text{ bar}) = 0.000273 \text{ mol/kg}$$

Henry's law is accurate at low pressure of dilute species



<< Gibbs-Duhem Equation

- From L35, $dG = -SdT + VdP + \sum \mu_i dn_i$

- At fixed T, P , $dG = \sum \mu_i dn_i$

$$G = \sum \mu_i n_i$$

- Total derivative $dG = \sum \mu_i dn_i + \sum n_i d\mu_i$

> Gibbs-Duhem eqn

$$\sum \mu_i dn_i = 0$$

$$\sum n_i d\mu_i = 0$$

<< Colligative Property (Solvent effects)

- Consider dilute A in solvent, derive chemical potential of solvent μ_{solvent}

- Gibbs-Duhem eqn

$$0 = \sum x_i d\mu_i$$

$$0 = x_A d\mu_A + x_{\text{solvent}} d\mu_{\text{solvent}}$$

$$0 = x_A d\mu_A + (1-x_A) d\mu_{\text{solvent}}$$

$$0 = \frac{x_A}{x_A} RT dx_A + (1-x_A) d\mu_{\text{solvent}}$$

$$\int d\mu_{\text{solvent}} = \int \frac{RT}{(1-x_A)} dx_A$$

$$\mu_{\text{solvent}} = RT \ln(1-x_A) + C$$

> Colligative property

$$\mu_{\text{solvent}} = RT \ln(1-x_A) + \mu_{\text{solvent}}^0$$

$$\left\{ \begin{array}{l} \mu_A = \mu_A^0 + RT \ln(x_A) \\ d\mu_A = RT \frac{1}{x_A} dx_A \end{array} \right.$$

$$\left\{ \begin{array}{l} \text{initial condition} \\ x_A = 0, \mu_{\text{solvent}} = \mu_{\text{solvent}}^0(T) \\ \Rightarrow C = \mu_{\text{solvent}}^0 \end{array} \right.$$

- chemical potential of solvent depends on properties of solvent (μ_{solvent}^0) and concentration of solute (x_A), but not properties of solute

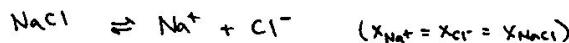
Freezing Point Depression

- Consider brine and ice in eqn, determine $x_{\text{NaCl}}(T)$.

- At eqm

$$\begin{cases} T_{\text{ice}} = T_{\text{brine}} \\ p_{\text{ice}} = p_{\text{brine}} \\ \mu_{\text{H}_2\text{O}}^{\text{ice}} = \mu_{\text{H}_2\text{O}}^{\text{brine}} \end{cases}$$
 $\rightarrow \mu_{\text{H}_2\text{O}}^{\text{brine}}$

- Calculate $\mu_{\text{H}_2\text{O}}^{\text{ice}}$ by first finding $\mu_{\text{NaCl}}^{\text{brine}}$



$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+} + \mu_{\text{Cl}^-}$$

$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+}^\circ + RT \ln x_{\text{Na}^+} + \mu_{\text{Cl}^-}^\circ + RT \ln x_{\text{Cl}^-}$$

$$\mu_{\text{NaCl}} = \mu_{\text{Na}^+}^\circ + 2RT \ln x_{\text{NaCl}}$$

$$d\mu_{\text{NaCl}} = \frac{2RT}{x_{\text{NaCl}}} dx_{\text{NaCl}}$$

- Gibbs-Duhem eqn gives

$$0 = \sum_i \mu_i$$

$$0 = x_{\text{H}_2\text{O}} d\mu_{\text{H}_2\text{O}} + x_{\text{NaCl}} d\mu_{\text{NaCl}}$$

$$0 = (1-x_{\text{NaCl}}) d\mu_{\text{H}_2\text{O}} + x_{\text{NaCl}} d\mu_{\text{NaCl}}$$

$$d\mu_{\text{H}_2\text{O}} = -\frac{x_{\text{NaCl}}}{1-x_{\text{NaCl}}} d\mu_{\text{NaCl}}$$

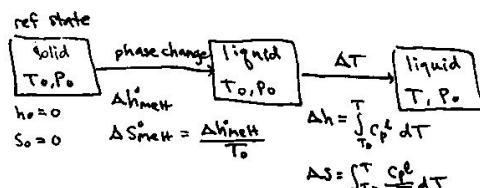
$$d\mu_{\text{H}_2\text{O}} = -\frac{x_{\text{NaCl}}}{1-x_{\text{NaCl}}} \frac{2RT}{x_{\text{NaCl}}} dx_{\text{NaCl}}$$

$$\int d\mu_{\text{H}_2\text{O}} = - \int 2RT \frac{dx_{\text{NaCl}}}{1-x_{\text{NaCl}}}$$

$$\mu_{\text{H}_2\text{O}}^{\text{brine}} = \mu_{\text{H}_2\text{O}}^\circ + 2RT \ln(1-x_{\text{NaCl}})$$

initial condition
 $x_{\text{NaCl}} = 0, \mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}^\circ$
 $\Rightarrow c = \mu_{\text{H}_2\text{O}}^\circ$

at ref state T_0, P_0 ,

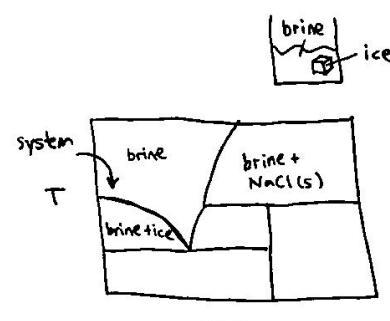


$$\mu_{\text{H}_2\text{O}}^{\text{liq}} = \bar{h}_{\text{H}_2\text{O}}^{\text{liq}} = \bar{h}_{\text{H}_2\text{O}}^{\text{liq}} - TS_{\text{H}_2\text{O}}^{\text{liq}}$$

$$= [\Delta h^{\circ\text{melting}} + C_p^L(T-T_0)] - T \left[\frac{\Delta h^{\circ\text{melting}}}{T_0} + C_p^L \ln \left(\frac{T}{T_0} \right) \right]$$

We therefore have $\mu_{\text{H}_2\text{O}}^{\text{brine}}$:

$$\mu_{\text{H}_2\text{O}}^{\text{brine}} = [\Delta h^{\circ\text{melting}} + C_p^L(T-T_0)] - T \left[\frac{\Delta h^{\circ\text{melting}}}{T_0} + C_p^L \ln \left(\frac{T}{T_0} \right) \right] + 2RT \ln(1-x_{\text{NaCl}})$$



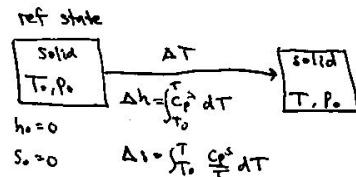
X_{NaCl}

$$\begin{aligned} h^{\text{L}} &= h_0 + \sum \Delta h \\ &= 0 + \Delta h^{\text{melting}} + \int_{T_0}^T C_p^L dT \\ &= \Delta h^{\text{melting}} + C_p^L (T - T_0) \\ S^{\text{L}} &= S_0 + \sum \Delta S \\ &= 0 + \frac{\Delta h^{\circ\text{melting}}}{T_0} + \int_{T_0}^T \frac{C_p^L}{T} dT \\ &= \frac{\Delta h^{\circ\text{melting}}}{T_0} + C_p^L \ln \left(\frac{T}{T_0} \right) \end{aligned}$$

« Freezing Point Depression (cont.)

$\rightarrow \mu_{\text{H}_2\text{O}}^{\text{ice}}$

- Use hypothetical path with ref state of solid at T_0, P_0



$$h^s = h_0 + \sum \Delta h$$

$$= C_p^s (T - T_0)$$

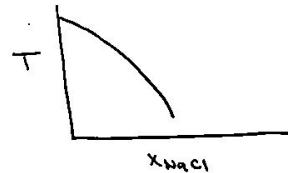
$$s^s = s_0 + \sum \Delta s$$

$$= C_p^s \ln\left(\frac{T}{T_0}\right)$$

$$\begin{aligned} \mu_{\text{H}_2\text{O}}^{\text{ice}} &> \bar{h}_{\text{H}_2\text{O}}^{\text{ice}} = \bar{h}_{\text{H}_2\text{O}}^s - T \bar{s}_{\text{H}_2\text{O}}^s \\ &= C_p^s (T - T_0) - T C_p^s \ln\left(\frac{T}{T_0}\right) \end{aligned}$$

\rightarrow Chemical equilibrium

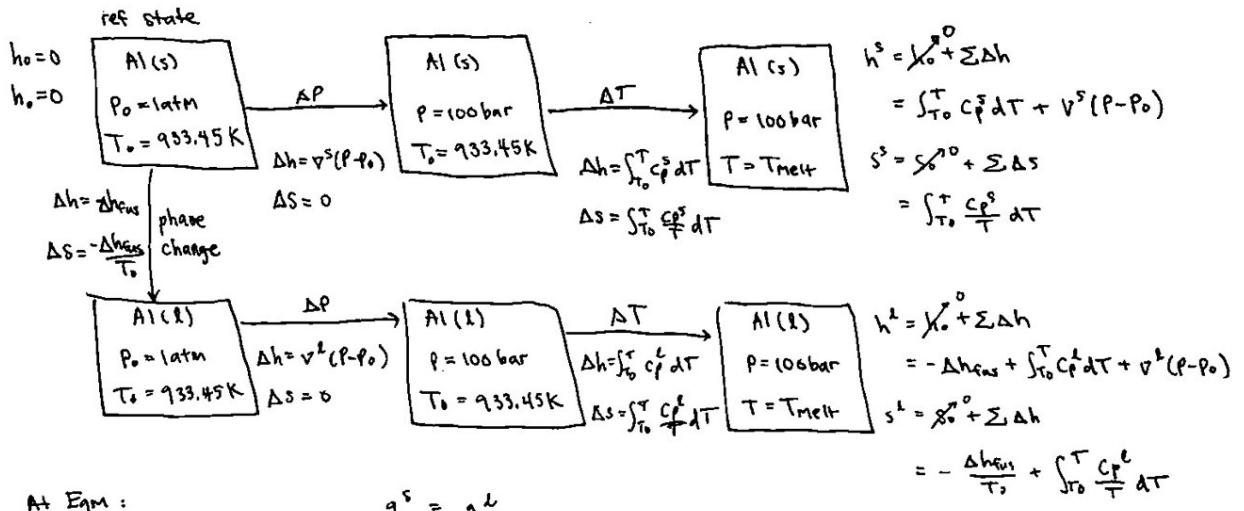
$$\begin{aligned} \mu_{\text{H}_2\text{O}}^{\text{brine}} &= \mu_{\text{H}_2\text{O}}^{\text{ice}} \\ [\Delta h_{\text{melt}} + C_p^s (T - T_0)] - T \left[\frac{\Delta h_{\text{melt}}}{T_0} + C_p^s \ln\left(\frac{T}{T_0}\right) \right] + 2RT \ln(1 - x_{\text{NaCl}}) &= C_p^s (T - T_0) - T C_p^s \ln\left(\frac{T}{T_0}\right) \\ x_{\text{NaCl}} &= 1 - \exp \left[-\frac{1}{2RT} (C_p^s - C_p^i) [(T - T_0) - T \ln\left(\frac{T}{T_0}\right)] + \Delta h_{\text{melt}} (1 - \frac{T}{T_0}) \right] \end{aligned}$$



** Single Component Egm

Ex1 Calculate the melting temperature of Aluminum at $P=100\text{ bar}$ using

- $T_{\text{melt}}(1\text{ atm}) = 933.45\text{ K}$
- $\Delta h_{\text{fus}}(1\text{ atm}) = -10711 \text{ J/mol}$
- $C_p^L = 31.748 \text{ J/mol K}$
- $C_p^S = [20.068 + 0.0138T] \text{ J/mol K}$
- $\rho^L = 2300 \text{ kg/m}^3, v^L = 1/\rho^L$
- $\rho^S = 2700 \text{ kg/m}^3, v^S = 1/\rho^S$



At Egm:

$$g^S = g^L$$

$$h^S - T s^S = h^L - T s^L$$

$$\int_{T_0}^T C_p^S dT + V^S(P - P_0) - T \int_{T_0}^T \frac{C_p^S}{T} dT = -\Delta h_{\text{fus}} + \int_{T_0}^T C_p^L dT + V^L(P - P_0) - T \left[-\frac{\Delta h_{\text{fus}}}{T_0} + \int_{T_0}^T \frac{C_p^L}{T} dT \right]$$

$$0 = -\Delta h_{\text{fus}} \left(1 - \frac{T}{T_0} \right) + \int_{T_0}^T (C_p^L - C_p^S) dT - T \left[\int_{T_0}^T \frac{C_p^L - C_p^S}{T} dT \right] + (V^L - V^S)(P - P_0)$$

$$0 = -\Delta h_{\text{fus}} \left(1 - \frac{T}{T_0} \right) + \left[A(T - T_0) - \frac{B}{2}(T^2 - T_0^2) \right] - T \left[A \ln \left(\frac{T}{T_0} \right) - B(T - T_0) \right] + (V^L - V^S)(P - P_0)$$

$$T = 934.95\text{ K}$$

$$\Delta T = 1.5\text{ K}$$

ccc Multicomponent Eqm

Ex2 Calculate vapor pressure of an aqueous solution that has a solute mole fraction of 0.1.
Vapor pressure of water is 25.756 mmHg at 25°C.

- If solute does not vaporize, the solvent (water) vaporizes to create vapor pressure.

- Raoult's law

$$x_{\text{H}_2\text{O}}^{\text{g}} P = x_{\text{H}_2\text{O}}^{\text{l}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$P_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}}^{\text{l}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$\left. \begin{array}{l} x_{\text{H}_2\text{O}}^{\text{l}} = 1 - x_{\text{solute}}^{\text{l}} = 1 - 0.1 = 0.9 \\ P_{\text{H}_2\text{O}}^{\text{sat}} (25^\circ\text{C}) = 25.756 \text{ mmHg} \\ x_{\text{H}_2\text{O}}^{\text{g}} = 1 - x_{\text{solute}}^{\text{g}} = 1 - 0 = 1 \end{array} \right\}$$

$$P_{\text{H}_2\text{O}} = (0.9)(25.756 \text{ mmHg}) = 23.18 \text{ mmHg}$$

Ex3 The vapor pressure of an aqueous solution is 24.90 mmHg at 25°C.
The vapor pressure of water is 25.756 mmHg at 25°C.
Calculate mole fraction of solute in solution.

- Raoult's law

$$x_{\text{H}_2\text{O}}^{\text{g}} P = x_{\text{H}_2\text{O}}^{\text{l}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$x_{\text{H}_2\text{O}}^{\text{l}} = \frac{x_{\text{H}_2\text{O}}^{\text{g}} P}{P_{\text{H}_2\text{O}}^{\text{sat}}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{\text{sat}}} \quad \left. \begin{array}{l} P_{\text{H}_2\text{O}} = 24.90 \text{ mmHg} \\ P_{\text{H}_2\text{O}}^{\text{sat}} = 25.756 \text{ mmHg} \end{array} \right\}$$

$$x_{\text{H}_2\text{O}}^{\text{l}} = \frac{24.90 \text{ mmHg}}{25.756 \text{ mmHg}} = 0.967$$

$$x_{\text{solute}}^{\text{l}} = 1 - x_{\text{H}_2\text{O}}^{\text{l}} = 1 - 0.967 = 0.023$$

Ex4 How many grams of nonvolatile compound B ($M = 97.8 \text{ g/mol}$) would need to be added to 250g of water to produce a solution with vapor pressure of 23.756 torr?
The vapor pressure of water at this temperature is 42.362 torr.

- Raoult's law

$$x_{\text{H}_2\text{O}}^{\text{g}} P = x_{\text{H}_2\text{O}}^{\text{l}} P_{\text{H}_2\text{O}}^{\text{sat}}$$

$$x_{\text{H}_2\text{O}}^{\text{l}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{\text{sat}}} = \frac{23.756 \text{ torr}}{42.362 \text{ torr}} = 0.5608$$

- Definition of mol frac

$$x_{\text{H}_2\text{O}}^{\text{l}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{solute}}}$$

$$0.5608 = \frac{(250 \text{ g}) \left(\frac{1 \text{ mol}}{18 \text{ g}} \right)}{(250 \text{ g}) \left(\frac{1 \text{ mol}}{18 \text{ g}} \right) + n_{\text{solute}}} \Rightarrow n_{\text{solute}} = 10.87 \text{ mol}$$

- Convert to mass

$$m_{\text{solute}} = M n_{\text{solute}} = (97.8 \text{ g/mol})(10.87 \text{ mol}) = 1063 \text{ g}$$

Ex5 Calculate T_{bp} of hexane at 0.5 atm. Given $\Delta h_{\text{vap}} = 30.8 \text{ kJ/mol}$, $T_{\text{bp}}(1 \text{ atm}) = 68.9^\circ\text{C} = 341.9 \text{ K}$

- Clausius-Clayperon eqn

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

$$\ln \left(\frac{1 \text{ atm}}{0.5 \text{ atm}} \right) = \frac{30.8 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K mol}} \left(\frac{1}{T_2} - \frac{1}{341.9 \text{ K}} \right)$$

$$T_2 = 321 \text{ K} = 48.85^\circ\text{C}$$