Lecture 03/30

Monday, March 30, 2009
9:46 AM

Notes 0330

Audio recording started: 10:02 AM Monday, March 30, 2009

- Chapter 1: Ideal Gases
    - Macroscopic properties of gases
    - Equation of state

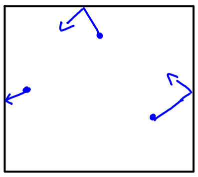
$$PV = nRT$$

Once 3 variables are known, the state of the system is known:

U, H, A, G, S

$U(P,T)$

- Pressure: force molecules assert on container walls



Collisions of molecules on container wall

$$\frac{\text{Force}}{\text{Area}} = \text{Pressure}$$

$$\text{dimensions} \quad \frac{\text{mass}\cdot\text{length}}{\text{time}^2\cdot\text{length}^2} = \frac{\text{mass}}{\text{time}^2\cdot\text{length}}$$

$$\text{mks units: pascal} = \frac{1\,N}{m^2} = \frac{kg}{s^2\,m}$$

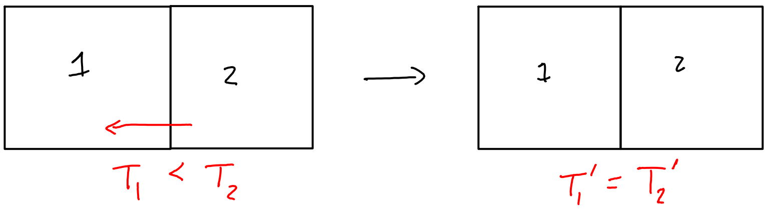
$$10^5\ \text{pascal} = 1\ \text{bar} \equiv p^{\ominus}\ (\text{STD Pressure})$$

$$1\,\text{atm} = 1.013\ \text{bar}$$

$$1\ \text{torr} = \frac{1}{760}\ \text{atm}$$

- $PV = $ Energy

- Temperature ~ Ave. KE of system

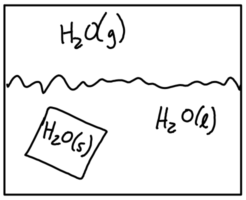


A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then A is in thermal equilibrium with C

Designing thermometer (object B is thermometer)

How do we define temperature scale?

Thermodynamic temperature scale: (Kelvins) K

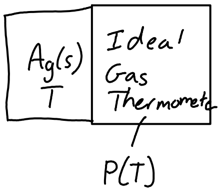


Tripple point of H_2O

always occurs at same temp

$$T_{T.P.} = 273.16K$$

Thermometer is an ideal gas at constant volume and number moles of material doesn't change



pressure is measurement of temperature

$$\boxed{T(\text{OBJECT}) = \frac{P_{\text{OBJECT}}}{P_{T.P.}} \times 273.16\text{K}}$$

Pressure cannot be less than zero, so temperature will never be below 0.

$$T \geq 0$$

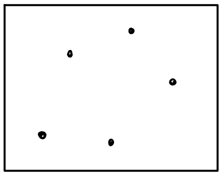
Celsius scale, 0^0 is melting point of water and 100^0 is boiling point of water

$$\theta/°C = T/K - 273.15$$

$PV = nRT$ Kelvin

$$\lim_{P \to 0} \text{all gases} = \text{ideal gas}$$

Ideal Gas



Molecules are very far apart in respect to their molecular size, so low pressure gives this

Then forces between molecules do not interact

R - universal gas constant

T always K

n always moles

$R = 8.314\ J/K\,mol$ (pascal,

$R = 8.21 \times 10^{-2}\ atm \cdot L$ (atm, L)

$$\overline{}\,\mathrm{K\cdot mol}$$

$$R = 8.314\times10^{-2}\ \frac{\mathrm{bar\cdot L}}{\mathrm{K\cdot mol}} \quad (\mathrm{bar},\ L)$$

$$R = 62.36\ \frac{\mathrm{torr\cdot L}}{\mathrm{K\cdot mol}} \quad (\mathrm{torr},\ L)$$

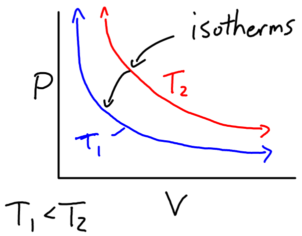
Applications of ideal gas law, set 2 variables constant and investigate dependence of one on other

n = constant

T = constant

PV = constant

$$P = \frac{\text{const}}{V}$$



constant T & n

$$P_1V_1 = P_2V_2$$

Discussion 03/31

Tuesday, March 31, 2009
9:47 AM

TA: Luan Vu
lvu@chem.ucla.edu
Office Hours: Geology 4607
Tue 11am-12pm
Thurs 2-3pm

Other TA: Terry
Office hours geology 4607
Wed 4-5pm
Fri 9-10am

Problem set problems not posted yet

Ideal Gas Laws

P1.1

$V = 1.00 \text{ dm}^3$

$m_{\text{methane}} = 5.00\text{g}$

$P = 1.00 \times 10^6 \text{Pa}$ flask explodes → t_0 atm

moles methane: $5\text{g} \times \frac{1\text{mol}}{30.068\text{g}} = 0.166 \text{ mol } C_2H_6 = n$

$PV = nRT$

$T = \frac{PV}{nR} = \frac{\qquad}{(0.166)(8.314)}$

P1.8

Lecture 04/01

Wednesday, April 01, 2009
9:53 AM

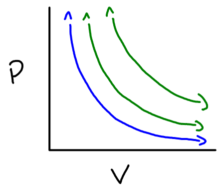
Notes 0401

Audio recording started: 10:02 AM Wednesday, April 01, 2009

Office Hours Geology 4607
Terry W 4-5, F 9-10
Luan T 11-12, R 2-3

Midterms are in CS24 (29th april & 28th of may)

- Chapter 1 Continued: Description of ideal gasses PV=nRT
    - n, T held constant

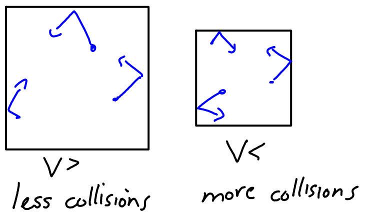


$PV = f(n,T)$

isotherms

hyperbola

microscopically

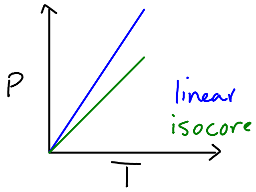


- n, V held constant

$$\frac{P}{T} = g(n,V)$$

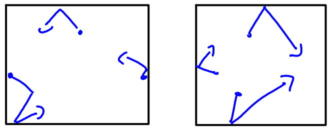
$P \sim T$

Charles' Law



linear

isocore



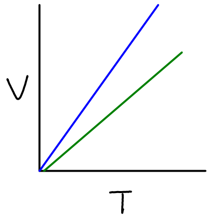
T~ Ave kinetic energy → velocity inc

Coll. freq. → $\sqrt{T}$

coll. freq. × force per collision → $\sqrt{T}$

low T   high T

- n, P constant



linear

isobar

$$V_m \equiv \frac{V}{n} \equiv \frac{1}{\rho}$$

molar volume

\# density

molar density mol/V

molar mass g/mol or kg/mol

$$\left.\begin{aligned} PV_m &= RT \\ P &= \rho RT \end{aligned}\right\} \quad \rho_m = \rho M$$

$$P = \frac{\rho_m}{M} RT$$

Consider orders of magnitude

V_m at STP (0°C, 1atm)

$V_m = 22.414$ L/mol

$V_m^{\ominus} \equiv V_m$ at SATP (25°C, 1 bar)

$V_m = 24.790$ L/mol

- Mixture of gases

$$x_i = \frac{n_i}{n}$$

mol fraction of species "i"

total # moles

$$\sum_{j=1}^{N} x_j = 1$$

$$P_i = x_i P$$

partial pressure

total pressure

P_i applies to ideal & nonideal gases

$$P_i = \frac{n_i RT}{V}$$

<-only true for ideal
approximate for non ideal

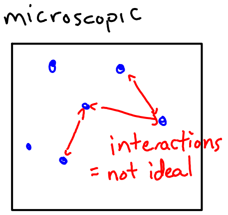
why? $P_i = x_i P$

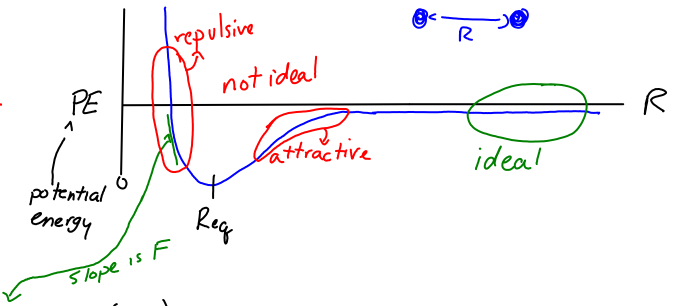
only true ideal gas

$$= \frac{n_i P}{n} = \frac{n_i}{n}\left(\frac{nRT}{V}\right) = \frac{n_i RT}{V}$$

- Real Gas Behavior

$PV \neq nRT$
why?





$$F = -\frac{d(PE)}{dR}$$

  - Van der Waals

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

rewritten molar volume

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

repulsive

$a, b > 0$
constants that depend on chemical identity only

1) Start $P = \frac{nRT}{V}$

2) modify with excluded V $b \Rightarrow \frac{\text{volume}}{\text{mol}}$ excluded volume

$$P = \frac{nRT}{V-nb}$$

3) attractive, reduces velocity so F_{on} wall is less
P will be decreased $\sim \left(\frac{n}{V}\right)^2$
$P = \underline{nRT} - a\left(\underline{n}\right)^2$

$$\overline{V-nb} \qquad (\overline{V})$$

- Chapter 2: First Law of Thermodynamics

$$\underset{\text{change in internal energy}}{\Delta U} = \underset{\text{heat}}{q} + \underset{\text{work}}{w}$$

Definitions:

- "System" - part of the universe we have a special interest in
- "Surroundings" - rest of the universe from the system
- "Boundary"
  - "Permeable" - matter/energy can be transferred back and forth between system and surroundings (open system)
  - "impermeable" - matter cannot (energy can) be transferred back and forth between system and surroundings (closed system).
  - "diathemic" boundary - heat can be transferred
  - "adiabatic" boundary - no heat can be transferred
  - Impermiable + adiabatic = closed system
- Internal energy
  - Internal: molecules IE beaker at rest, not in movement
  - Energy: kinetic + potential

Lecture 04/03

Friday, April 03, 2009
9:57 AM

Midterm open book. 1 page front and back
Final open back. 3 pages front and back

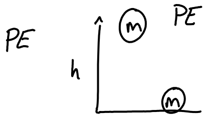
- Chapter 2: First Law of Thermodynamics

$$\Delta U = q + w$$

$$U = KE + PE$$

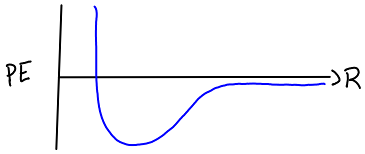
$$KE_i = \frac{m_i v_i^2}{2}$$

$$KE = \sum_{i=1}^{n} \frac{m_i v_i^2}{2}$$

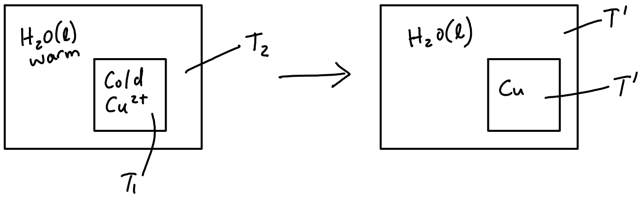


$$PE(\vec{r}) = \int_{\vec{r}_0}^{\vec{r}} -\vec{F}\cdot d\vec{l}$$

(1) PE is relative quantity (ref. position)
(2) U is extensive (scales w/ size of system)
(3) U is a state function
(change only depends on initial & final state)

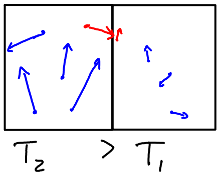


Heat: q



$T_1 < T' < T_2$

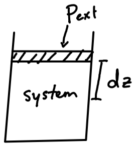
q>0 if heat is absorbed by system



Work: w

$$w = \int_{\vec{r}_0}^{\vec{r}} \vec{F}\cdot d\vec{l}$$

PV work



$$dw = F_{ext}\cdot dz$$

$F_{ext} = P_{ext}\cdot \text{Area}$ $\qquad -Adz = dV$

$dw = (P_{ext}\cdot A)\left(\frac{-dV}{A}\right)$ $\qquad dz = -\frac{dV}{A}$

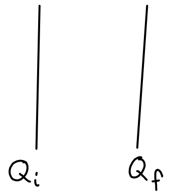
w>0 if work is done on system
w<0 if work is done by system

$$\boxed{dw = -P_{ext}A}$$

$w_{PV} > 0$ for contraction

$w_{PV} < 0$ for expansion

Current Work



$w = z(\varphi_f - \varphi_i)$

$w_{el} = \underset{\text{constant current}}{I}\,\underset{\text{time}}{t}\,\phi \leftarrow$ potential difference

Surface Expansion

$w_{SE} = \iint \underset{\text{surface tension}}{\gamma}\, dv$

similar to spring

$w = -\int \gamma\, dl$

$\Delta U = q + w \leftarrow$ 1st law of thermodynamics
only for closed system
also statement of conservation of energy

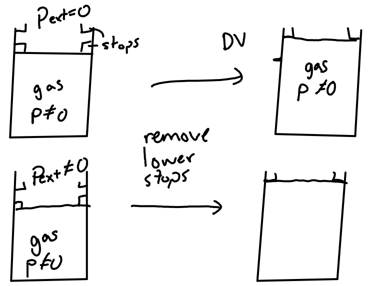
$\Delta U = 0$

$d\underset{\text{state function}}{U} = \underset{\text{not state functions}}{dq + dw}$

Back to PV Work

$dw = -P_{ext}\, dV$

Free Expansion

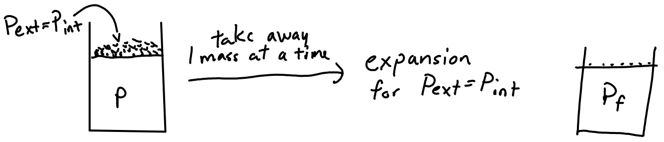


$dw = -P_{ext}\, PV$

$\int dw = \int 0\, dV$

$w = 0$

$\int_i^f dw = -\int_{V_i}^{V_f} P_{ext}\, dV = -P_{ext}\Delta V$



$dW = -P_{ext}\, dV$

$dw = -P\, dV$

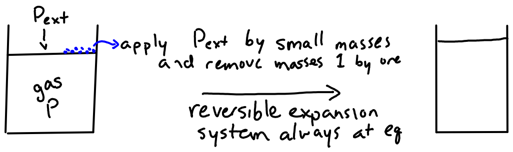
Lecture 04/06

Monday, April 06, 2009
9:49 AM

Lecture 0406

Audio recording started: 10:01 AM Monday, April 06, 2009

- PV work
    - Free expansion
    - Reversible expansion -



- Always in equilibrium
- Impossible to actually achieve since time would have to be taken to infinity
- Useful to consider as a limit

$$W = -\int_i^f P_{ext}\,dV$$

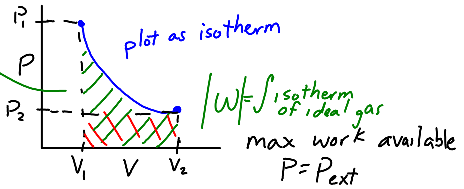
$$W_{rev} = -\int_i^f P\,dV$$

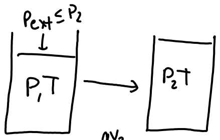
- 2 cases:
    1. Ideal gas: Isothermal reversible expansion

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

$$W_{rev} = -\int_i^f \frac{nRT}{V}\,dV$$ in isothermal, temp is constant

$$= -nRT\int_i^f \frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$$





$$W_{irrev} = -\int_{V_1}^{V_2} P_2\,dV$$
$$= -P_2(V_2 - V_1)$$

$$|W| = -P_2(V_2 - V_1)$$

Reversible gives rise to maximum amount of work.
Irreversible gives less work than reversible

2. Reversible Adiabatic expansion of real gas (cover this next time)

- Relationship between internal energy and heat

$$\Delta u \Rightarrow q$$

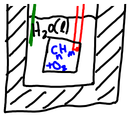
1st law: $dU = đq + đw$

- +consider system that only expansion work can be done
+consider constant V process

$$\longrightarrow dU = đq - P_{ext}\,dV \quad (dV = 0)$$
$$dU_v = đq_v$$
$$\Delta U_v = q_v$$

this can be measured to get U by constant V calorimetry

Calorimetry



constant V

$$\Delta T = \frac{q}{C}$$

C ← heat capacity

$$q = c\Delta T$$

$$q_v = \Delta U_v$$
$$q_v = c\Delta T$$
$$\Delta U_v = c\Delta T$$

how to determine c?

run rxn in container that we know ΔU for

$$\frac{\Delta U_{known}}{\Delta T_{known}} = c$$

or run constant current over time & measure heat transfer

$$\frac{W_{elect}}{\Delta T_{elect}} = c$$

$$\Delta H_p = q_p$$

$\overset{\uparrow}{?}$enthalpy

$$H \equiv U + PV$$

Enthalpy is a state function (only depends on initial and final state) since ΔU and ΔPV are also state functions

$$\Delta H = \Delta U + \Delta PV$$

1) Only expansion work possible
2) Constant pressure process
3) $P_{sys}=P_{ext}$

$$dH_p = dU + d(PV)$$
$$dH_p = dU + PdV + VdP$$
$$= đq + đw + PdV + VdP$$

$đw$: $-P_{ext}dV = -PdV$

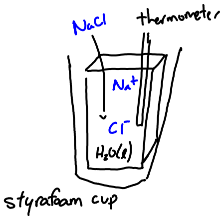
constant $P \rightarrow dVP=0$

$$dH_p = đq - PdV + PdV + VdP = dq_p + dV\cancel{P}$$
$$dH_p = dq_P$$

take integral

$$\Delta H_p = q_P$$

Constant P calorimeter



$$q_P = c\Delta T = \Delta H_p$$

$\Delta H<0$ exothermic $q_p<0$ heat loss by system
$\Delta H>0$ endothermic $q_p>0$ heat absorbed by system

$$H = U + PV, \quad \Delta H \neq \Delta U$$
$$\Delta H = \Delta U + \Delta(PV)$$

ΔH differs ΔU only when ΔPV is considerable

for condensed phases $\Delta(PV) << DU$ so $\Delta H \approx \Delta U$ (no gasses involved)

if gasses are involved ΔPV can be significant

↳ $\Delta PV \cong \Delta(nRT) \overset{generally}{\approx} RT(\Delta n)$

$PV = nRT$ when $\Delta n \neq 0$ then ΔPV is not negligable compared to ΔU

$$\Delta H = \Delta U + \Delta(nRT)$$

$$\Delta H = \Delta U + \Delta(nRT)$$
$$\Delta H \cong \Delta U + RT\Delta n$$

- Heat Capacity

ΔU and ΔH changes with T

$$q = c\Delta T$$
$$\text{đ}q = c\,dT$$

- Heat capacities are not general, every system/material has its own heat capacity
- Heat capacities depend on state of system (temperature, pressure, volume)
  - C(T,P)
  - C(T,V)
- Heat capacities depend on nature of process taking place
  - C corresponding to constant volume process is not same as c for constant pressure process

$$C_v \neq C_p$$

At constant volume:

$$\text{đ}q_v = dU_v = c_v\,dT$$

Definition of constant volume heat capacity:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

At constant pressure:

$$\text{đ}q_p = dH_p = c_P\,dT$$

Definition of constant pressure heat capacity:

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

$$C_P \neq C_V$$

generally $C_P > C_V$

Lecture 04/08

Wednesday, April 08, 2009
10:01 AM

- Finishing Chapter 2

1) Closed system
2) constant composition = no chem transformation

$$\left\{ \begin{array}{l} U(T,V) \text{ or } U(T,P) \text{ or} \ldots \\ H(T,V) \text{ or } U(T,P) \text{ or} \ldots \end{array} \right.$$

or

$T(H,P)$ Need 2 independent variables

$$\Delta U = \int_{\#1}^{\#2} dU = \int_{V_1}^{V_2}\left(\frac{\partial U}{\partial V}\right)_T dV + \int_{T_1}^{T_2}\left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV + \left(\frac{\partial H}{\partial T}\right)_V dT$$

U and H are state functions,

$$\begin{tikzcd} V_1T_1 \arrow[rr] \arrow[dr, "dV=0"'] & & V_2T_2 \\ & V_1T_2 \arrow[ur, "dT=0"'] & \end{tikzcd}$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

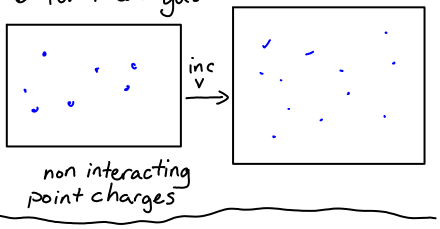
$$\downarrow \qquad \downarrow$$

$$dU = \pi_T \, dV + C_V dT$$

heat capacity const. V

ideal gas: $dU = C_V dT$

$\pi_T = 0$ for ideal gas



$$\overset{(T,P)}{dH} = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\downarrow \qquad \downarrow$$

$$dH = -\mu_{JT} C_P + C_P dT$$

joule thompson coeffient

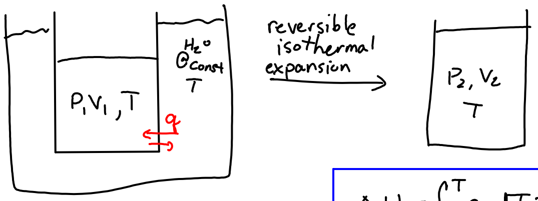
cons. P heat capacity

ideal gas: $dH = C_P dT$

$-\mu_{JT} = 0$ for ideal gas

$$\mu_J = \left(\frac{\partial T}{\partial P}\right)_H$$

Isothermal reversible expansion of an ideal gas:



before: $dW \overset{rev}{=} -PdV \overset{ideal\ gas}{=} -\frac{nRT}{V} dV$

$$W = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

$$\boxed{\begin{array}{l} \Delta U = \int_T^T C_V dT = 0 \\ \Delta H = \int_T^T C_P dT = 0 \end{array}}$$

Heat involved in process?

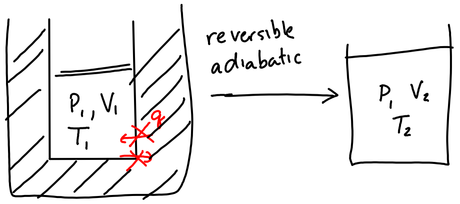
$$\Delta U = q + w$$

$$0 = q - nRT \ln \frac{V_2}{V_1}$$

$$q = nRT\ln\frac{V_2}{V_1}$$

$$\Delta H = \underset{0}{\Delta U} + \Delta(PV)$$
$$\qquad\qquad \underset{0}{\Delta(nRT)}$$
$$\Delta H = 0$$

Reversible adiabatic expansion of an ideal gas



Given variables such as V1,T1, V2 or V1, T1, P2

$V_1 T_1$ $\qquad$ V_2

$\Delta U = w$, b/c $q=0$ for adiabatic

$$dU = dw = -P_{ext}\,dV = -P\,dV$$

cannot do $\frac{nRT\,dV}{V}$ $\int$ integrate b/c don't know how temp changes w/ volume

$$dU = c_v\,dT$$

$$-P\,dV = c_v\,dT$$
$$-\frac{nRT\,dV}{V} = c_v\,dT$$
$$-\frac{nR\,dV}{V} = \frac{c_v\,dT}{T}$$

integrate

$$-nR\ln\frac{V_2}{V_1} = c_v\ln\frac{T_2}{T_1}$$

$C_{V(\text{ideal gas})} = \text{constant}$
$C_{P(\text{ideal gas})} = \text{constant}$
$\underbrace{C_{P,m} - C_{V,m}}_{\text{molar heat capacity}} = R$

exponentiate both sides

$$\left(\frac{T_2}{T_1}\right)^{c_v} = \left(\frac{V_1}{V_2}\right)^{nR}$$

take both sides to power $1/c_v$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/c_v} = \left(\frac{V_1}{V_2}\right)^{\frac{c_{p,m}-c_{v,m}}{c_{v,m}}}$$

$$\gamma \equiv \frac{c_{p,m}}{c_{v,m}} = \frac{c_p}{c_v}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\Delta U = C_v\Delta T \qquad \Delta U = \int dU = \int_{T_1}^{T_2} C_v\,dT$$

$$\Delta U = C_v T_1\left(\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right)$$

$$\Delta H = C_p T_1\left(\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right)$$

$$W = \underset{0}{q} + u$$

$$w = \Delta U = C_v T_1\left(\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right)$$

$$\downarrow$$
$$0$$

$$w = \Delta U = C_v T_1\left(\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right)$$

suppose given other variables

$$\boxed{\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1}\right)^{-\gamma}$$

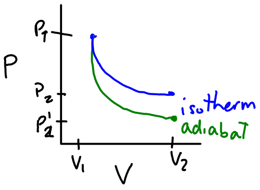
$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$$

$$PV^{\gamma} = \text{constant}$$

$$P = \frac{\text{constant}}{V^{\gamma}} \rightarrow \text{adiabat}$$

Isotherm: connection between pressure and volume where T is constant

$$P = \frac{\text{const}}{V} \quad \text{isotherm}$$



Adiabat falls off faster than isotherm

$$C_P > C_V$$

$$\frac{C_P}{C_V} = \gamma > 1$$

Notes 04/13

Monday, April 13, 2009
10:02 AM

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T \overset{\text{show this}}{\overset{?}{=}} 0$$ for ideal gas

$$\hookrightarrow dU = T\Delta S - PdV$$

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\overset{=0}{\left(\frac{\partial V}{\partial V}\right)_T}$$

maxwell relation

$$dA = -SdT - PdV$$

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

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

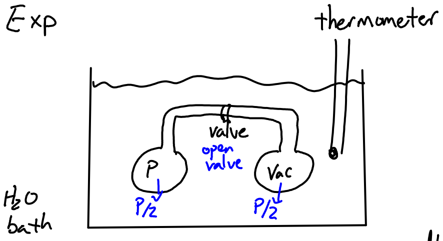
$$\Pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial\left(\frac{nRT}{V}\right)}{\partial T}\right)_V = \frac{nR}{V}$$

$$\Pi_T = \frac{nRT}{V} - P = 0$$

How to measure Π_T for gas

Joule's Exp



$W = 0$

$-P_{ext} = 0$ so $w = 0$

$$dU = đq = \Pi_T dV + C_V dT$$

$$\hookrightarrow (C_{APP} - C_{\text{ideal gas}})\,dT = \Pi_T dV + C_V dT$$

$$\underbrace{(C_{APP} - C_{\text{ideal gas}} - C_V)}\,dT = \Pi_T dV$$

$$C\Delta T = \Pi_T \Delta V$$

$$\Delta T = 0$$

$$\Pi_T = 0$$

Indicated internal pressure of gas is relatively small quanity
Not very sensitive experiment because specific heat capacity of water is very large

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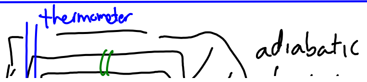
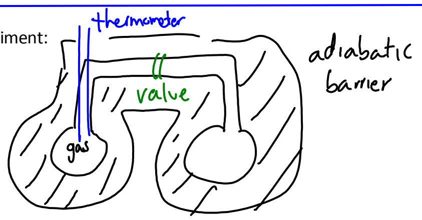
More sensitive experiment:



$w = 0$

More sensitive experiment:



This experiment shows U_J tends to be very small for real gases and 0 for ideal gases

$$w = 0$$
$$q = 0$$
$$dU = 0 = \pi_T dV + C_V dT$$
$$\left(\frac{\partial T}{\partial V}\right)_U = \mu_J \text{ (Joule coefficient)}$$
$$\pi_T dV_u = -C_V dT_u$$
$$\pi_T = -C_V \left(\frac{\partial T}{\partial V}\right)_u$$

$dU = \pi_T dV + C_V dT$ convert to P & T as indep. variables

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

$$\left(\frac{\partial U}{\partial P}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V \left(\frac{\partial T}{\partial T}\right)_P = \pi_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

isobaric coefficent of thermal expansion (β)

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\beta \pi_T V + C_V$$

now other derivative

$$\left(\frac{\partial U}{\partial P}\right)_T = \pi_T \left(\frac{\partial V}{\partial T}\right)_T + C_V \overset{0}{\left(\frac{\partial T}{\partial P}\right)_T}$$

isothermal compresability (K)

$$K \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

derivative always neg, so $-\frac{1}{V}$ used

$$= -\pi_T V K$$

So...

$$dU = -\pi_T V K dP + (\beta \pi_T V + C_V) dT$$

Enthalpy

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\left(\frac{\partial H}{\partial T}\right)_P \equiv C_P$$

$\left(\frac{\partial H}{\partial P}\right)_T$ don't know measure enthalpy, but can measure P, T

oiler chain relation

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

mult both sides by inverter

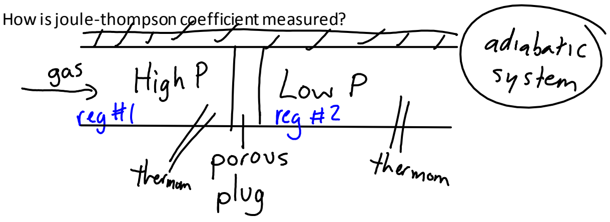
$$\left(\frac{\partial H}{\partial P}\right)_T = -\underbrace{\left(\frac{\partial T}{\partial P}\right)_H}_{\mu_{JT}} \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{C_P}$$

hold enthalpy const. in exp?

μ_{JT} (joule-thompson coefficient)

$$= -\mu_{JT} C_P$$

How is joule-thompson coefficient measured?

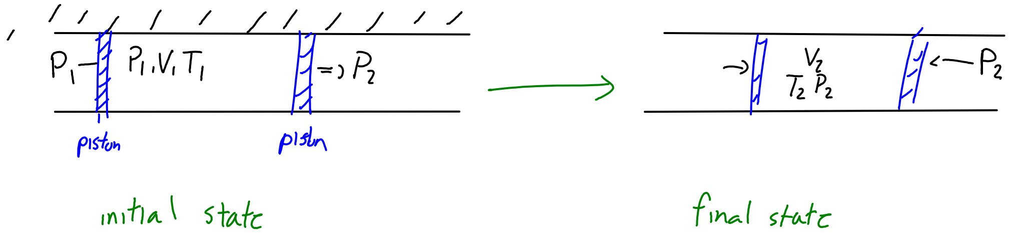


exp reaches steady state

conserves enthalpy of container

$$\left(\frac{T_2 - T_1}{P_2 - P_1}\right)_H \equiv \mu_{JT}$$

How do we know enthalpy (H) is constant? Consider analogous system:



We know enthalpy doesn't change by making use of definition of enthalpy:

$$H_1 = U_1 + P_1 V_1$$

$$H_2 = U_2 + P_2 V_2$$

$$\Delta H = \Delta U + P_2 V_2 - P_1 V_1$$

$$\Delta U = \underset{\text{adiabatic}}{\underset{0}{q}} + w = -P_1(0 - V_1) - P_2(V_2 - 0)$$

$$\Delta U = P_1 V_1 - P_2 V_2$$

$$\Delta H = P_1 V_1 - P_2 V_2 + P_2 V_2 - P_1 V_1 = 0$$

so...

$$\left(\frac{T_2 - T_1}{P_2 - P_1}\right)_H = \mu_{JT}$$

Show why $U_{JT} = 0$ for ideal gases and small number for real gases?

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu_{JT} C_P$$

plug in def of enthalpy $(H = U + PV)$

$$\underbrace{\left(\frac{\partial U}{\partial P}\right)_T}_{-\pi_T K V} + \underbrace{\left(\frac{\partial (PV)}{\partial P}\right)_T}_{V + \left(\frac{\partial V}{\partial P}\right)_T P}$$

$$-\pi_T K V + V - VPK$$

$$-\mu_{JT} C_P = -\pi_T K V + (V)(1 - PK)$$

$$\mu_{JT} = \frac{V}{C_P}\underbrace{\left((\pi_T + P)K - 1\right)}_{\text{evaluate for ideal}}$$

$$\rightarrow \frac{P}{P} - 1 = 0$$

$$\pi_T = 0$$

$$K = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{-1}{V}\left(\frac{\partial \frac{nRT}{P}}{\partial P}\right)_T$$

$$= \frac{1}{P}$$

Lecture 04/15

Wednesday, April 15, 2009
10:04 AM

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu_{JT} C_P = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$\left(\frac{\partial U}{\partial P}\right)_T = \underset{\underset{\textstyle \pi_T}{\shortparallel}}{\left(\frac{\partial U}{\partial V}\right)_T} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\pi_T(-VK) = -\pi_T VK$$

$$\left(\frac{\partial (PV)}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T + V = V(1-PK)$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$\pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$= \frac{T\beta}{K} - P$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}\left([\pi_T + P]K - 1\right) = \frac{V}{C_P}\Big[\ldots$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial P}\right)_T = V(1-\beta T)$$

$$\mu_{JT} = \frac{V}{C_P}\left(\beta T - 1\right)$$

$$\beta \equiv \frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right) = \frac{nR}{PV} = \frac{1}{T} \quad \text{for ideal gas}$$

$$\mu_{JT} = \frac{V}{c_P}\left(\frac{1}{T}\cdot T - 1\right) = 0 \quad \longleftarrow \text{for ideal gas}$$

μ_{JT} for van der walls

$$\mu_{JT} = \frac{V}{C_p}(\beta T - 1)$$

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \text{... see above}$$

van der walls: $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$

algebra is tedius for $\left(\frac{\partial V}{\partial T}\right)_P$ so.... $\left(\frac{\partial P}{\partial V}\right)_T$ or $\left(\frac{\partial P}{\partial T}\right)_V$ are easier by Oiler chain rule

---

Real gases $\mu_{JT} \neq 0$

$\underline{\text{at STP}}$

$\mu_{JT}(CO_2) = 1.11\ K/atm$

if μ_{JT} is positive, then T decreases by $\left(\frac{\partial T}{\partial P}\right)_H$

$\mu_{JT}(N_2) = 0.25\ K/atm$

$\mu_{JT}(H_2) = -0.06\ K/atm$

As gas expands, species become further apart. If species have attractive force, they must overcome this energy by kinetic energy via temperature to move further apart.
There are also repulsive interactions, so if repulsive forces are predominant, then there is decrease in potential energy and goes to kinetic energy which increases the temperature.

Real gases differ from ideal gasses by that of their intermolecular interactions

---

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV + \left(\frac{\partial H}{\partial T}\right)_V dT$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_T$$

$$= \frac{-\mu_{JT} C_p}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\mu_{JT} C_p}{KV}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu_{JT} C_p$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial V}{\partial P}\right) = -KV$$

$$dH = -\mu_{JT} C_p dP + C_p dT$$

$$\left(\frac{\partial H}{\partial T}\right)_V = -\mu_{JT} C_p \left(\frac{\partial P}{\partial T}\right)_V + C_p \overset{1}{\overset{\shortparallel}{\left(\frac{\partial T}{\partial T}\right)_V}}$$

$$= -\mu_{JT} C_p \frac{\beta}{K} + C_p$$

$$= C_p\left(1 - \mu_{JT}\frac{\beta}{K}\right)$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

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

Connection C_p & C_v

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

$$\left(\frac{\partial U}{\partial T}\right)_P = \pi_T \beta V + \underset{\overset{\shortparallel}{C_V}}{\left(\frac{\partial U}{\partial T}\right)_V}$$

$$C_P - C_V = \beta \pi_T V + \left(\frac{\partial (PV)}{\partial T}\right)_P$$

$$= \beta \pi_T V + PV\beta \qquad \left(\frac{\partial (PV)}{\partial T}\right)_P = PV\beta$$

$$C_P - C_V = \beta V(\pi_T + P)$$

$$C_{pm} - C_{vm} = \beta V_m(\pi_T + P)$$

$$\pi_T = \frac{\beta T}{K} - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$C_{pm} - C_{vm} = \frac{\beta^2 V_m T}{K}$$

for an ideal gas sample $C_{pm} - C_{vm}$

need to evaluate β, K, V_m

$$\beta_{i.g.} = \frac{1}{T}$$

$$K_{i.g.} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial \frac{nRT}{P}}{\partial P}\right)_T = \frac{1}{PV \cdot P_V} \cdot nRT = \frac{1}{P}$$

$$C_{pm} - C_{vm} = \frac{\frac{1}{T^2} \cdot TV_m}{\frac{1}{P}} = \frac{PV_m}{T} = R$$

Constant pressure heat capacity is higher than constant volume heat capacity because constant pressure heat capacity can do work while constant volume heat capacity goes to kinetic energy.

For a given increment of heat, the temperature goes up more for a constant pressure process than a constant volume process.

In general, there is a possibility that the heat that goes into the system can increase the potential energy: That's where π_T comes from.

Typically beta and V_m are much smaller for condensed phase systems (solid or liquid) are much smaller than for gases

$$\beta_{s,l} \ll \beta_g$$

$$V_{m(s,l)} \ll V_{m,g}$$

Summary

$$\mu_{JT} = \left(\frac{\partial T}{\partial V}\right)_U$$

$$(\partial U) = \pi = T(\partial P) - P = RT - P = -\mu\ C$$

$$\left(\frac{\partial U}{\partial V}\right)_T \equiv \pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{\beta}{K}T - P = -\mu_{JT}C_V$$

$$\left(\frac{\partial U}{\partial T}\right)_V \equiv C_V$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -\pi_T K V = (KP - \beta T)V$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \beta \pi_T V + C_V = \beta V\left(\frac{\beta}{K}T - P\right) + C_V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu_{JT} C_P = V\left(1 - [\pi_T + P]K\right) = V(1 - \beta T)$$

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$\mu_{JT} = \frac{V}{C_P}\left(\beta T - 1\right)$$

$$\left(\frac{\partial H}{\partial T}\right)_P \equiv C_P$$

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{\mu_{JT} C_P}{KV} = \frac{(\beta T - 1)}{K}$$

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P\left(1 - \mu_{JT}\frac{\beta}{K}\right) = C_P - \frac{\beta V}{K}(\beta T - 1)$$

$$C_{P,m} - C_{V,m} = \frac{\beta^2 T V_m}{K}$$

$$\int_{\#1}^{\#2} dU = \Delta U = \int_{V_1}^{V_2} \pi_T \, dV + \int_{T_1}^{T_2} C_V \, dT$$

Notes 04/20

Monday, April 20, 2009
10:01 AM

- Chapter 4

$\Delta H^\ominus$

$$A-B(g) \longrightarrow A(g) + B(g)$$

$$HO-H(g) \longrightarrow OH(g) + H(g) \qquad \Delta H^\circ \equiv D_{O-H}$$

$$\left.\begin{array}{ll} CH_4(g) \longrightarrow CH_3(g) + H(g) & D_{CH} \\ CH_3CH_2CH_3(g) \longrightarrow CH_3CH_2CH_2 + H(g) & D_{C-H} \end{array}\right\} \text{similar } D_{C-H}$$

Pg 69 - table 4.3 - tabulated of mean bond disassociation energies.

$$\begin{tikzcd} H_2(g) \arrow[d, "D_{H-H}"] & + \tfrac{1}{2} O_2(g) \arrow[d, "D_{O=O}"] & \arrow[r] & H_2O(g) \\ 2H(g) & O(g) & \arrow[ur, "-2D_{O-H}"] & \end{tikzcd}$$

$$\Delta H_{rxn} = D_{O-H} + D_{O=O} - 2D_{O-H}$$

Enthalpies of atomization

$$C_6H_6(l) \longrightarrow 6C(g) + 6H(g) \qquad \Delta H_a$$

$$Fe(s) \longrightarrow Fe(g) \qquad \Delta H_a$$

Example

$$\begin{tikzcd} C(s,gr) \arrow[d, "\Delta H_1"'] & + 2H_2(g) \arrow[d, "\Delta H_2"'] & \arrow[r] & CH_4(g) \\ C(g) & + 4H(g) & \arrow[ur, "\Delta H_3"'] & \end{tikzcd}$$

find ΔH_{rxn}

$$\Delta H_1 = \Delta H_a(C(s,gr))$$

$$\Delta H_2 = 2D_{H-H}$$

$$\Delta H_3 = -4D_{C-H}$$

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

How the enthalpy of reaction depends on temperature and pressure?

Temperature:

$$\text{Reactants} \xrightarrow{\Delta H_T^\circ} \text{Products} \qquad T, 1\,\text{bar} \quad \cancel{=} 298K$$

$$\Delta H_T^\circ \neq \sum_J^{\text{all species}} \nu_J \Delta H^\circ_{f,298K}(J)$$

Go from reactants to products by any path

$$\begin{tikzcd} T & \text{Reactants} \arrow[r] \arrow[d, "\Delta H_1"] & \text{Product} & \\ \cancel{T}=298K & \text{Reactants} \arrow[r, "\Delta H_2"] & \text{Products} \arrow[u, "\Delta H_3"'] & \cancel{T} \end{tikzcd}$$

$$\Delta H_2 = \Delta H^\circ_{\cancel{T}} = \sum_J^{\text{all species}} \nu_J \Delta H_{f,\cancel{T}}(J)$$

$$\Delta H_1 = q_1 = \int_T^{\cancel{T}} C_{p(\text{reactants})}\, dT = -\int_{\cancel{T}}^T C_{p(\text{react})}\, dT$$

$$\Delta H_3 = q_3 = \int_{\cancel{T}}^T C_{p(\text{products})}\, dT$$

$$\Delta H_3 = q_3 = \int_{T^{\ominus}}^{T} C_p(\text{products})\,dT$$

$$\Delta H_1 + \Delta H_3 = \int_{T^{\ominus}}^{T} \underbrace{\left[C_p(\text{products}) - C_p(\text{react})\right)}_{\Delta C_p} dT$$

$$\Delta H_T^{o} = \Delta H_{T^{\ominus}}^{o} + \int_{T^{\ominus}}^{T} \Delta C_p\, dT$$

$$\Delta C_p \equiv \sum_{J}^{\text{all Species}} \nu_J C_m(J)$$

$$C_{p,m}(J,T) = \underset{\substack{\uparrow \\ \text{constant}}}{a_J} + \underset{\substack{\uparrow \\ \text{linear}}}{b_J T} + \underset{\substack{\uparrow \\ \text{porpotional to } \frac{1}{T^2}}}{\frac{C_J}{T_2}}$$

so $C_{p,m}$ may have dependence on T

Determine ΔH_{rxn}

$$\begin{tikzcd}
320K & 6C(s,gr) + 3H_2(g) \arrow[r] \arrow[d, "\Delta H_1"'] & C_6H_6(l) \\
298K & 6C(s,gr) + 3H_2(g) \arrow[r, "\Delta H_2"] & C_6H_6 \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

$T = 320K$, 1 bar

back of text

$$\Delta H^{o}_{rxn}(320K) = \Delta H^{\ominus}_{f,298K}(C_6H_6\,l) + \int_{298.15}^{320} \left[1\,\text{mol}\; C_{p,m}(C_6H_6(l)) - 6\,C_m(C(s,gr)) - 3\,C_{p,m}\,H_2(g)\right] dT$$

How enthalpy relates to pressure:

$$\begin{tikzcd}
P & \nu_A A + \nu_B B \arrow[r, "\Delta H_{rxn}"] \arrow[d, "\Delta H_1"] & \nu_C C + \nu_D D & \\
1\text{ bar} & \nu_A A + \nu_B B \arrow[r, "\Delta H_2"] & \nu_C C + \nu_D D \arrow[u, "\Delta H_3"'] & 1\text{ bar}
\end{tikzcd}$$

$P \neq P^{\ominus} = 1\,\text{bar}$

$$dH = V(1-\underset{\substack{\uparrow \\ \left(\frac{\partial H}{\partial P}\right)_T}}{\beta} T)\,dP + \cancel{C_p dT}^{\,0} \;(\text{no temp change})$$

$$\Delta H_1 = \int_{P}^{1\text{bar}} \left[\nu_A V_{m,A}(1-\beta_A T) + \nu_B V_{m,B}(1-\beta_B T)\right] dP$$

$$\Delta H_3 = \int_{1\text{bar}}^{P} \left[\nu_C V_{m,C}(1-\beta_C T) + \nu_D V_{m,D}(1-\beta_D T)\right] dP$$

$$\Delta H_{(P)} = \Delta H^{\ominus} + \int_{1\text{bar}}^{P} \Delta(V(1-\beta T)]\,dP$$

$$\Delta(V(1-\beta T) = \left[\nu_C V_{m,C}(1-\beta_C T) + \nu_D V_{m,D}(1-\beta_D T) - \nu_A V_{m,A}(1-\beta_A T) - \nu_B V_{m,B}(1-\beta_B T)\right]$$

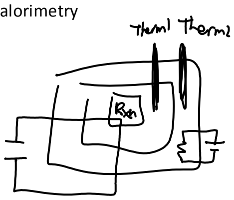
$$0 = \sum_{J}^{\text{all species}} \nu_J J$$

$$\Delta H(P) = \Delta H^{o} + \int_{1\text{bar}}^{P} \Delta[(V(1-\beta T)]\,dP$$

$$\Delta[V(1-\beta T)] \equiv \sum_{J}^{\text{all species}} \nu_J V_{m,J}(1-\beta_J T)$$

Temperature can have a significant effect on enthalpies since heat capacity is involved. The effects of pressure on enthalpy of reaction tends not to be very large.

Bomb calorimetry



$w=0 \quad \Delta V=0$

$q=0$

$\Delta U=0=\Delta U_{rxn}+C_{calorimeter}\Delta T+C_{P,H_2O}\Delta T$

$\Delta U_{rxn}\cong\Delta U^\circ$

$\Delta H^\circ=\Delta U^\circ+\Delta(PV)$

Lecture 04/22

Wednesday, April 22, 2009
9:57 AM

Finishing Chapter 4

$$\Delta H = \Delta U + \Delta(PV)$$

$V_m(s), V_m(l) << V_m(g)$ @STP

$$\Delta(PV) = P_f V_f - P_i V_i$$

* don't need to consider condensed phase (s) + (l)

$$\Delta(PV) \cong \Delta(nRT)$$

$$= RT\Delta n$$

^ change # moles of gaseous species in rxn

Ex: $CaCO_3(s) \longrightarrow CaO(s) + O_2(g)$

$\Delta n = 1$ (gas species)

$$\Delta H = \Delta U + RT$$

$$\Delta H \cong \Delta U + RT\Delta n$$

Ex $C_6H_6(l) + \frac{15}{2}O_2(s) \xrightarrow{\Delta H_{rxn}} 6CO_2(g) + 3H_2O(l)$

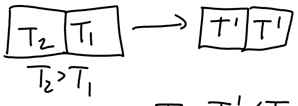
$$\Delta H^\circ_{rxn} = 6\Delta H^\circ_f(CO_2(g)) + 3\Delta H_2O^\circ_f(l) - \Delta H^\circ_f(C_6H_6(l))$$

Exam1 covers chapter 1-4
Best way to study for exam: do problems by yourself

Chapter 5

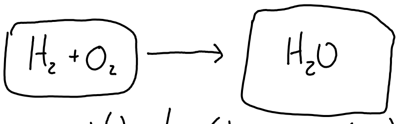
Spontaneity = direction of change

- Entropy, 2nd law of thermodynamics



$T_2 > T_1$

$T_1 < T' < T_2$



$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l,g)$

^ depends on temperature

$\Delta H < 0$ exothermic

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H << 0$

$C_6H_6(s) \longrightarrow C_6H_6(l)$ $\Delta H > 0$

$C_6H_6(s) \longrightarrow C_6H_6(\ell) \quad \Delta H > 0$

S- entropy

$\Delta S_{universe} > 0$ for spontaneous process

< 0 won't occur

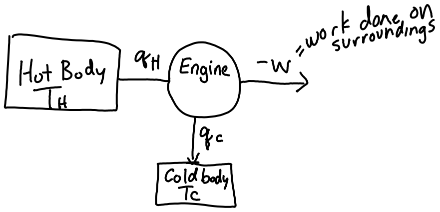
$= 0$ equilibrium

microscopically defined
but we are only concerned
macriscopic view

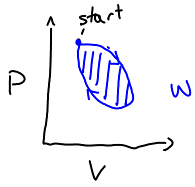
$S = k_B \ln \Omega$ <- # of microstates, measure degree of randomness

$\hat{\iota}\ \dfrac{R}{N_A\,(\text{avagadro's \#})}$

Heat Engine

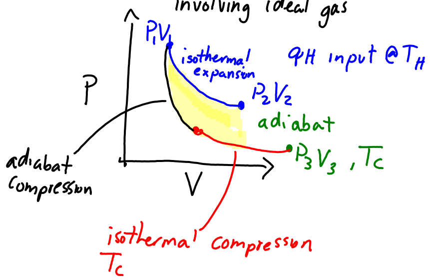


$|w|_{max} = ?$



w = area under curve

Carnot cycle
involving ideal gas



W = area under curve

To maximize work, each step must be reversible. If each step takes place reversibly then work is maximized by engine.

Ex Carnot Cycle (ideal gas)

step 1 isothermal expansion

$$W_1 = -nRT_H \ln\left(\frac{V_2}{V_1}\right) = -q_H$$

$$\Delta U_1 = 0$$

step 2 adiabatic expansion

$$q_2 = 0$$

$$w_2 = \Delta U_2 = \int_{T_H}^{T_c} C_v\, dT$$

step 3 isothermal compression

$$w_3 = -nRT_c \ln\left(\frac{V_4}{V_3}\right) = -q_c$$

step 4 adiabatic compression

$q_4 = 0$

$w_4 = \Delta U_4 = \int_{T_C}^{T_H} C_V \, dT$

$q = q_H + q_C$

$w_{TOTAL} = n\left[-RT_H \ln\left(\frac{V_2}{V_1}\right) - RT_C \ln\left(\frac{V_4}{V_3}\right)\right]$ $(^* w_2 + w_4 = 0)$

adiabatic expansion in general

$\left(\frac{V_i}{V_f}\right)^{\gamma-1} = \frac{T_f}{T_i}$ $\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^{\frac{1}{\gamma-1}}$ $\gamma = \frac{C_P}{C_V}$

adiabatic expansion

$\frac{V_2}{V_3} = \left(\frac{T_C}{T_H}\right)^{\frac{1}{\gamma-1}}$

adiabatic compression

$\frac{V_4}{V_1} = \left(\frac{T_H}{T_C}\right)^{1/\gamma-1}$

$$\left.\right\} \frac{V_2}{V_3} = \frac{V_1}{V_4} \rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$w_{TOTAL} = -nR(T_H - T_C)\ln\frac{V_2}{V_1}$$

100% efficient $w = q_H = nRT_H \ln\left(\frac{V_2}{V_1}\right)$

efficency: $\frac{|w_{TOTAL}|}{q_H} = \frac{nR(T_H - T_C)\ln\left(\frac{V_2}{V_1}\right)}{nRT_H \ln\left(\frac{V_2}{V_1}\right)} = \boxed{\frac{T_H - T_C}{T_H}}$ always < 1

Notes 04/24

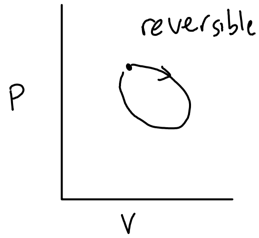
Tuesday, May 05, 2009
12:42 AM

$$\varepsilon = \frac{|w|}{q_H} = \frac{T_H - T_C}{T_H}$$

$$\oint \frac{dq}{T} = \frac{q_H}{T_H} + \frac{q_C}{T_C} = \frac{nR\cancel{T_H}\ln\frac{V_2}{V_1}}{\cancel{T_H}} + \frac{nR\cancel{T_c}\ln\frac{V_4}{V_3}}{\cancel{T_c}} = 0$$

$\oint dS = 0$ $\quad dS = \frac{dq_{rev}}{T} = 0$ for carnol-cycle

$$\varepsilon = 1 + \frac{q_c}{q_H} = \frac{T_H - T_c}{T_H} \Rightarrow \frac{q_c}{q_H} = \frac{-T_C}{T_H}$$



-fill area w/ infinitely small carnol cycles

$$\oint \frac{dq_{rev}}{T} = 0$$

Entropy

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T}$$

Principple of Clasius

Isolated system -> no mechanical contact
No thermal contact
No material transfer

$(dS)_{U,V} \geq 0$ spontaneous process

Inequality of Clasius

Closed system, const. comp, only PV work available

$$\begin{aligned} dU &= dq + dW \\ &= dq_{rev} - PdV \\ &= TdS - PdV \end{aligned}$$

$TdS = dq + (P - P_{ext})dV$ $\qquad (P - P_{ext})dV > 0$ spontaneous

$TdS > dq$ spontaneous

$$dS_{surr} = -\frac{dq}{T}$$

$$dS - \frac{dq}{T} \geq 0$$

$$dS + dS_{surr} \geq 0$$

$$\boxed{dU = TdS - PdV}$$

A) Heating at constant V

ΔS?

$$dU = \pi_{\cancel{T}}\, dV + C_v dT = Tds - \cancel{Pd}V$$

$$\Delta S = \int_{T_1}^{t_2} \frac{C_v dT}{T}$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T}}$$

B) Constant P

$$dH = -\mu_{JT} C_p dP + c_p dT = dU + PdV + VdP = TdS - \cancel{P}dV + \cancel{Pd}V + VdP$$

$$= TdS + VdP$$

$$-\mu_{JT} \cancel{C_p} dP + c_p dT = TdS + V\cancel{dP}$$

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

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

c) Constant T

$$TdS - PdV = \pi_T dV + C_v dT$$

$$Tds = \pi_T\, dV + PdV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\pi_T + P}{T} = \frac{\beta}{K}$$

Notes 04/27

Tuesday, May 05, 2009
12:53 AM

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$dU = \pi_T dV + C_V \overset{0}{\overset{\shortparallel}{dT}} = TdS - PdV$$

$$(\pi_T + P)dV = TdS$$

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

$$\partial H = V(1-\beta T)\,dP + C_P dT$$

$$= TdS + VdP$$

$$[V(1-\beta T) - V]\,dP = TdS_T$$

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

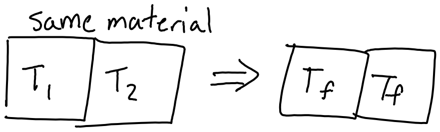
$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$= \frac{\beta}{K} dV + \frac{C_V}{T} dT$$

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

$$= -\beta V dP + \frac{C_P}{T} dT$$

Heat transfer @ constant P



$$dS = \frac{C_P dT}{T} - \beta V \overset{0}{\overset{\shortparallel}{dP}}$$

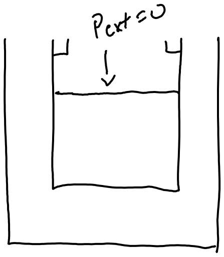
$$dS = \frac{C_P dT}{T} \Rightarrow \int_{\#1}^{\#2} dS = \int_{T_1}^{T_2} \frac{C_{P1}}{T_1} dT + \int_{T_2}^{T_f} \frac{C_{P2}}{T_2} dT$$

$$\Delta S = C_P\left[\ln\frac{T_f}{T_1} + \ln\frac{T_f}{T_2}\right]$$

$$q_P = \Delta H = 0$$

$$\Delta H_1 + \Delta H_2 = C_P(T_f - T_1) + C_P(T_f - T_2) = 0$$

$$\Delta S = c_p \ln \frac{(T_1+T_2)^2}{4T_1T_2} > 0$$



$$đq = 0$$
$$đw = 0$$

$$dU = 0 = TdS - PdV$$
$$TdS = PdV$$
$$\int_i^f dS = \int_{V_i}^{V_f} \frac{P}{T} dV > 0$$
$$= \int_{V_i}^{V_f} \frac{nR}{V} dV \text{ for i.g.}$$

$H_2O(s) \longrightarrow H_2O(l)$ 1 bar const P, T 273.15K

$$TdS = đq_{rev,P} = dH$$
$$\int dS = \int \frac{dH}{T}$$
$$\Delta S = \frac{\Delta H}{T} \text{ @ phase changes}$$
$$\Delta H = \Delta H^\circ_{f\,298K}(H_2O_{(l)}) - \Delta H^\circ_{f,298K}(H_2O_{(s)}) + \int_{298}^{273} (\Delta C_{p,m})\, dT$$

3rd Law of Thermodynamics

$$S = k_B \ln \Omega$$

$$S^\circ_T(A)$$
$$S^\circ_{T=0K}(A) = 0$$

$A(g), T,$ 1bar $S^\circ_T(A_{(g)})$

$$\underset{\text{1bar}}{\underset{T=0K}{A(s)}} \xrightarrow{S_1} \underset{\text{bar}}{\underset{T_{fus}}{A(s)}} \xrightarrow{S_2} \underset{\text{1bar}}{\underset{T_{fus}}{A(l)}} \xrightarrow{S_3} \underset{\text{1bar}}{\underset{T_B}{A(l)}} \xrightarrow{S_4} \underset{\text{1bar}}{\underset{T_b}{A(g)}} \xrightarrow{S_5} \underset{\text{1bar}}{\underset{T}{A(g)}}$$

$$\Delta S_1 = \int_{0K}^{T_{fus}} \frac{C_p(s)}{T} dT, \quad \Delta S_2 = \frac{\Delta H_{fus}}{T_{fus}}, \quad \Delta S_3 = \int_{T_{fus}}^{T_{vap}} \frac{C_p(l)}{T} dT$$

$$\Delta S_4 = \frac{\Delta H_{vap}}{T_{vap}}, \quad \Delta S_5 \int_T^T \frac{C_p(g)}{T} dT$$

$$\Delta S_T^\circ(A) = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

$$\Delta S_{rxn}^\circ = \sum S_{(products)} - \sum S_{(reactants)}$$

Notes 05/01

Friday, May 01, 2009
10:03 AM

$G = H - TS$

$dG_{T,P} < 0$ spontaneous

$dG_{T,P} = 0$ equilibrium

$dG_{T,P} > 0$ impossible

$\Delta G_f^\circ(A)$

$$\begin{matrix}\text{constit elements} \\ \text{in reference states} \\ @T\end{matrix} \xrightarrow{\Delta G_{rxn} \equiv \Delta G_{f,T}^\circ(A)} \begin{matrix}1A \\ \text{T, STD STATE}\end{matrix}$$

$$0 = \sum_{J=1}^{\text{all species}} \nu_J S_J$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$$

$$0 = H_2O(\ell) - H_2(g) - \tfrac{1}{2}O_2(g)$$

$$\Delta G_{rxn}^\circ = \sum_{J=1}^{\text{all speres}} \nu_J \Delta G_f^\circ(S_J)$$

---

equations

$dU = TdS - PdV$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

relations

1) $\left(\frac{\partial U}{\partial S}\right)_V = T$ 2) $\left(\frac{\partial U}{\partial V}\right)_S = -P$

3) maxwell relations

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

$H \equiv U + PV$

$dH = dU + VdP + PdV$

$dH = TdS + VdP$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

3 more relations

1) $\left(\frac{\partial H}{\partial S}\right)_P = T$ 2) $\left(\frac{\partial H}{\partial P}\right)_S = V$ 3) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

$A = U - TS$

$dA = dU - TdS - SdT$

$dA = -SdT - PdV$

$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial V}\right)_T dV$

1) $\left(\frac{\partial A}{\partial T}\right)_V = -S$ 2) $\left(\frac{\partial A}{\partial V}\right)_T = -P$ 3) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K}$

more useful relation $\left(\frac{\partial P}{\partial T}\right)_V$ easy to measure. $= \left(\frac{\beta}{K}\right)$

$dG = -SdT + VdP$

$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$

1) $\left(\frac{\partial G}{\partial T}\right)_P = -S$ 2) $\left(\frac{\partial G}{\partial P}\right)_T = V$ 3) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = \beta V$

$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\beta}{K} - P$

$dU = TdS - PdV$

divide both sides dV & impose const. T

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

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

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\beta}{K} - P}$$

$dG = VdP - SdT$

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

first look at T dependence

$\left(\frac{\partial G}{\partial T}\right)_P = -S = -\frac{(H-G)}{T} = \frac{G-H}{T}$

multiply by $\frac{1}{T}$

$\frac{1}{T}\left(\frac{\partial G}{\partial T}\right) - \frac{G}{T^2} = \frac{-H}{T^2}$

$$\underbrace{\frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}} = \frac{-H}{T^2}$$

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + \frac{G}{-T^2}$$

$$\boxed{\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{-H}{T^2}}$$ — Gibbs Helmholtz Equation

---

$\Delta G(T) = G_P(T) - G_R(T)$

how does this depend on T?

$$\left(\frac{\partial\left(\frac{\Delta G(T)}{T}\right)}{\partial T}\right)_P = \left[\frac{\partial\left(\frac{G_P(T)}{T} - \frac{G_R(T)}{T}\right)}{\partial T}\right]_P$$

evaluatable by Gibbs Helmholtz

$$= -\frac{H_P}{T^2} + \frac{H_R(T)}{T^2} = \frac{-\Delta H(T)}{T^2}$$

$$\left(\frac{\partial\left(\frac{\Delta G^{(T)}}{T}\right)}{\partial T}\right)_P = \frac{-\Delta H(T)}{T^2}$$

integrate by mult both sides dT

$$\int_{\frac{\Delta G(T_1)}{T_1}}^{\frac{\Delta G(T_2)}{T_2}} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \frac{-\Delta H}{T^2}\, dT_P$$

suppose ΔH is independent of T

$$\Delta H\left(\frac{1}{T^2} - \frac{1}{T^2}\right) = \frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1}$$

if ΔH is dependent on T then evaluate integral taking that into regard.

$$\frac{\Delta G^\circ}{T} = -R\ln K$$

$$\cancel{R}\left[\ln K(T_2) - \ln K(T_1)\right] = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

divide both sides R

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$dG_T = VdP_T$$

$$G(P_2) = G(P_1) + \int_{P_1}^{P_2} VdP$$

2 cases: ¹⁾ condensed matter (l & s) and ²⁾ gas

1) for condensed phase systems

$$V(P) \simeq V \qquad K << 1$$

$$G(P_2) = G(P_1) + V\Delta P$$

example

1 mol $H_2O(l)$ @ 298K, 1bar

$$\underset{\substack{298K\\1bar}}{H_2O(l)} \longrightarrow \underset{\substack{298K\\2bar}}{H_2O(l)}$$

$V\Delta P = (0.018L)(1bar) = 1.8\times10^{-2}$ bar·L $= \boxed{1.8J}$ — this is very small

so $G(P) \simeq G$ (condensed phase)

2) for gaseous systems

$$G(P_2) = G(P_1) + \int_{P_1}^{P_2} VdP$$

$$G(P_2) = G(P_1) + \int_{P_1}^{P_2} \frac{nRT}{P}\, dT$$

$$= G(P_1) + nRT\ln\left(\frac{P_2}{P_1}\right)$$

example

1 mol gas @ 298K $\qquad P_1 = 1bar \rightarrow P_2 = 2bar$

$RT\ln 2 \simeq \boxed{1700J}$ — much larger by orders of magnitude than condensed phase.

How Gibbs Free Energy depends on composition of system

$$G(P=1bar) = G^\circ$$

$$G(P) = G^\circ + nRT\ln\left(\frac{P}{P^\circ}\right)$$

$$G_m(P) = G_m^\circ + RT\ln\left(\frac{P}{P^\circ}\right)$$

$$G_m(P) = G_m^{\circ} + RT\ln\left(\frac{P}{P^{\circ}}\right)$$

μ : chemical potential for a pure substance

$$\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{T,P} = G_m$$

$$\mu = \mu^{\circ} + RT\ln\left(\frac{P}{P_0}\right)\Bigg\}\text{perfect gas} \qquad \mu^{\circ} = G_m^{\circ}$$

Notes 05/04

Monday, May 04, 2009
10:01 AM

- Open Systems w/ changes of composition

$$dG_{T,P} \begin{array}{l} <0 \\ =0 \end{array}$$

$$dG = -SdT + VdP$$

system w/ 2 components (#1, #2)
#1: n_1
#2: n_2

so need 4 independent variables

$$dG(T,P,n_1,n_2) = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2$$

nomenclature

$$* \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} \equiv \left(\frac{\partial G}{\partial T}\right)_{P,n}$$

$$* \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n \neq n_i}$$

These are same as closed system constant composition

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

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

so:

$$dG = -SdT + VdP + \left(\frac{\partial G}{\partial n_1}\right)_{T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,n_1} dn_2$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \mu_1 \quad \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} = \mu_2$$

$\mu \equiv$ chemical potential

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

$$\boxed{dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i}$$

open systems with changes in composition

i refers to different compounds & states

Fundamental Equation of Thermodynamics

$$\mu_i(T,P,n_1,n_2)$$
$$\mu_i(T,P,\{n_i\})$$

$\mu_i(T, P, \{n\})$

example: $10^{-5}\,m\ (CH_3)_2CO_2$ in H_2O
$10^{-2}\,m$ " "

definition chemical potential (μ)

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n\neq n_i}$$

μ can also be expressed as U, H, A

$$dG = -SdT + \sum_{i=1}^{N} \mu_i dn_i = dH - SdT - TdS$$

solve for dH

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

which mathmatically:

$$dH = \underset{\overset{\downarrow}{=T}}{\left(\frac{\partial H}{\partial S}\right)_{P,n}} dS + \underset{\overset{\downarrow}{=V}}{\left(\frac{\partial H}{\partial P}\right)_{S,n}} dP + \sum_{i=1}^{N} \underset{\overset{\downarrow}{\mu_i}}{\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n\neq n_i}} dn_i$$

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

$$dU + d(PV) = dH =$$

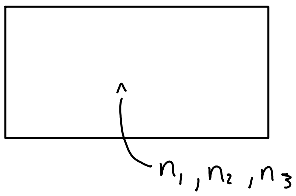
$$dU = TdS - PdV + \sum_{i=1}^{n} \mu_i dn_i$$

$$\left(\frac{\partial U}{\partial n_1}\right)_{S,V,n\neq n_1} = \mu_1 \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n\neq n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n\neq n_i}$$

$$dA = -SdT - PdV + \sum_{i=1}^{n} \mu_i dn_i$$

---

initial state



at T&P constant

chemical potential constant of system

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n\neq n_i}$$

integrate $dG = -\underset{0}{\underset{\|}{SdT}} + \underset{0}{\underset{\|}{VdP}} + \sum_{i=1}^{N} \mu_i dn_i$

$$\int^{G} dG = \sum^{N} \int^{n_i} \mu_i dn_i$$

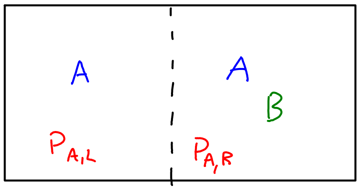
$$\int_0^G dG = \sum_{i=1}^{N} \int_0^{\overset{\overset{\shortparallel}{0}}{n_i}} \overset{\overset{\shortparallel}{0}}{\mu_i}\, dn_i$$

$$\boxed{G = \sum_{i=1}^{N} \mu_i n_i} \leftarrow \text{for constant } P, V$$

Determine of chemical potential of an ideal gas in a mixture

$$\mu = \mu^\circ + RT\ln\frac{P}{P^\ominus} \quad \Big\} \text{ pure ideal gas (not mixture)}$$

Consider system divided into two parts with semi permeable membrane. Membrane only passes species A through. A and B are ideal gases.



at equilibrium

$$P_{A,L} = P_{A,R}$$

$$dG_{TOT} = 0 = dG_L + dG_R = 0$$

$$dG_L = \mu_{A,L}\, dn_{A,L} \qquad dG_R = \mu_{A,R}\, dn_{A,R}$$

$$\mu_{A,L}\, dn_{A,L} + \mu_{A,R}\, dn_{A,R} = 0$$

$$\underbrace{(\mu_{A,L} - \mu_{AR})}_{\text{must be } 0} \underbrace{dn_{A,L}}_{\text{can't be } 0} = 0$$

$$\mu_{A,L} = \mu_A^\ominus + RT\ln\frac{P_{A,L}}{P^\ominus}$$

$$\overset{\shortparallel}{\mu_{A,B}} = \mu_A^\circ + RT\ln\left(\frac{P_{A,R}}{P^\ominus}\right) \leftarrow \text{true for mixture}$$

$$= \mu_A^\circ + RT\ln\frac{X_A P}{P^\circ} = \left(\mu_A^\ominus + RT\ln\frac{P}{P^\ominus}\right) + RT\ln X_A$$

$$\mu_A = \mu_A^{pure}(T,P) + RT\ln\frac{P}{P_0}$$

Thermodynamics of mixing of an ideal gas

Initial state: (pure A, pure B, pure C, pure D) all at pressure P

Might be different mole amounts but they have the same pressure P

$$A + B + C + D \qquad \text{total } P_i = P$$

Find ΔG_{mix}

$$G_i = n_A\mu_A^{pure}(T,P) + n_B\mu_B^{pure}(T,P) + n_C\mu_C^{pure}(T,P) + n_D\mu_D^{pure}(T,P)$$

$$\mu_A = \mu_A^{pure}(T,P) + RT\ln X_A$$

$$G_f = n_A[\mu_A^{pure}(T,P) + RT\ln X_A] + n_B[\mu_A^{pure}(T,P) + RT\ln X_B] + \ldots$$

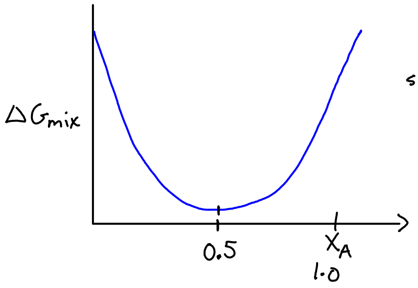
$$\Delta G_{mix} = G_f - G_i = n_A RT\ln X_A + n_B RT\ln X_B + n_C RT\ln X_C + n_D RT\ln X_D$$

def. of mole fraction $\frac{n_i}{n} = x_i$

$$\boxed{nRT\sum \ln x_i = \Delta G_{mix}}$$

What does G_{mix} mean?

Mole fractions are always less than or equal to 1, so $\Delta G_{mix} < 0$ always so spontaneous



2 component system (A&B)

Entropy/Enthalpy change during mixing

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

$$\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{P,n} = -\Delta S_{mix} \longrightarrow = +nR\sum_{i=1}^{N} x_i \ln X_i$$

$$\Delta S_{mix} = -nR\sum_{i=1}^{N} x_i \ln X_i$$

$\Delta S_{mix} > 0$ always

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$$
$$= 0$$

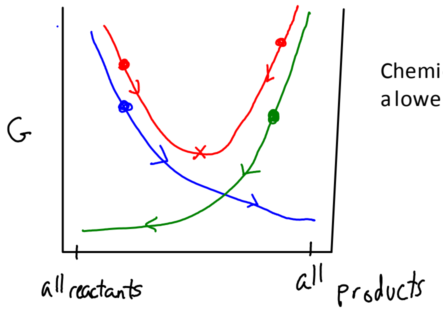
Notes 05/06

Wednesday, May 06, 2009
10:01 AM

Thermodynamics to Chem. Rxns

$$\Delta G^{\circ}_{rxn} = -RT\ln K$$

$$dG_{T,P} < 0$$



Chemical reaction will evolve toward an equilibrium that has a lower G

$$A \rightleftharpoons B$$

$$dn_A = dn_B$$

$$\varepsilon \equiv \text{extent of rxn}$$

$$d\varepsilon \equiv -dn_A = dn_B$$

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

Constant temp and pressure

$$\shortparallel \qquad\qquad \shortparallel$$
$$0 \qquad\qquad 0$$

$$dG_{T,P} = \mu_A dn_A + \mu_B dn_B = d\varepsilon(-\mu_A + \mu_B) = (\mu_B - \mu_A)d\varepsilon$$

Divide both sides by dE

$$\frac{dG_{T,P}}{d\varepsilon} = \underset{\equiv}{\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P}} = \mu_B - \mu_A$$

ΔG_r = rxn Gibbs function

$dG_{T,P} < 0$ spontaneous

$d\varepsilon > 0$ fwd rxn

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} < 0 \quad \text{fwd rxn spontaneous}$$

$dG_{T,P} < 0$ spontaneous

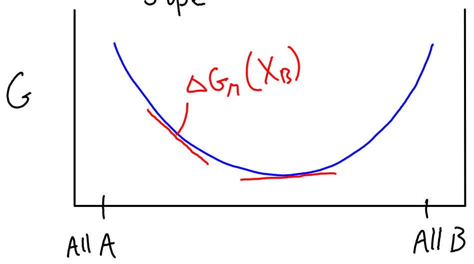
$d\xi < 0$ rev. rxn

$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} > 0$ rev. rxn spontaneous

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} \equiv \Delta G_r = 0$$

What is ΔG_r? $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G_r$

slope



$$A \xrightarrow{\Delta G_{rxn}} B$$

$$G(B) - G(A) = \Delta G_{rxn}$$

suppose have $N_A A + N_B B \longrightarrow (N_A - 1)A + (N_B + 1)B$

where N_A & N_B are very large

$$\Delta G \equiv \Delta G_r$$

$\Delta G_r = \mu_B - \mu_A$

$\Delta G(x_B) = \mu_B(x_B) - \mu_A(x_B)$

$\Delta G_r < 0$ $\mu_B < \mu_A$ spontaneous rxn in fwd direction $A \to B$

$\Delta G_r > 0$ $\mu_B > \mu_A$ spontaneous rxn in rev direction $B \to A$

$\Delta G_r = 0$ $\mu_B = \mu_A$ equilibrium

$\Delta G_r = \mu_B - \mu_A$ where A & B are ideal gases

$$\mu_A = \mu_A^\circ + RT\ln\left(\frac{P_A}{P^\circ}\right)$$

$$\mu_B = \mu_B^\circ + RT\ln\left(\frac{P_B}{P^\circ}\right)$$

$$\Delta G_r = \mu_B - \mu_A = (\mu_B^\circ - \mu_A^\circ) + RT\ln\left(\frac{P_B/P^\circ}{P_A/P^\circ}\right)$$

$$\mu_B = G^\circ_{m,B} \qquad \mu_A^\circ = G^\circ_{m,A}$$

$$\Delta G^\circ_{rxn} = \Delta G^\circ_{m,B} - \Delta G^\circ_{m,A}$$

$$\Delta G_r = \Delta G^\circ_{rxn} + RT\ln\left(\frac{P_B/P^\circ}{P_A/P^\circ}\right)$$

$$\Delta G_{r,eq.} = 0 = \Delta G^\circ_{rxn} + RT\ln\left(\frac{P_B/P^\circ}{P_A/P^\circ}\right)$$

$$\Delta G^\circ_{rxn} = -RT\ln\left(\frac{P_B/P^\circ}{P_A/P^\circ}\right) \qquad K_{eq} \equiv \left(\frac{P_B/P^\circ}{P_A/P^\circ}\right)$$

$$\Delta G^\circ_{rxn} = -RT\ln \underset{\overset{\|}{K_P}}{K_{eq}}$$

$$Q \equiv \text{rxn quotient} \equiv \left(\frac{P_B/P^\circ}{P_A/P^\circ}\right) \neq K_{eq}$$

$$(Q)_{eq} = K_{eq}$$

$$\Delta G_r = \Delta G^\circ + RT\ln Q$$

when $\Delta G^\circ = 0$, $Q = K$, $\Delta G_r = \Delta G^\circ_{rxn}$

$\Delta G^\circ_{rxn} < 0$ $\quad RT\ln K > 0$, $K_{eq} > 1$ } system at equilibrium that favors products

$\Delta G^\circ_{rxn} > 0$ $\quad RT\ln K < 0$, $K_{eq} < 1$ } system at equilibrium that favors reactants

---

$$A + 2B \longrightarrow 3C + 2D$$

$0 = \sum_J \nu_J S_J$ general

$\nu_A = -1,\ \nu_B = -2,\ \nu_C = 3,\ \nu_D = 2$

$$dn_A = \frac{dn_B}{2} = -\frac{dn_C}{3} = -\frac{dn_D}{2}$$

$$\boxed{dn_J = \nu_J\, d\xi}$$

$$d\xi \equiv -dn_A$$

$$dn_A = -d\xi$$

$$dn_B = -2d\xi$$

$$dn_C = 3d\xi$$

$$dn_D = 2d\xi$$

$$dG_{T,P} = \mu_A dn_A + \mu_B dn_C + \mu_D dn_D$$

$$= (-\mu_A - 2\mu_B + 3\mu_C + 2\mu_D)\, d\varepsilon$$

$$dG_{T,P} = \left(\sum_J \nu_J \mu_J\right) d\varepsilon$$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} = \Delta G_\Lambda = (3\mu_C + 2\mu_D - \mu_A - 2\mu_B)$$

$$\boxed{\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} = \sum_J \nu_J \mu_J}$$

For perfect gas

$$\mu_J = \mu_J^\circ + RT\ln\left(\frac{P_J}{P^\circ}\right)$$

$$\left(\frac{\partial G}{\partial \varepsilon}\right)_{T,P} = \underbrace{(3\mu_C^\circ + 2\mu_D^\circ - \mu_A^\circ - 2\mu_B^\circ)}_{\Delta G^\circ_{rxn}} + RT\ln\left[\underbrace{\frac{(P_C/P^\circ)^3 (P_D/P^\circ)^2}{(P_A/P^\circ)(P_B/P^\circ)^2}}_{K_P}\right]$$

$$\Delta G_\Lambda = 0 = \Delta G^\circ_{rxn} + RT\ln K_P$$

$$\Delta G^\circ_{rxn} = -RT\ln K_P$$

Notes 05/08

Friday, May 08, 2009
9:56 AM

Finish Chapter 6

$$0 \sum_J \nu_J S_J$$

$$dG = \left(\sum_J \nu_J \mu_J\right) d\xi \overset{\text{equilibrium}}{=} 0$$

$$dn_J = \nu_J \, d\xi$$

$$\sum_J \nu_J \mu_J = \sum_J \nu_J \left(\mu_J^\circ + RT\ln\left(\frac{P_J}{P^\circ}\right)\right)$$

$$\sum_J \nu_J \mu_J^\circ = \Delta G^\circ_{rxn}$$

$$\sum \nu_J RT\ln\left(\frac{P_J}{P^\circ}\right) = RT\ln\left(\prod_J \frac{P_J}{P^\circ}\right)^{\nu_J}$$

$$\Delta G^\circ_{rxn} = -RT\ln\left(\prod_J \frac{P_J}{P^\circ}\right)^{\nu_J} \qquad \uparrow K_p$$

$$\Delta G^\circ_{rxn} = -RT\ln K_p$$

$$K_p = \prod_J \left(\frac{P_J}{P^\circ}\right)^{\nu_J}$$

$$\left(\frac{P_1}{P^\circ}\right)^{\nu_1}\left(\frac{P_2}{P^\circ}\right)^{\nu_2}$$

$$A + 2B \longrightarrow 3C + 2D$$

$$K_p = \frac{\left(\frac{P_C}{P^\circ}\right)^3 \left(\frac{P_D}{P^\circ}\right)^2}{\left(\frac{P_A}{P^\circ}\right)\left(\frac{P_B}{P^\circ}\right)^2}$$

This ↑ was only for ideal gas

$$\mu_J \underset{m_J}{(x_J)}$$

for real gas $\mu_J \neq \mu_J + RT\ln\left(\frac{P_J}{P^\circ}\right)$

For condensed phase systems:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$\Delta G_r = \sum_J \nu_J \mu_J = 0$$

$$\mu_{eq}(NaCl(s)) - \tfrac{1}{2}\mu_{eq}(Cl_2(g)) - \mu_{eq}(Na(s)) = 0$$

$$\mu(Cl_2(g)) = \mu^\circ_{Cl_2} + RT\ln\left(\frac{P_{Cl_2}}{P^\circ}\right)$$

$$\mu = G_m \qquad d\mu = dG_m \Rightarrow (dG = VdP - \cancel{S}dT)$$

$$d\mu = V_m dP$$

$$\int_{\mu^\circ}^{\mu(P)} \underset{\shortparallel}{d\mu} = \int_{P^\circ}^{P} V_m dP = V_m(P-P_0)$$

$$\mu(P)-\mu^\circ = V_m(P-P_0)$$

$\mu^\circ \simeq \mu(P)$ For condensed phase, pressure is negligible when not too far from atmospheric pressure

$$\mu_{eq}(Na(s)) = \mu^\circ(Na(s))$$
$$\mu_{eq}(NaCl(s)) = \mu^\circ(NaCl(s))$$
$$\mu^\circ(NaCl(s)) - \mu^\circ(Na(s)) - \frac{1}{2}\left(\underset{\substack{\shortparallel\wr \\ 0}}{\mu^\circ Cl_2(g)} + RT\ln\left(\frac{P_{Cl_2}}{P^\circ}\right)\right)$$

$$\Delta G^\circ_{rxn} + RT\ln\left(\frac{P_{Cl_2}}{P^\circ}\right)^{\frac{1}{2}} = 0$$

$$-RT\ln K_p = \Delta G^\circ_{rxn}$$

$$K_p = \left(\frac{P_{Cl_2}}{P^\circ}\right)^{-\frac{1}{2}}$$ Kp only refers to gas phase (does not include condensed phase)

For all rxns that include condensed phase and ideal gases, can write Kp as

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$
$$K_p = \left(\frac{P_{CO_2}}{P^\circ}\right)$$
$$\Delta G^\circ_{rxn} = -RT\ln K_p$$

$$\nu_A A(s) + \nu_B B(g) \longrightarrow \nu_C(g) + \nu_D D(l)$$
$$K_p = \frac{\left(\frac{P_C}{P^\circ}\right)^{\nu_C}}{\left(\frac{P_B}{P^\circ}\right)^{\nu_B}}$$
$$\Delta G^\circ_{rxn} = \nu_C \Delta G^\circ_f(C(g)) + \nu_D \Delta G^\circ_f(D(l)) - \nu_A \Delta G^\circ_f(A(s)) - \nu_B \Delta G^\circ_f(B(g))$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$K_c = [H_3O^+][OH^-]$ (no $H_2O(l)$ → μ_J doesn't change essentially. Condensed phase)

$$K_p = \prod_J^{\text{gases}} \left(\frac{P_J}{P^\circ}\right)^{\nu_J}$$

Can re-express in terms of mole fractions: $P_J = x_J P$

$$K_p = \underbrace{\left(\prod_J x_J^{\nu_J}\right)}\left(\frac{P}{P^\circ}\right)^{\Delta\nu} \quad \text{where } \Delta\nu = \sum_J \nu_J$$

$K_x \equiv \prod_J x_J^{\nu_J}$ (make definition)

$$K_p = K_x\left(\frac{P}{P^\circ}\right)^{\Delta\nu}$$

$$\Delta G^\circ = -RT\ln K_p$$

Kp, and G, not dependent on pressure. Kx is

$$K_x = K_p\left(\frac{P}{P^\circ}\right)^{-\Delta\nu}$$

Kx and Kp have different values if delta(v) does not = 0

$$P_J = \frac{n_J}{V}RT = \overset{\text{concentration}}{C_J}RT$$

$$K_p = \prod_J\left(\frac{P_J}{P^\circ}\right)^{\nu_J} = \left(\prod_J C_J^{\nu_J}\right)\left(\frac{RT}{P^\circ}\right)^{\Delta\nu}$$

$$\text{define } K_c \equiv \prod_J\left(\frac{C_J}{C^\circ}\right)^{\nu_J} \qquad C^\circ \equiv \text{standard concentration (typically } 1\text{mol/L)}$$

$$\prod_J C_J^{\nu_J} = K_c (C^\circ)^{\Delta\nu}$$

$$K_p = K_c\left(\frac{C^\circ RT}{P^\circ}\right)^{\Delta\nu}$$

$$K_c = K_p\left(\frac{C^\circ RT}{P}\right)^{-\Delta\nu}$$

Unlike mole fraction equilibrium constant, Kc doesn't depend on pressure
Kp will depend on our choice of C^0 and P^0 (usually 1mol/L & 1bar, though a different standard can be chosen)

Temperature dependence

$$\ln K_p = -\frac{\Delta G^\circ}{RT}$$

differentiate both sides for T dep.

$$\frac{d\ln K_p}{dT} = -\frac{1}{R}\frac{d\left(\frac{\Delta G^\circ_{rxn}}{T}\right)}{dT} \longleftarrow * \ \frac{\partial(G/T)}{\partial T} = \frac{-H}{T^2}$$

$$= \frac{\Delta H^\circ_{rxn}}{RT^2}$$

endothermic $\Delta H^\circ_{rxn} > 0$, K_p inc w/ temp
exothermic $\Delta H^\circ_{rxn} < 0$, K_p dec w/ temp

$$\int_{\ln K_p(T_0)}^{\ln K_p(T_f)} d(\ln K_p) = \int_{T^\circ}^{T_f}\frac{\Delta H^\circ_{rxn}}{RT^2}\,dT$$

make assumpton ΔH°_{rxn} indep on T (ie T° & T_f close)

$$\ln K_p(T_f) - \ln K_p(T_0) = \frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_0} - \frac{1}{T_f}\right)$$

$$K_p(T_f) = \underset{\substack{\uparrow\\ \text{can get from } \Delta G^\circ_f}}{K_p(T_0)}\exp\left(\underset{\substack{\uparrow\\ \text{can get from } \Delta H^\circ_{rxn}}}{\frac{\Delta H^\circ_{rxn}}{R}}\left(\frac{1}{T_0} - \frac{1}{T_f}\right)\right)$$

Pressure Dependence

$$A(g) \rightleftharpoons 2B(g)$$

$$K_p = \frac{\left(\frac{P_B}{P_0}\right)^2}{\left(\frac{P_A}{P_0}\right)}$$

start n mol A 0 mol B
end $n-\alpha$ mol A 2α mol B

@ equilibrium $X_A = \frac{1-\alpha}{1+\alpha}$ $X_B = \frac{2\alpha}{1+\alpha}$

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2\left(\frac{P}{P^0}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\left(\frac{P}{P_0}\right)} = \frac{4\alpha^2}{(1-\alpha)^2}\frac{P}{P_0}$$

In general: $\underset{\substack{\uparrow\\ \text{depends}}}{K_x} = \underset{\uparrow}{K_p}\left(\frac{P}{P^\circ}\right)^{-\Delta\nu} \longleftarrow \text{pressure}$

In general: $K_x = K_P \left(\frac{P}{P^\circ}\right)$

depends on P

pressure indep

pressure varies

Not talk about RNA/DNA stuff at end.

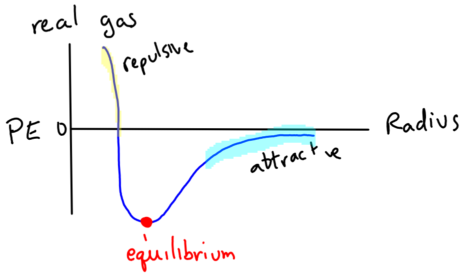
6.15, delta H and delta U changes, maxwell relations, state functions etc. Go through those examples closely.

Notes 05/11

Monday, May 11, 2009
10:01 AM

Chapter 7

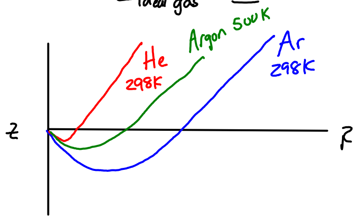
- Ideal gas - point charges that do not interact together
- Real gas - there are interactions between real gases



z (compressibility ratio)

$$z = \frac{PV_m}{RT}$$

$$z_{\text{ideal gas}} = 1$$



$z = \frac{PV_m}{RT} < 1$ easier to compress than ideal gas because attractive forces dominate

$z > 1$ harder to compress because repulsive forces dominate

At small and intermediate pressures, z<1 because average distances tend to be less
As pressure increases, will encounter repulsive wall. Repulsive forces dominate z>1

Virial Equation of State

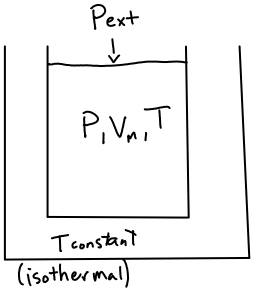
$$PV_m = RT \text{ at low } P$$

$$PV_m = RT(1 + B'(T)P + C'(T)P^2 + \dots)$$

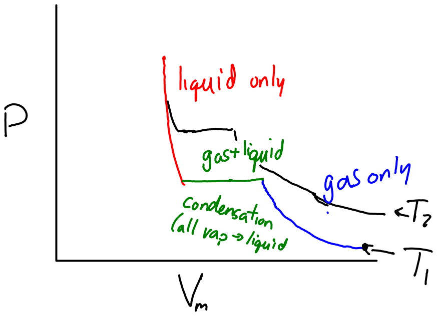
2nd virial coefficient 3rd

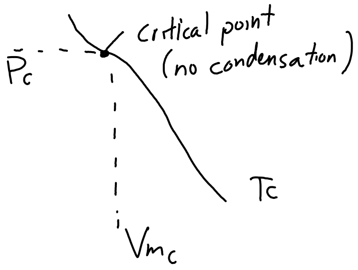
$$P \cong \frac{k}{V_m}$$

$$PV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots\right)$$



V_m decreases
P increases
PV_m = constant
↓ inc pressure
$PV_m \neq$ constant
⇓ dec. V_m
P remains same } condensation (reached vapor pressure) $\xrightarrow{\text{small dec. } V_m}$ large inc. in pressure





$T_c, P_c, V_{m,c}$ = constant for each gas

inflection point → critical point is inflection point

$$\left(\frac{\partial P}{\partial V_m}\right)_T = 0 \quad \& \quad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = 0$$

solve crit point for Van der Walls

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

$$-\frac{RT}{(V_m-b)^2} + \frac{2a}{V_m^3} = 0$$

$$\frac{2RT}{(V_m-b)^3} - \frac{6a}{V_m^4} = 0$$

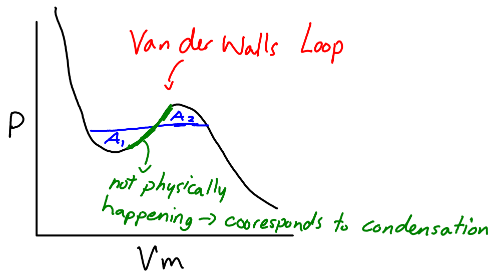
2 equations, 2 unknowns

Van der Walls gas

$$T_c = \frac{8a}{27Rb}$$

$$V_{m,c} = 3b$$

$$P_c = \frac{a}{27b^2}$$



Real gases obey Principle of Corresponding States.
Express in reduced variables

$$P_r \equiv \frac{P}{P_c} \qquad T_r \equiv \frac{T}{T_c} \qquad V_r \equiv \frac{V_m}{V_{m,c}}$$

for van der walls

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

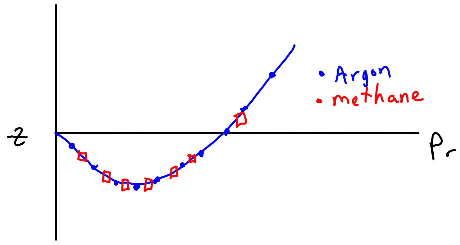
$$P_r P_c = \frac{R T_r T_c}{V_r V_{m,c} - b} - \frac{a}{(V_r V_{m,c})^2}$$

plug in T_c, P_c, $V_{m,c}$

$$\boxed{P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}}$$

→ applies to any gas as long as it obeys van der walls

z vs. P_r (for different gases at same T_r)



Lecture 05/13

Wednesday, May 13, 2009
10:04 AM

Fugacity

$$\mu_{real} \neq \mu_{ideal} = \mu^{\circ} + RT \ln \frac{P}{P^{\circ}}$$

$$\mu_{real} = \mu^{\circ} + RT \ln \frac{f}{f^{\circ}}$$

$\uparrow$

diff. for f

$$f^{\circ} = P^{\circ}$$

$$\lim_{P \to 0} f = P$$

$$\lim_{P \to 0} \mu_{real} = \mu_{ideal}$$

$$dG = VdP - SdT$$

const temp

$$dG = VdP$$

divide by n

$$dG_n = V_m \, dP_T$$

$$d\mu_T = V_m \, dP_T$$

$$\left.\begin{array}{l} d\mu_{ideal} = V_m^{ideal} \, dP \\ d\mu_{real} = V_m^{real} \, dP \end{array}\right\} \text{subtract from one another} \quad -$$

$$d\mu_{real} - d\mu_{ideal} = (V_m^{real} - V_m^{ideal}) \, dP$$

integrate from $P' = 0 \longrightarrow P = P$

$$\mu_{real}(P) - \cancel{\mu_{real}(0)} - (\mu_{ideal}(P) - \cancel{\mu_{ideal}(0)}) = \int_0^P (V_m^{real} - V_m^{ideal}) \, dP$$

as $P \to 0$, $\mu = 0$

$$\mu_{real}(P) - \mu_{ideal}(P) = \int_0^P (V_m^{real} - V_m^{ideal}) \, dP$$

$$\left(\cancel{\mu^{\circ}} + RT \ln \frac{f}{f^{\circ}}\right) - \left(\cancel{\mu^{\circ}} + RT \ln \frac{P}{P^{\circ}}\right) = \int_0^P (V_m^{real} - V_m^{ideal}) \, dP$$

$$RT \ln f - RT \ln P = \int_0^P (V_m^{real} - V_m^{ideal})$$

$$\ln f = \ln P + \frac{1}{RT} \int_0^P (V_m^{real} - V_m^{ideal}) \, dP'$$

$$z = \frac{PV_m^{real}}{RT} = \frac{V_m^{real}}{V_m^{ideal}}$$

express in terms of z

$$V_m^{real} = z V_m^{ideal}$$

$$V_m^{real} - V_m^{ideal} = (z - 1) V_m^{ideal}$$

$$\frac{V_m^{ideal}}{RT} = \frac{1}{P}$$

so...

$$\ln f = \ln P + \int_0^P \frac{(z-1)}{P'}\,dP'$$

$$f = P\underbrace{\left[\exp\left(\int_0^P \frac{(z-1)}{P}\,dP'\right)\right]}_{\gamma(P,T)\,\equiv\,\text{frugacity coefficient}}$$

$\gamma = 1$ ideal gas behavior
$\gamma \neq 1$ not ideal gas behavior

2 cases

(a) $z > 1$ for all P
then $\gamma > 1$ & $f = Pe^{a}$ where $a>0$
so $f > P$
repulsive forces dominate

(b) $z<1$ for $P'=0 \rightarrow P$
then $f = P\exp(-a)$ $a>0$
$f < 0$

$$\mu_{real} = \mu^{\theta} + RT\ln\frac{f}{f^{\theta}}$$

why is this?
recipe for equilibrium constant for real & ideal gases

recall law mass action gases (for ideal gases only)

$$aA + bB \ldots \longrightarrow cC + dD \ldots$$

$$K_p = \frac{P_C^{\,c}\,P_D^{\,d}}{P_A^{\,a}\,P_B^{\,b}}$$

real gas:

$$\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \longrightarrow NH_3(g)$$

$$\mu_{NH_3} - \frac{3}{2}\mu_{H_2} - \frac{1}{2}\mu_{N_2} = 0$$

$$\mu^{\theta}_{NH_3} + RT\ln\frac{f_{NH_3}}{f^{\theta}} - \frac{3}{2}\left(\mu^{\circ}_{H_2} + RT\ln\frac{f_{H_2}}{f^{\theta}}\right) - \frac{1}{2}\left(\mu^{\circ}_{N_2} + RT\ln\frac{f_{N_2}}{f^{\circ}}\right) = 0$$

$$\underbrace{\left(\mu_{NH_3} - \frac{3}{2}\mu^{\circ}_{H_2} - \frac{1}{2}\mu^{\theta}_{N_2}\right)}_{\Delta G^{\theta}{}_{rxn}} + RT\ln\underbrace{\left[\frac{f_{NH_3}/f^{\circ}}{\left(\frac{f_{H_2}}{f^{\circ}}\right)^{3/2}\left(\frac{f_{N_2}}{f^{\circ}}\right)^{1/2}}\right]}_{K} = 0$$

$$\Delta G^{\theta} = -RT\ln K$$

$f_i = \gamma_i P_i$

$$K = \frac{f_{NH_3}/f^\circ}{\left(\frac{f_{H_2}}{f^\circ}\right)^{3/2}\left(\frac{f_{N_2}}{f^\circ}\right)^{\frac{1}{2}}} = \frac{\left(\frac{\gamma_{NH_3}P_{NH_3}}{P^\circ}\right)}{\left(\frac{\gamma_{H_2}P_{H_2}}{P^\circ}\right)^{3/2}\left(\frac{\gamma_{N_2}P_{N_2}}{P^\circ}\right)^{1/2}} = K_P\left(\frac{\gamma_{NH_3}}{\gamma_{H_2}^{3/2}\gamma_{N_2}^{1/2}}\right)$$

$K \neq K_P$

$K = K_P$ at P close to 1 bar

Chapter 8

Phase Behavior (certainly something on final with this topic)

When are these in equilibrium?

- Solid-liquid
- Solid-gas
- Liquid-gas

$$\boxed{dG = -SdT + VdP + \sum_J \mu_J dn_J}$$

→ apply this where J applies to different phases of the same compound

at equilibrium

$dG_{T,P} = 0$, $-SdT = 0$, $VdP = 0$

so

$\sum_J \mu_J dn_J = 0$ at equilibrium

consider phase 1 & phase 2

$\mu_1 dn_1 + \mu_2 dn_2 = 0$

$dn_1 = -dn_2$

$(\mu_1 - \mu_2)dn_1 = 0$

so $\mu_1 = \mu_2$

Pure substance

$\mu_1 = \mu_2 = \mu_3$ (at triple point)

Triple point - 3 phases in equilibrium

Ie liquid, solid, gas

Ie liquid water, liquid water type 2, etc

$dG_{T,P} < 0$

$dG_{T,P} = (\mu_1 - \mu_2)dn_1 < 0$

$\left\{\begin{array}{l} dn_1 < 0 \\ \mu_1 > \mu_2 \end{array}\right.$ $1 \to 2$

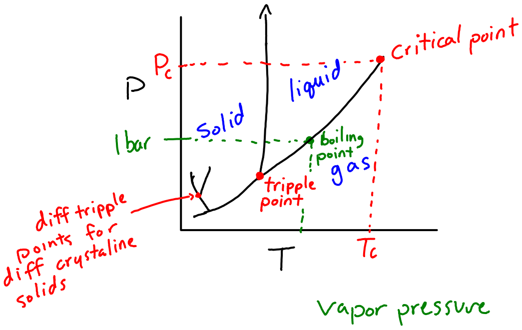
$\left\{\begin{array}{l} dn_1 > 0 \\ \mu_1 < \mu_2 \end{array}\right.$ $2 \to 1$

System proceeds spontaneously toward lower chemical potential

---

Review some phase coexistance

Phase Diagrams



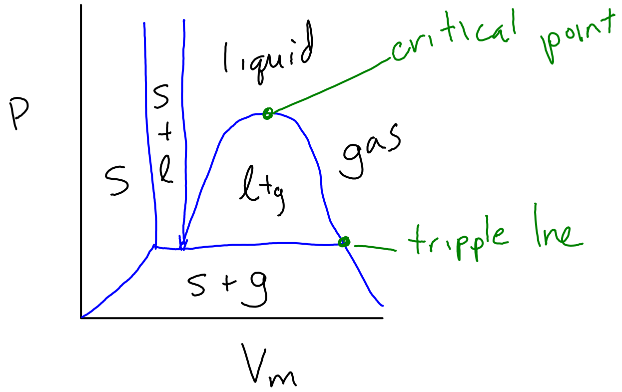
Lines that divide up regions of stable single phases are phase boundaries

Phase coexistence in equilibrium

Vapor pressure $P(T)$

Lecture 5/15

Wednesday, May 27, 2009
11:14 PM



$\mu_1 = \mu_2$ (coexistance

(phase #1
phase #2)

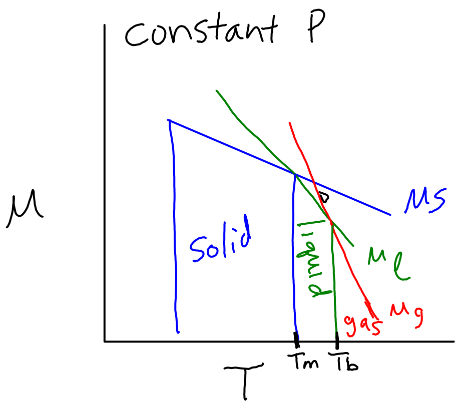
T-dependence of μ's @ constant P

$dG = - dT + \cancel{VdP} + \mu dn$

$$-\left(\frac{\partial S}{\partial n}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,n} = -S_m$$

$S_m > 0$ μ decreases with T

$S_{g,m} > S_{l,m} > S_{s,m}$



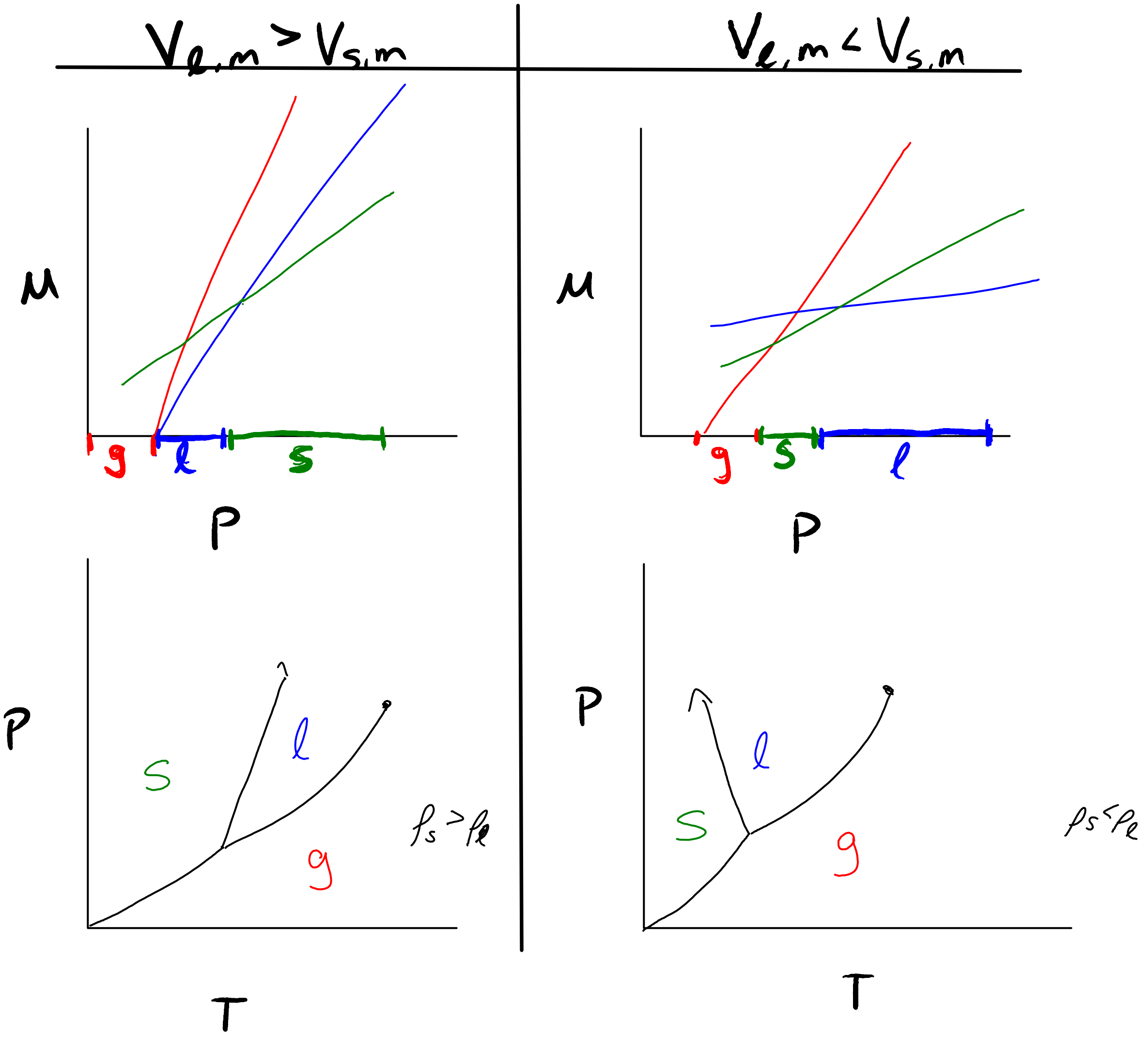
$dG = -SdT + VdP + \mu dn$

$$\left(\frac{\partial V}{}\right) = \left(\frac{\partial \mu}{}\right) = V_m$$

$$\left(\frac{\partial V}{\partial n}\right)_{T,P} = \left(\frac{\partial \mu}{\partial P}\right)_{T,n} = V_m$$

a) $V_m > 0$ μ increases w/ P @ const. T

b) $V_{g,m} > V_{\ell,m}, V_{s,m}$



$$\mu_1(P,T) = \mu_2(P,T)$$

$$d\mu_1 = d\mu_2$$

$$-S_{1,m}dT + V_{1m}dP = -S_{2,m}dT + V_{2,m}dP$$

$$\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{phase}\\ \text{boundary}}} = \frac{S_{2,m} - S_{1,m}}{V_{2,m} - V_{1,m}}$$

$$= \frac{\Delta S_m}{\Delta V_m}$$ Clapeyron Equation

$$= \frac{\Delta H_m}{T \Delta V_m}$$

$$\Delta S_m = \frac{\Delta H_m}{T}$$

$$\frac{\partial P}{\partial T} = \frac{\Delta H_{fus}}{T \Delta V_{fus}} = \frac{\Delta H_{fus}}{T(V_{m,l} - V_{m,s})}$$

Lecture 5/18

Thursday, May 28, 2009
12:25 AM

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$

$$\int_{P_0}^{P} dP' = \int \frac{\Delta H_m(T)}{T\Delta V_m(T)}\, dT$$

ΔH_{fus} & ΔV_{fus} are T independent

$$P \cong \frac{\Delta H_{fus}}{\Delta V_{fus}} \ln\frac{T}{T_0} + P_0 \cong P_0 + \frac{\Delta H_{fus}}{\Delta V_{fus}}\left(\frac{T-T_0}{T_0}\right)$$

Example: H_2O $\Delta V_{fus} = -0.0018\ \text{L/mol}$ $\Delta H_{fus} = 8700\ \text{J/mol} = 87\ \text{bar}\cdot\text{L}$

$P \cong -20\ \text{bar/K}$

$$\frac{\partial P}{\partial T} = \frac{\Delta H_{vap}}{\Delta V_{vap} T}$$

$\Delta V_{vap} \approx \Delta V_{g,m} = \frac{RT}{P}$ <– ideal gas

$$\frac{\partial P}{\partial T} = \frac{P\Delta H_{vap}}{RT^2} \Rightarrow \ln\frac{P}{P_0} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$P' = P_0' \exp\left[\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

$P = P'$ when $T = T$ of tripple point

$$T_{tripple} = \frac{\Delta H_{vap} - \Delta H_{sub}}{\left[R\ln\left(\frac{P_0'}{P_0}\right) - \frac{\Delta H_{sub}}{T_0} - \frac{\Delta H_{vap}}{T_2'}\right.}$$

Example: H_2O phase diagram

ΔH_{sub}, ΔH_{vap}, ρ_l, ρ_s are independent of T

vapor is an ideal gas

given: $\rho_l = 0.999\ \text{g/cm}^3$ $\rho_s = 0.91689\ \text{g/cm}^3$ $\Delta H_{fus} = 6010\ \text{J/mol}$

$C_{p,m}(l) = 72.29\ \text{J/K}\cdot\text{mol}$ $C_{p,m}(g) = 33.58\ \text{J/K}\cdot\text{mol}$

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

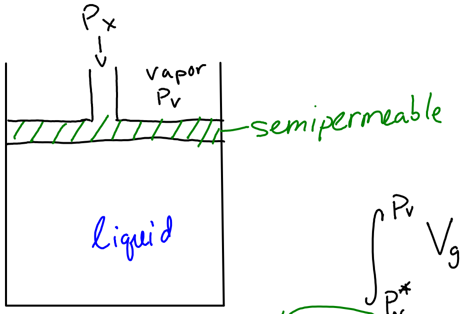
P, P_0, T, T_0 are given on a chart

(P, T)

(P_t, T_t)

$$P = P_0 + \frac{\Delta H_{fus}}{\Delta V_{fus}} \ln\left(\frac{T}{T_0}\right)$$

$$\begin{tikzcd} s \arrow[r, "\Delta H_{fus}"] \arrow[rr, bend right, "\Delta H_{sub}"'] & \ell \arrow[r, "\Delta H_{vap}"] & g \end{tikzcd}$$



$$\mu_g = \mu_\ell \qquad d\mu_g = V_{g,m}\, dP_v$$

$$d\mu_g = d\mu_\ell \qquad d\mu_\ell = V_{\ell,m}\, dP = V_{\ell,m}\, d(P_x + P_v)$$

$$\int_{P_v^*}^{P_v} V_{g,m}\, dP' = \int_{P_v^*}^{P_x+P_v} V_{\ell,m}\, dP'$$

P_v^* = v.p. with no excess P

$$RT \ln\left(\frac{P_v}{P_v^*}\right) = V_{\ell,m}\left(P_v + P_x - P_v^*\right)$$

Discussion 05/19

Tuesday, May 19, 2009
10:01 AM

Ch. 5
- Carnot cycle
  - Switching between isotherm and adiabatic
  - Efficiency = 1- (tc/th)
  - Work -> heat 100% efficiency
  - Heat -> work <100% efficient
- Entropy

$\Delta S = \frac{q_{rev}}{T}$ $\quad$ ΔS_{sys} (talking about rev)

isotherm $\Delta S = nR\ln\frac{V_f}{V_i}$

const $V \Rightarrow q = U$ (no w) $\quad \Delta S = \int \frac{nC_v dT}{T} = nC_v \ln\frac{T_f}{T_i}$

const $P \Rightarrow q = H \quad \Delta S = \int nC_p \ln\frac{T_f}{T_i}$

$V_1T_1 \rightarrow V_2T_2$

$\Delta S = nR\ln\frac{V_f}{V_i} + nC_v\ln\frac{T_f}{T_i}$

phase changes (const P assumed) $\quad \frac{\Delta H_p}{\Delta T_p}$

Arbitrary $\quad$ s, l, or g

$P_1T_1 \rightarrow V_2T_2 \quad \Delta S = C_v\ln\frac{T_f}{T_i} + \frac{\beta}{K}(V_f - V_i)$

$P_1T_1 \rightarrow P_2T_2$

$C_p\ln\frac{T_f}{T_i} + V\beta(P_f - P_i)$

$$\Delta S_{TOT} = \overset{\text{must be rev}}{\overset{\uparrow}{\Delta S_{sys}}} + \underset{\downarrow}{\Delta S_{surr}}$$

$\frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T} \Rightarrow$ doesn't have to be rev

5.11) 1 mol I.G. w/ $C_v = \frac{5}{2}R$ $\quad$ ($\frac{5}{2}R \rightarrow$ diatomic gas)

$T_1 = 250K \quad P_1 = 1.00 bar$

$q, w, \Delta U, \Delta H, \Delta S$

a) gas rev. adiabatic expanson

$P_f = \frac{1}{2}P_i$

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

$\Delta U = nC_v\Delta T$

$P_iV_i^{\gamma} = P_fV_f^{\gamma}$ where $\gamma = \frac{C_p}{C_v} = \frac{7}{5}$ $\quad$ ($C_p = C_v + R$)

$P_i V_i^{\gamma} = P_f V_f^{\gamma}$ where $\gamma = \frac{C_p}{C_v} = \frac{7}{5}$ $(C_p = C_v + R)$

$V_i = \frac{nRT}{P_i} = (.08314)(250k) = 20.79L$

$P_i (20.74)^{7/5} = \frac{1}{2} P_i V_f^{7.5}$

$P_i = 34.11L$

rev process only $\Big\}$ $\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma}$

$\frac{T_f}{T_i} = 0.82$

$T_f = 205K$

$\Delta U = w = (1mol)(\frac{5}{2}R)(8.314 J/Kmol)(205 \cdot 250k) = -935.3J$

$\Delta H = \frac{7}{5} \Delta U = -1.3kJ$

$\Delta S = 0$ (rev. process)

c) exp. against const. $P_{ext} = 0$ $P_f = \frac{1}{2} P_i$

free expansion: $w = 0$ (assumed happens so quickly no time for T change)

$\Delta T = 0$

$\Delta U = \Delta H = 0$ $q = 0$

$\Delta S = \frac{q_{rev}}{T}$

take rev path: isothermal rev. expansion

$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{P_i}{P_f} = (8.314 J/Kmol)(\ln 2) = 5.76 J/K$

5.15

$\frac{C_p}{J/Kmol} = 46.94 + 34.31 \times 10^{-3} \frac{T}{K} - 11.30 \times 10^{5} \frac{T^2}{K^2}$

$\beta = 0.3530 \times 10^{-4} K^{-1}$

$V_m = 22.6 cm^3/mol$

what is ΔS_m (25°C 1atm) → (225C, 1000atm)

$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{P_i}^{P_f} V \beta dP = 46.94 \ln \frac{498K}{298K} + 34.31 \times 10^{-3}(498-298) - 5.65 \times 10^{-5}(498^2 - 298^2) J/Kmol$

$- 22.6 cm^3/mol \times \frac{1m^3}{10^6 cm^3} \times \frac{0.353 \times 10^{-4}}{K} \times (999atm \times \frac{1.01325 \times 10^5 Pa}{1atm})$

$= 22.11 J/Kmol - 0.0807 J/Kmol = 21.88 J/Kmol$

Chapter 6

Maxwell Relations

$$dU = TdS - PdV \rightarrow \overset{T}{\overset{\parallel}{\left(\frac{\partial U}{\partial S}\right)_V}} dS - \overset{-P}{\overset{\parallel}{\left(\frac{\partial U}{\partial V}\right)_S}} dV$$

$$\left.\begin{aligned} dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}\right\}$$ can do for these eq. too

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

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

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

Ex] Derive an expression for molar entropy of isothermal expansion of V.W. gas

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

Find $\left(\frac{\partial S}{\partial V_m}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m - b}$

$$\Delta S = \int_{V_i}^{V_f} \frac{R}{V_m - b}\, dV$$

$$= R\ln\left(\frac{V_{mf} - b}{V_{mi} - b}\right)$$

Ex] Show

$$\left(\frac{\partial U}{\partial P}\right)_T = V_m(\kappa P - \beta T)$$

RT hand side $= V_m\left(\frac{-1}{\cancel{V_m}}\left(\frac{\partial V_m}{\partial P}\right)_T P - \frac{1}{\cancel{V_m}}\overset{\left(-\frac{\partial S}{\partial P}\right)_P}{\overset{\parallel}{\left(\frac{\partial V}{\partial T}\right)_P}} T\right)$

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

Lft hand side $= \left(\frac{\partial U}{\partial P}\right)_T$

$$dU = TdS - PdV$$

@ const T → $T\left(\frac{\partial S}{\partial P}\right)_T - \overset{0}{\cancel{\frac{\partial P}{\partial P}}} V - P\left(\frac{\partial V}{\partial P}\right)_T$

RT side = Lft side

6.12

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

T	600 °C	1000°C
K_p	0.900	0.396

$\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$ at 600°K

$\Delta G = \Delta G^\circ + RT \ln Q_p$

at eq $\Delta G^\circ = -RT \ln K_p = 765\ J/mol$

ΔH $\ln K(T_2) - \ln K(T_1) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\Delta H = -18.96\ kJ/mol$

$\Delta S = ?$

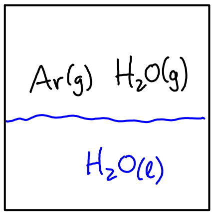
$\Delta G = \Delta H - T\Delta S$

$\Delta S = -22.6\ J/K$

X_{CO_2}

Lecture 5/20

Thursday, May 28, 2009
12:42 AM



$P_v^* \longrightarrow P_v$ $\qquad P_x, P_v, P_v^*$

$\mu_\ell = \mu_g$

$$\int_{P_v^*}^{P_x+P_v} V_{\ell,m}\, dP_\ell = \int_{P_v^*}^{P} V_{g,m}\, dP_g$$

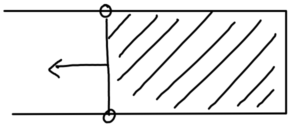
$$RT\ln\left(\frac{P_v}{P_v^*}\right) = V_{\ell,m}\left(P_x + P_v - P_v^*\right)$$

$$P_v = P_v^* \exp\left[\frac{V_{\ell,m}\Delta P}{RT}\right] \simeq P_v^* \exp\left[\frac{V_{\ell,m}P_x}{RT}\right]$$

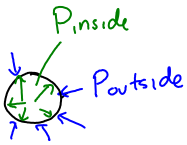
$$\exp\left[\frac{V_{\ell,m}P_x}{RT}\right] = \exp\left[\frac{(0.018L)(P_x)}{(0.083)(298)}\right]$$

10 bar $\quad$ 1.0074

100 bar $\quad$ 1.076



$$dw = \underset{\text{surface tension}}{\gamma}\, \underset{\text{change in surface area}}{d\sigma}$$



$$\frac{dw}{dr} = F = \frac{\gamma\, d\sigma}{dr} = \frac{\gamma 8\pi r\, dr}{dr} = 8\pi\gamma r$$

$\sigma = 4\pi r^2$

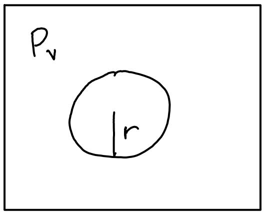
$d\sigma = 8\pi r\, dr$

$$\frac{F_{s.t.}}{4\pi r^2} = \frac{8\pi r\gamma}{4\pi r^2} = \frac{2\gamma}{r}$$

$P_{out} + P_{s.T.} = P_{in}$

constant V, T @ equilibrium

constant V, T @ equilibrium



$$dA_{T,V} = 0 = (\mu_\ell - \mu_g)\,dn_\ell$$

$$\mu_\ell = \mu_g$$

$$dA_{T,V} = dA_\ell + dA_g$$

$$dA_g = -\cancelto{0}{S_g\,dT} - P_g\,dV_g + \mu_g\,dn_g$$

$$dA_\ell = dU_\ell + d(TS)_\ell$$

$$= -S_\ell\,dT - P_\ell\,dV_\ell + \gamma\,d\sigma + \left(\frac{\partial A}{\partial n_\ell}\right)_{T,V,\sigma} dn_\ell$$

$$V_\ell = \frac{4}{3}\pi r^3 \qquad \sigma = 4\pi r^2$$

$$dV_\ell = 4\pi r^2\,dr \qquad d\sigma = 8\pi r\,dr$$

$$d\sigma = \frac{2}{r}\,dV_\ell$$

$$dA_\ell = -S_\ell\,dT_\ell + dV_\ell\left(-P_\ell + \frac{2\gamma}{r}\right) + \mu_\ell\,dn_\ell$$

$$dA_\ell + dA_g = 0 = \left(-P_\ell + \frac{2\gamma}{r}\right)dV_\ell + \mu_\ell\,dn_\ell - P_g\,dV_g + \mu_g\,dn_g$$

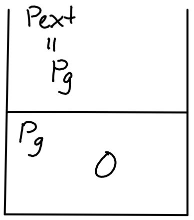
$$dn_g = dn_\ell$$

$$dV = 0 = dV_\ell + dV_g$$

$$dA_{V,T} = \left(P_v - \cancelto{0}{P_\ell} + \frac{2\gamma}{r}\right)dV_\ell + (\cancelto{0}{\mu_\ell - \mu_g})\,dn_\ell = 0$$

$$P_\ell = P_v + \frac{2\gamma}{r}$$

$$P_g = P_v$$



constant P + T

$$dG = 0 \Rightarrow \mu_\ell = \mu_g$$

$$\mu_g = \mu_g^\circ + RT\ln\frac{P_g}{P_0} = \mu_\ell^* + \frac{2\gamma V_{\ell,m}}{r}$$

$$dG_\ell = -S_\ell\,\cancelto{0}{dT} + V_\ell\,dP_\ell + \gamma\,d\sigma + \left(\frac{\partial G}{\partial n_\ell}\right)_{T,P,V} dn_\ell$$

$$\left(\frac{\partial G}{\partial n_\ell}\right)_{T,P} \equiv \mu_\ell$$

$$\left(\frac{\partial G}{\partial n_\ell}\right)_{T,P,\sigma} = \mu_\ell^*$$

$$d\sigma = \frac{2}{r}\, dV_\ell = \frac{2}{r} V_{\ell,m}\, dn_\ell$$

$$dG_\ell = V_\ell\, dP_\ell + \left(\mu_\ell^* + \frac{2V_{\ell,m}}{r}\right) dn_\ell = dG_\ell$$

$$\mu_\ell = \mu_\ell^* + \frac{2\gamma V_{\ell,m}}{r}$$

$$\mu_\ell^* = \mu_g^\ominus + RT\ln\frac{P^*}{P^\ominus} \leftarrow \text{V.P. of bulk liquid}$$

$$RT\ln\left(\frac{P_g}{P_g^*}\right) = \frac{2\gamma V_{\ell,m}}{r}$$

$$P_g = P_g^* \exp\left[\frac{2\gamma V_{\ell,m}}{rRT}\right]$$

Lecture 5/22

Thursday, May 28, 2009
1:06 AM

Missed

Lecture 05/27

Wednesday, May 27, 2009
9:57 AM

Chapter 9

Colligative Property: depends only on amount of solvent and amount of solute.

- ○ Magnitude of the effect depends on nature of solvent and molality (amount of solute in species). Doesn't depend on nature of solute

1. BP elevation
2. FP depression
3. Osmotic pressure

- ○ Chemical potential of substance in solution is lower than pure substance

- Assume
  1. solute is nonvolatile
  2. Solute is insoluble in solid solvent
  3. Solution is ideal solution

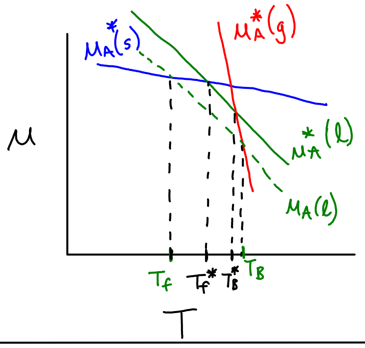
Let A=solvent, B=solute

$$\mu_A(l) = \mu_A^*(l) + RT\ln X_A$$

X_A always <1

so $\mu_A(l) < \mu_A^*(l)$

$$\mu_A(s) = \mu_A^*(s)$$
$$\mu_A(g) = \mu_A^*(g)$$



$$\left(\frac{\partial U}{\partial T}\right)_P = -S$$

Entropic effect

B.P. Elevation

$$\mu_A(g) \equiv \mu_A(l)$$
$$\mu_A^*(g) = \mu_A^*(l) + RT\ln X_A$$

$$RT\ln X_A = RT(1-X_B) = \mu_A^*(g) - \mu_A^*(l) = \Delta G_{A,vap}^{*\,(T=T_B)}$$

$$\ln(1-X_B) = \frac{\Delta G^*_{vap,A}(T_b)}{RT_B} = \frac{\Delta H^*_{A,vap}(T_B)}{RT_B} - \frac{\Delta S^*_{A,vap}(T_B)}{R}$$

assume $X_B \ll 1$ (dilute solution)

replace log by taylor series expansion

$$\ln(1-X_B) \cong -X_B$$

$$\frac{\Delta H^*_{vap,A}}{T_B^*} = \Delta S_{vap,A}$$

$$X_B = \left(\frac{\Delta H^*_{A,vap}}{R}\right)\left(\frac{-1}{T_B} + \frac{1}{T_B^*}\right)$$

$$\Delta T \equiv T_B - T_B^*$$

$$\Delta T << T_B,\ T_B^*$$

$$\frac{1}{T_B^*} - \frac{1}{T_B} = \frac{T_B - T_B^*}{T_B T_B^*} = \frac{\Delta T_B}{(T_B^* + \cancel{\Delta T_B})T_b^*}$$

$$X_B = \frac{\Delta H_{A,vap}}{R}\frac{\Delta T_B}{(T_B^*)^2}$$

$$\boxed{\Delta T_B = \frac{R(T_B^*)^2}{\Delta H_{A,vap}} X_B}$$

$w_B \equiv$ mass solute

$w_A \equiv$ mass solvent

$m_B \equiv$ mol. wt solute

$m_A \equiv$ mol. wt solvent

$$X_B << 1$$

$$X_B = \frac{\mu_B}{\mu_B + \mu_A} \simeq \frac{\mu_B}{\mu_A} = \frac{\left(\frac{w_B}{m_B}\right)}{\left(\frac{w_A}{m_A}\right)}$$

$$X_B = \frac{\Delta H_{vap,A}}{R} = \frac{\Delta T_B}{(T_B^*)^2}$$

$$T_b = \frac{R(T_B^*)^2}{\Delta H_{vap,A}} X_B = \Delta T_B = \frac{R T_B^{*2}}{\Delta H_{vap,A}} m_A \left(\frac{\frac{w_B}{m_B}}{w_A}\right) = K_B m_B$$

F.P. depression

$$\mu_A^*(s) = \mu_A(l) = \mu_A^*(l) + RT\ln X_A$$

$$-X_B = -\frac{\Delta H^*_{fus,A}}{RT_f} + \frac{\Delta S^*_{fus,A}}{R}$$

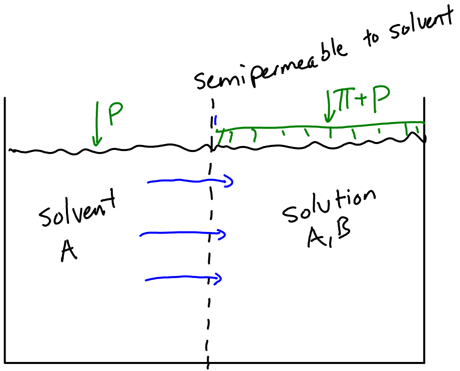
$$\frac{\Delta H^*_{fus,A}}{T_f} = \Delta S^*_{fus,A}$$

$$\Delta T_f <<< T_f, T_f^*$$

$$\Delta T_f = -\left(\frac{R T_f^{*2}}{\Delta H_{fus,A}}\right) X_B$$

$$\Delta T_f = -\underbrace{\left(\frac{M_A R T_f^2}{\Delta H^*_{fus,A}}\right)}_{K_f} m_B = -K_f m_B$$

Osmosis



$$\mu_A^*(l) \overset{?}{>} \mu_A(l)$$

$$\mu_A(l) = \mu_A^*(l) + RT\ln X_A$$

Π = osmotic pressure

$$\mu_A^*(P) = \mu_A(P+\Pi) \quad \text{for equilibrium}$$

$$\mu_A^*(P) = \mu_A(P+\Pi) + RT\ln X_A$$

$$\mu_A^*(P+\Pi) - \mu_A(P) = -RT\ln X_A$$

$$d\mu_T = V_m dP \quad \text{or} \quad \left(\frac{\partial U}{\partial P}\right)_T = V_m$$

$$\mu_A^*(P+\pi) - \mu_A^*(P) = V_{A,m}^*(\pi)$$

$$\Pi = \frac{-RT\ln X_A}{V_{A,m}^*} \overset{\text{always}}{>} 0$$

$$\ln X_A = \ln(1-X_B) \approx -X_B$$

$$\boxed{\Pi = \frac{RT x_B}{V_{A,m}^*}}$$

$$X_B = \frac{n_B}{n_A}$$

$$n_A V_{A,m} \cong V$$

algebra....

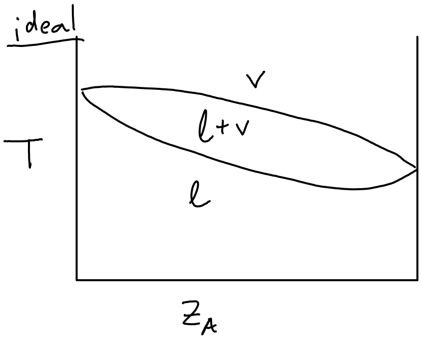
$$\Pi = \frac{RT\mu_B}{V} = [B]RT$$

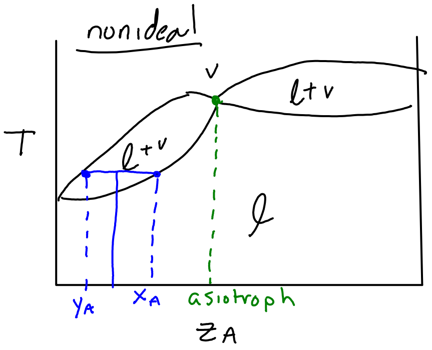
Lecture 06/01

Monday, June 01, 2009
10:01 AM

No lecture Fri (just complete evaluations)

Nonideality





H_2O/EtOH azıotroph
4% H_2O in EtOH

Chemical potential

ideal $\mu_i = \mu_i^* + RT\ln X_i$

real ?

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w \cong [H_3O^+][OH^-] = (a_{H_3O^+})(a_{OH^-})$$

for ideal

a=activity for nonideal

applies to solutions that behave Rault's Law

$$\boxed{\begin{aligned} \mu_i &= \mu_i^* + RT\ln a_i \\ \mu_i &= \mu_i^* + RT\ln \frac{P_i}{P_i^*} \end{aligned}}$$

(ideal gas)

$$a_i = \frac{P_i}{P_i^*}$$

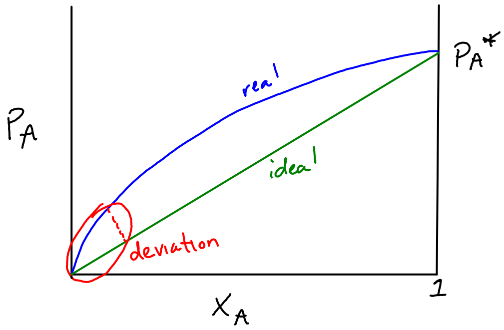
$$a_i = \frac{x_i P_i^*}{P_i^*} = x_i \quad \text{(for ideal solutions)}$$

$\lim a_i = x_i$ for solution that obeys Rault's Law

$a_i = \gamma_i x_i$

activity coefficient (depends on composition: $\gamma_i(x_i)$)

$\gamma_i \to 1$



$$\mu_i = \mu_i^* + RT\ln a_i$$

in dilute solution: $\mu_A = \mu_A^* RT\ln a_A$

$$a_A \neq X_A$$

$$a_A = \gamma_A X_A$$

where γ_A is far from 1

B is solute in dilute solution

$P_B = K_B^H X_B$ Henry's Law

$$\mu_B = \mu_B^* + RT\ln\frac{P_B}{P_B^*}$$

$$\mu_B = \mu_B^* + RT\ln\frac{K_B^H X_B}{P_B^*} = \underbrace{\mu_B^* + RT\ln\left(\frac{K_B^H}{P_B^*}\right)}_{\text{let } = \mu_B^+} + RT\ln X_B$$

$$= \mu_B^+ + RT\ln X_B$$

$$\lim_{\substack{\text{ideal}\\\text{dilute}\\\text{solution}}} a_B = X_B$$

$$a_B = \frac{P_B}{K_B^H}$$

$$\mu_B = \mu_B^+ + RT\ln a_B$$

$$= \left(\mu_B^* + RT\ln\frac{\cancel{K_B^H}}{P_B^*}\right) + RT\ln\frac{P_B}{\cancel{K_B^H}}$$

$$= \mu_B^* + RT\ln\frac{P_B}{P_B^*}$$

$$\lim_{x_B \to 0} a_B = x_B$$

$$a_B \equiv \frac{P_B}{K_B^H}$$

$$a_B = \gamma_B X_B$$

$$\lim_{X_B \to 0} \gamma_B = 1$$

Pure B that obeys Henry's Law ($P_B = K_B^H X_B$)

$\mu_A = \mu_A^* + RT\ln a_A$

$\mu_B = \mu_B^+ + RT\ln a_B$

pure solvent

$= \mu_B^* + RT\ln \frac{K_B^H}{P_B^*}$

A second convention for measuring chemical potential based on molality rather than mole fraction

$$x_B = k\frac{m_B}{m^\ominus}$$

n_B/1kg solvent

$m^\ominus$ = 1mol/kg

unitless constant

$$X_B \simeq \frac{n_B}{n_A}$$

$\mu_B = \mu_B^+ + RT\ln X_B$ for ideal dilute solution

$= \mu_B^+ + RT\ln k + RT\ln\left(\frac{m_B}{m^\ominus}\right)$

define $\mu_B^\ominus = \mu_B^+ + RT\ln k$

$\mu_B = \mu_B^\ominus + RT\ln\left(\frac{m_B}{m^\ominus}\right)$

standard state ≡ ideal dilute solution of B that has molality $= m^\ominus$

$a_B = \gamma_B \frac{m_B}{m^\ominus}$

$\gamma_B \to 1$ as $m_B \to 0$ (as solution becomes more and more dilute)

$\mu_B = \mu_B^\ominus + RT\ln\left(\frac{m_B}{m^\ominus}\right) + RT\ln\gamma_B$

For Solvent

1) $\mu_A = \mu_A^* + RT\ln a_A$ $\qquad a_A = \frac{P_A}{P_A^*} = \gamma_A X_A$

For Solute

1) $\mu_B = \mu_B^+ + RT\ln a_B$ $\qquad a_B = \frac{P_B}{K_B^H} = \gamma_B X_B$

2) $\mu_B = \mu_B^\ominus + RT\ln a_B$ $\qquad a_B = \frac{m_B}{m^\ominus}\cdot X_B$ $\qquad x_B \to 1$ as $m_B \to 0$

What exactly are activities?

$a_A(x_A) = \frac{P_A(x_A)}{{}^{*}}$ $\qquad a_B(x_B) = \frac{P_B(x_B)}{{}^{H}}$

$$a_A(x_A) = \frac{P_A(x_A)}{P_A^*} \qquad a_B(x_B) = \frac{P_B(x_B)}{K_B^H}$$

Not cover for nonvolatile solvent