15

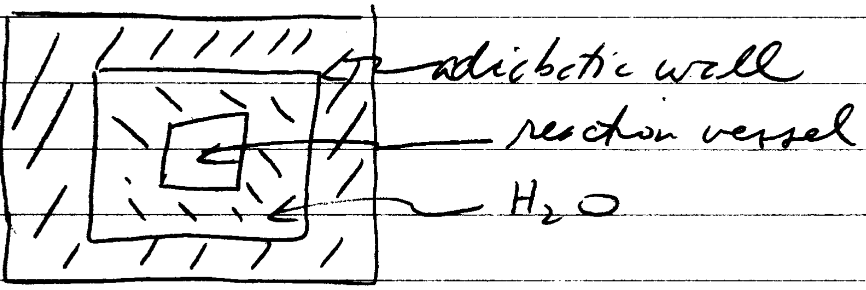
Thermochemical Calculations

Consider a flask with chemicals in it. They react, the flask heats up. Heat flowed in. It can be related to changes in state functions. These changes can be used to predict, whether other reactions - which we want to know about, but don't want to experiment on yet - are possible.

Collections of thermochemical data are VERY useful, for this reason. How are thermochem tables set up? This is the subject of the next lectures.

Calorimetry

The quantitative measurement of heat.



universe reservoir (surr.) system

for system = water + reaction vessel $q = 0$ since adiabatic. If reaction vessel fixed V, then $W = 0$. And

$\Delta U = q = 0$

Now $q = q_{water} + q_{reaction}$. Thus $q_{water} = -q_{reaction}$

Could heat water electrically to get a temperature rise ΔT. And (Calibrate "heat content" of water)

q_{water} = Voltage · Current · time, so known amount

$C_{V(\text{calor})} = q_{\text{water}}/\Delta T$ for calorimeter.

Then let reaction happen. Know $C_V(\text{calor})$ and ~~that~~ measure $\Delta T_{\text{for reaction}}$ Then have

$$-q(\text{reactn}) = C_{V(\text{calor})}\,\Delta T_{\text{for reaction}} \qquad \Delta U = q = 0 \Rightarrow \Delta U_{rxn} = q_{rxn}$$

Very schematic: Actual devices very complicated to achieve above idealization.

Standard states and reference states

We measure $\Delta J^{\text{in lab (transformation)}}$ ($J = H, U$ etc) values. Not J values in thermo. So need values of J in a reference state. Then

$$J = J - J_{ref} + J_{ref} = \underbrace{\Delta J}_{\text{measured}} + J_{ref}$$

To define J_{ref}. lets first define Standard states

Solid or liquid J^{0}_{T} ← 1 atm. pressure ← absolute temp.

Gas J_T^{0} ← 1 atm. ← absolute T and ideal gas

In chemical transformations, don't change elements into other elements (ie, no fission, fusion, decay) $O_2^{16} \rightarrow O_2^{18}$ — T of interest

Thus, elements are always the same. So assign them to have standard values.

15 I USE $\bar{J}$ for molar, LV uses J_m

Enthalpy – $\bar{H}^\circ_{298.15} \equiv \bar{H}^\circ_{298} = 0$ each element in its stable (at this T,p) form.

($\bar{H}^\circ_{298} = 0$ graphite $\neq 0$ diamond since graphite is stable form at this T,p). $Br_2(l) = 0$ $Br_2(g) = 7.39$ $C(graph) = 0$ $C(dia) = .453$
$C(gas) = 171.3$ got units kcal/mol from 47.2 $\times 4.184 \frac{J}{kcal}$

Then $\bar{H}(Tp) = \Delta\bar{H} + 0$

FROM

and $\Delta\bar{H}(Tp) = \int_{298}^{T} \bar{C}_p(T', p=1)\,dT' + \int_1^p [\bar{V}(Tp') - T\bar{V}\alpha]\,dp'$

From experimental values of $\bar{C}_p$ and α, get $\Delta\bar{H}(Tp)$ at any T p.
And need $\bar{V}(T = T_{const}, p)$.

For compounds what is the enthalpy? We define an Enthalpy of formation (Heat of formation), as $\Delta H^\circ_{f,T}$
[form ⇒ from the elements].

$\bar{H}^\circ_T(\text{compound}) - \sum \bar{H}^\circ_T(\text{elements that make up compound}$
– in their standard states)

Since $\bar{H}^\circ_T(\text{elements s.s.}) = 0.$ at $T = 298$

$$\Delta H^\circ_{f,298} = \bar{H}^\circ_{298}(\text{compound})$$

How do we measure $\Delta\bar{H}^\circ_{f,T}$ for a compound? Put it in a calorimeter and measure q_p (heat at constant pressure) for formation from the elements, IN THEIR FORMS(S) THAT ARE STABLE

Ex. $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$

$$\Delta H^\circ_{f,298} = q_p \text{ at } 298^\circ \text{ 1 atm.}$$

Now, the above reaction goes if a pinch of catalyst is added. But, what if you want, say,

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

This won't go at $T = 25°C$ say and $p = 1 atm$.

But add up reactions that will go – and have been measured in a calorimeter. ALL COMBUSTION RXNS – THEY "GO".

combustion reactions – usually ΔH < 0

(1) $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$ $\Delta H^\circ_{298} = -212.8$

(2) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ_{298} = -94.05 \frac{kcal}{mole}$

(3) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ_{~~298~~} = -68.32 \frac{kcal}{mol}$

WHAT WE WANT

$$\Delta \bar{H}^\circ_{f,CH_4} = \bar{H}^\circ_{CH_4(g)} - 2\bar{H}^\circ_{H_2(g)} - \bar{H}^\circ_{C(s)}$$

DON'T PUT ON BARS OR ZERO

DONT WRITE (g), (s)

$$\Delta \bar{H}_1^\circ = 2\bar{H}_{H_2O} + \bar{H}_{CO_2} - \bar{H}_{CH_4} - 2\bar{H}_{O_2} \quad / \quad \bar{H}^\circ_{CH_4} = -\Delta H_1^\circ + 2\bar{H}_{H_2O} + \bar{H}_{CO_2} -$$

$$\Delta \bar{H}_2 = \bar{H}_{CO_2} - \bar{H}_C - \bar{H}_{O_2} \quad / \quad \bar{H}_C = -\Delta \bar{H}_2 + \bar{H}_{CO_2} - \bar{H}_{O_2}$$

$$\Delta \bar{H}_3 = \bar{H}_{H_2O} - \bar{H}_{H_2} - \frac{1}{2}\bar{H}_{O_2} \quad / \quad \bar{H}_{H_2} = -\Delta \bar{H}_3 + \bar{H}_{H_2O} - \frac{1}{2}\bar{H}_{O_2}$$

Thinking $\Delta H^\circ_{f,CH_4} = H_{CH_4} - 2H_{H_2} - H_C$

$$\Delta H^\circ_{f,CH_4} = -\Delta \bar{H}_1^\circ + \Delta \bar{H}_2^\circ + 2\Delta \bar{H}_3^\circ + \overbrace{(2\bar{H}_{H_2O} - 2\bar{H}_{H_2O}) + (\bar{H}_{CO_2} - \bar{H}_{CO_2})(-2\bar{H}_{O_2} + \bar{H}_{O_2} + \bar{H}_{O_2})}^{\text{all cancel}}$$

so $\Delta H^{o}_{f,CH_4} = -\Delta \bar{H}_1^{o} + \Delta \bar{H}_2^{o} + 2\Delta \bar{H}_3^{o}$ ⊙

$= 212.8 - 94.05 - 2(68.32) = -17.89$ kcal/mole

Thus, the $\Delta \bar{H}^{o}_{f,T}$ for a reaction that won't go at usual T and p=1 atm can be obtained from reactions that do go.

This is known as <u>Hess' Law</u> - very important.

Also from

$\Delta \bar{H}_1^{o} = 2\bar{H}_{H_2O} + \bar{H}_{CO_2} - \bar{H}_{CH_4} - 2\bar{H}_{O_2}$ SKIP THIS

$= 2\Delta H^{o}_{f,H_2O} + \Delta H^{o}_{f\,CO_2} - \Delta H^{o}_{f,CH_4} - 2\Delta H^{o}_{f,O_2}$

we can tabulate just heats of formation of various compounds — which are doable — to get heats of other reactions i.e. reaction 1 above. And then add these to get ΔH_f for reactions that don't go.

What have we done in the above? THE ABOVE IS ⊙

$(-1)[\,CH_4 + 2O_2 = 2H_2O + CO_2\,]$

$(+1)[\,C + O_2 = CO_2\,]$

$+2[\,H_2 + \frac{1}{2}O_2 = H_2O\,]$

$= -CH_4 + C + 2H_2 = 0$, or

$CH_4 = C + 2H_2$

Thus, take

$$\Delta \bar{H}_f^\circ = -\Delta \bar{H}_1 + \Delta \bar{H}_2 + 2\Delta \bar{H}_3$$

in agreement with our long calculation

<u>Exothermic</u> - reaction has $\Delta H < 0$
<u>Endothermic</u> " " $\Delta H > 0$

<u>Since $\Delta H = q_p$ for p constant, Then</u>
exo $q_p < 0$ heat given off by system (the reactor), heat absorbed by surroundings (the H_2O) and $T \to T + \Delta T$ with ΔT positive. Thus <u>exo</u> reaction heats surroundings

General notation for reactions [illegible] in tables.

$$\overset{\text{reactants}}{aA + bB} = \overset{\text{products}}{cC + dD}$$

(can have more species, of course).

Then write this as

$$0 = -aA - bB + cC + dD \equiv \nu_A A + \nu_B B + \nu_C C + \nu_D D$$

The ν's are called stoichiometric coefficients

$\nu_i < 0$ reactant $\nu_i > 0$ product $\nu_i = 0$ non-participa

Thus, for this reaction

$$\Delta H_T^\circ = \nu_C \Delta H^\circ_{C,f,T} + \nu_D \Delta H^\circ_{D,f,T} - \nu_A \Delta H^\circ_{A,f,T} - \nu_B \Delta H^\circ_{B,f,}$$

And then for any reaction add others to get desired

L16

16 Temperature Dependence of Reaction Heat

Want to convert $\Delta H^\circ_{T_1} \rightarrow \Delta H^\circ_{T_2}$ where ΔH°_T is for given reaction at T. Then

$$\left.\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \frac{d\Delta H^\circ}{dT} \quad \text{(since } p = 1 \text{ atm.)}$$

And $$= \sum_i \nu_i \frac{dH_i^\circ}{dT} = \sum_i \nu_i C^\circ_{p_i} = \Delta C_p^\circ$$

Then

$$\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1} = \int_{T_1}^{T_2} \Delta C_p^\circ(T)\, dT$$

DONT CONFUSU

$\Delta H \rightarrow$ PROD − REA

S

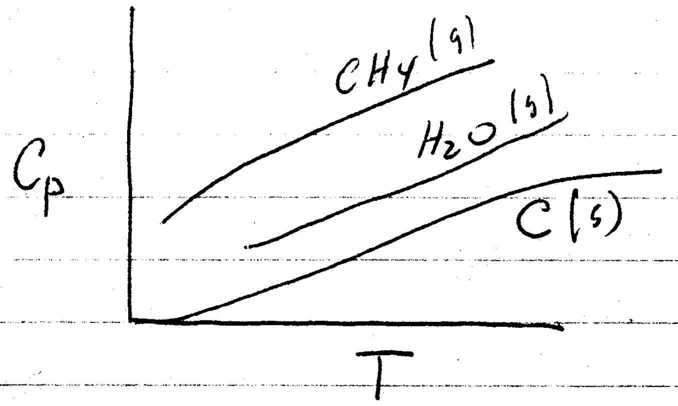
$\Delta H \rightarrow H(2) - H($

or,

$$\left[H^\circ_{T_2}(\text{products}) - H^\circ_{T_1}(\text{products})\right] - \left[H^\circ_{T_2}(\text{reactants}) - H^\circ_{T_1}(\text{reactants}\right.$$

$$= \int_{T_1}^{T_2} C_p^\circ(\text{products})\, dT - \int_{T_1}^{T_2} C_p^\circ(\text{reactants})\, dT$$

Typical heat capacity vs. T curves



Simple curves. Take

$$C_p^\circ = a + bT$$
$$C_p^\circ = a + bT + cT^2$$
$$C_p^\circ = a + bT + dT^{-2}$$

Usually not a big difference between ΔH°_T's for T's not too far away

Example

$$CO + \frac{1}{2} O_2 = CO_2$$

From Levine data ~~[illegible]~~,

$$\Delta H^\circ_{298} = -67.635 \text{ kcal/mol}$$

$$\Delta H^\circ_{1000} = -67.561 \text{ kcal/mol}$$

Very small difference. [could be larger]. But still ~;
See example 5.5

(~~[illegible] case is in ideal gas room T and above heat~~
Cap's are

Third "Law"

For a reversible process we found

$$\Delta S = \int dq_{rev}/T$$

At constant $p = 1$ atm say

$$\Delta S^\circ = \int_{T_1}^{T_2} \frac{C_p^\circ}{T} dT$$

Choose a reference state for entropy at $T_1 = 0$

$$S^\circ(T) = S_0^\circ + \int_0^T \frac{C_p^\circ}{T} dT$$

Need to know S_0°.

For elements in stable form at $T=0$ $S_0^\circ \equiv 0$.

Experimentally found that for chemical reactions – and lets think specifically about formation (from the elements) reactions that

$$\lim_{T\to 0} \left.\frac{\partial \Delta G_f}{\partial T}\right)_p \to 0$$

$$dG = -SdT + VdP$$

$$\left.\frac{dG}{dT}\right)_p = -S$$

but $\frac{\partial \Delta G_f}{\partial T} = -\Delta S_f$, so

$$\lim_{T\to 0} \Delta S_f^\circ \to 0$$

For formation reaction of a compound from its elements, we have

$$\Delta S_f^\circ = S^\circ_{compound} - S^\circ_{elements}$$

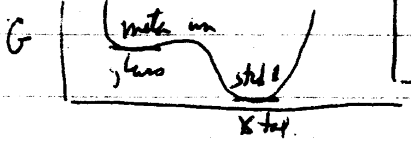
16

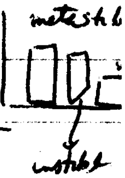
But S°_0 element $= 0$ Thus S°_0 compound $= 0$. (so that $\Delta S^\circ_0 =$

So $S^\circ_0 = 0$ element + compound

Third law - For any isothermal process involving only pure substances, each in internal equi,

$$\lim_{T\to 0} \Delta S \to 0.$$





Pure substances, internal equi ⇒ no randomness (crystalline material – no glasses, say).

Exception NO → T=0   NO NO ‖ ON ON .... so $\Delta S^\circ \neq 0$
But can calculate this residual entropy. And when included stat. mech calc. + exp. agree. $S = k\ln\Omega$ $\Omega = 2^N$ $S = R\ln 2$

From H°_T and S°_T all the other functions follow

$U^\circ_T = H^\circ_T - pV^\circ_T$ where V°_T is molar volume at $T, p=$ of substance. Easy to measure

$A^\circ_T = U^\circ_T - TS^\circ_T \quad \Rightarrow \quad A^\circ_0 = U^\circ_0$

$G^\circ_T = H^\circ_T - TS^\circ_T \quad \Rightarrow \quad G^\circ_0 = H^\circ_0$

$H = U + pV$
$G = A + pV$
$G = U - TS + pV$
$= U + pV - TS = H - T$

For substances that undergo phase change say solid → liquid.

$$S^\circ_T = \int_0^{T_m} \frac{C_p^\circ(\text{solid})}{T}\,dT + \frac{\Delta H^\circ_m}{T} + \int_{T_m}^{T} \frac{C_p^\circ(l)}{T}\,dT$$

need low T C_p behavior ~~Δ Theory provides~~ HARD TO MEASURE | GO
ABSOLUT
Z

Now one can calculate ΔJ_T°, $J = S, U, H, G, A.$, as we did for ΔH_f° i.e. from tabulated values.

Also temp. changes. For example Δ HERE MEANS (PROD.-REAC

skip did previous page

$$\Delta S_{T_2}^\circ - \Delta S_{T_1}^\circ = \int_{T_1}^{T_2} \frac{\Delta C_p^\circ}{T}\, dT \quad \text{at constant } p = 1 \text{ atm}$$

To calculate $\Delta G_{T_f}^\circ$ need either a table of ΔG or get it from ΔH and ΔS.

Consider the example

$$C_8H_{18}(g) + 12.5\, O_2(g) = 8\, CO_2(g) + 9\, H_2O(g)$$

$$\Delta H_{298}^\circ = 8\, \Delta H_{CO_2\, f,298}^\circ + 9\, \Delta H_{H_2O\, f,298}^\circ - \cancel{12.5\, \Delta H_{O_2\, 298}^\circ} - \Delta H_{C_8H_{18}\, f,298}^\circ$$

$\xleftarrow{\quad}$ FORMATION

Same for ΔS_{298}°

Get $\Delta H_{298}^\circ = -1219$ kcal/mol

$\Delta S_{298}^\circ = 100$ cal/K mol.

$$\Delta G_{298}^\circ = [-1219 - (298)(.1)] \text{ kcal/mol} = -1249 \text{ kcal/mol.}$$

This is maximum amount of useful work (work in addn. to pV work of process) obtainable

But 1 mol $C_8H_{18} = 8 \times 12 + 18 \times 1 = 114$ gms $\sim 100\ cm^3 = .1$ lit.

44 mol of $C_8H_{18} \sim 1$ gallon.

Thus ΔG°_{298} octane/gallon $\approx 44 \times 1250 \frac{kcal}{mol} \times \frac{4\ J}{cal}$

$\Delta G^\circ_{298} = 2.2 \times 10^8$ Joules.

Burn it in one second to get 10^8 Joules/sec $= 10^8$ watts $= 100$ megawatts. Roughly $\frac{1}{10}$ nuclear power plant's wattage.

Of course, can't get all of ΔG; combustion is an irreversible process, so infinite time to get all of ΔG. But still, that's why cars run on gasoline.

One tricky point in use of tables : $\overline{\Delta H}^0_{f,298}$, $\Delta\overline{G}^0_{f,298}$, $\overline{S}^0_{298}$

Want ΔG for some reaction. Can get ΔG from ΔH + ΔS where $\Delta H = \Sigma H(\text{prod}) - \Sigma H(\text{reac})$ etc. But Or if $G(\text{prod}) - G(r.)$ listed fine.

But, its $\Delta G_{f,i}$ thats listed, not G_i ..

Nevertheless $\Delta G^0_T = \sum_i \nu_i \Delta G^0_{f,T,i}$

because G is state function ail.

$$\begin{tikzcd}
\text{reactants} \arrow[rr, "①"] \arrow[dr, "②"'] & & \text{products} \\
& \text{elements in std. states at } T \arrow[ur, "③"'] &
\end{tikzcd}$$

can get from $R \to P$
by ② + ③
② $= -\Delta G_f(\text{reactants})$
③ $= +\Delta G_f(\text{products})$

$-\Delta G_f(\text{reactants}) + \Delta G_f(\text{prod}) = \Delta G_T$ ① - ②

If want $\overline{G}$ of some compound. Its not $\Delta G_{f,298,i}$ of table

But it is $\overline{G} = \Delta\overline{H}_f - T\overline{S}$

↳ $\overline{H}$ since $\overline{H}(\text{element}) = 0$ at 298

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17 So far we have only discussed *closed* systems i.e.

$$dU = \bar{d}q + \bar{d}w \qquad dS \geq \bar{d}q/T$$

no matter exchange. If matter exchanged, then heat transfer is ambiguous because matter carries energy with it.

Also $dU = TdS - pdV$

not applicable to *closed system* with irreversible composition change. If isolated $dU=0$, $dV=0 \Rightarrow dS=0$. But $dS > 0$ if *chem* reaction or *diffusive* mixing

[DYC GOOD ABOUT THIS] Also $dG=0$ if T,p fixed But if double system can do work
This arises because we implicitly assume that two variables fix state of system. This is only true for bodies of fixed composition. Thus must introduce mole numbers.

Consider *one phase* with k different substances with mole numbers $n_1 \ldots n_k$

$$U = U(S\, V\, n_1 \ldots n_k)$$

Really should be G T,p well define

$$dU = \left.\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left.\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_{i=1}^{k} \left(\frac{\partial U}{\partial n_i}\right)_{\substack{S,V,n_j \\ j \neq i}} dn_i$$

[EXPLAIN NOTATION].

Since $\left.\frac{\partial U}{\partial S}\right)_{V, n_i}$ has all n_i constant $= T$

$$\left.\frac{\partial U}{\partial V}\right)_{S, n_i} = -p$$

DEFINE $\mu_i = (\partial U/\partial n_i)_{S,V,n_j \; j \neq i}$ CHEM. POT.

17

(introduced by Willard Gibbs). Facilitates discussion of op
systems, or closed ones with composition changes.

$$\mu_i = \frac{U(n_i+dn_i, \dots)_{V,S\dots} - U(n_i)_{V,S\dots}}{dn_i}$$

how to keep V, S fixed? For V, just readjust p. For S, a
carries a certain amount of S with it, then take it out by
contact with heat bath, remove / $dq = T\,dS$.

$\Delta T \Rightarrow$ direction of heat flow
$\Delta p \Rightarrow$ direction of piston movement
$\Delta\mu \Rightarrow$ direction of chem reaction, or diffusion of a subs
from one phase to another (we will show)
KNOWING THESE DIRECTIONS VERY IMPORTANT [MIXING]

<u>Another form of μ_i</u>

$$dG = \left.\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left.\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum_{i=1}^{k} \left.\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

Again for p, n_i fixed $\left.\frac{\partial G}{\partial T}\right)_{p,n_i} = -S$ $\left.\frac{\partial G}{\partial p}\right)_{T,n_i} = V$.

$$dG = -S\,dT + V\,dp + \sum \mu_i\,dn_i$$

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$

Recall that G change gives amount of work other th
pV work doable by system, μ_i gives this amt

17

for dn_i added at fixed T, p. For example, electrochem cell adding substance increases cells ability to do electrical work.

Is $\mu_i \equiv \partial U/\partial n_i)_{S,V,n_j} = \partial G/\partial n_i)_{T,p,n_j}$?

Add $d(pV - TS)$ to both sides of $dU = TdS - pdV + \underline{\mu}\cdot d\underline{n}$

$\mu_i = \partial$

$$d(U + pV - TS) = TdS - pdV + d(pV - TS) + \underline{\mu}\cdot d\underline{n}$$
$$dG = -SdT + Vdp + \underline{\mu}\cdot d\underline{n}$$
$$\Rightarrow \quad \mu_i = \partial G/\partial n_i)_{T,p,n_j}$$

New Gibbsians dU -- dG

$$dA = -SdT - pdV + \underline{\mu}\cdot d\underline{n}$$
$$dH = TdS + Vdp + \underline{\mu}\cdot d\underline{n}$$

$$\mu_i = \partial G/\partial n_i)_{T,p..} = \frac{\partial U}{\partial n_i}\Big)_{S,V,n_j} = \frac{\partial H}{\partial n_i}\Big)_{S,p,n_j} = \frac{\partial A}{\partial n_i}\Big)_{T,V,n_j}$$

Comments

1. μ_i is intensive - ratio of extensive quantities

2. if n_i const. during process $\mu_i dn_i = 0$
   if n_i diminishes " " $dn_i < 0$

3. $$dU = \underbrace{TdS}_{q} \underbrace{- pdV}_{W} + \underbrace{\sum \mu_i dn_i}_{W_{\text{chem, bio}}}$$ reversibly / closed system

if open can't sep heat TdS & work

Can do work without pV change. ↳ i.e. lift a weight still without pV change

↑ Ex. O.K. Interpretation changes

FOR REVERSIBLE

At equilibrium $dG = đw_{other}$ (T, p fixed).

Then, since G minimum at equi $dG = 0$ and

$$đw_{other} = \sum_{i=1}^{n} \mu_i \, dn_i = 0$$

NO MATERIAL FLOW

Thus $\sum_i \mu_i \, dn_i = 0$ at equi, fixed T, p., closed!!

Same conclusion for dU, dH, dA eq. at their fixe quantities,

Thus, in general $\sum_i \mu_i \, dn_i = 0$ closed, equ (chem. reac.).

Also: At equi - so rev. processes.

$\underbrace{dG = -SdT + V}_{\text{to zero.}}dp \Rightarrow \sum_i \mu_i \, dn_i = 0$

$\boxed{\text{One component: } \mu = \frac{\partial G}{\partial n} = \bar{G} = G/n}$

Consider chem. reaction explicitly now, at equilibrium

$$\sum_i \nu_i A_i = 0$$

B Define extent of reaction ξ (Xi) via (units of n_i

$n_i = n_{i,0} + \nu_i \xi$ $\quad n_{i,0}$ initial amounts

Then in reaction, ξ is same for all n_i changes. ie

$$2C + O_2 = 2CO$$

$\nu_C = -2 \quad \nu_{O_2} = -1 \quad \nu_{CO} = 2$

$n_{O_2,0} \qquad n_{CO,0}$

$n_C = n_{C,0} - 2\xi \quad n_{O_2} = n^{\circ}_{O_2} - \xi \quad n_{CO} = n_{0,CO} + 2\xi$

since 2 molecules of C react with 1 of O_2 to give 2 C

now $dn_i = \nu_i \, d\xi$

(plenty of molecules in dn_i so can treat it as continuous, diff.

The equi. condition is $\sum \mu_i dn_i = 0$, Thus

$$\sum \mu_i dn_i = \left(\sum_i \mu_i \nu_i\right) d\xi = 0 \Rightarrow$$

$$\sum_{i=1}^{k} \nu_i \mu_i = 0 \quad \text{(closed system).} \circledast$$

i.e. just replace species A_i by their respective μ_i to get condition of reaction equi

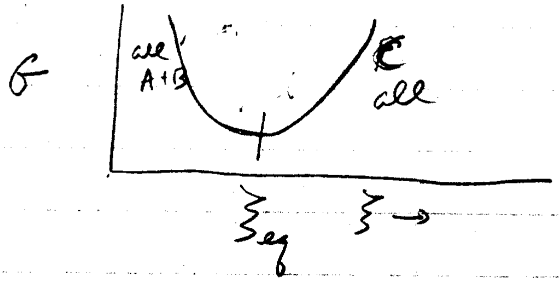
⊛ Levine says (~~cf eq.~~ 4.111) PV work only – but of course reaction itself does work.

For const. T, p, $dG = \sum \mu_i dn_i$

$$dG = \left(\sum_i \mu_i \nu_i\right) d\xi, \quad dG/d\xi = \left(\sum_i \mu_i \nu_i\right) \equiv -\mathcal{A}$$

Since G minimized at equi, dG = 0,

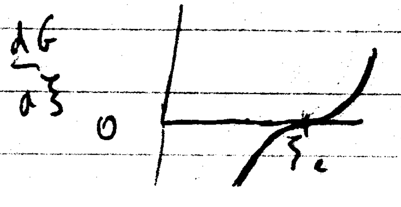
$\mathcal{A}$ Affinity De Donder

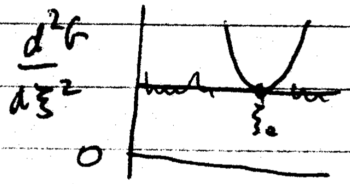


A + B → C

equi A, B and C.

Now lets explore connection between G and equi. constant of a reaction. And how to quantitatively obtain equi constants.





min value is > 0

Reaction Equilibrium in Ideal Gas Mixtures.

For a one component gas, we have from

$$dG = -SdT + Vdp + \mu dn \qquad G = G(Tpn)$$

$$dG = VdP \qquad T \text{ fixed} \quad n \text{ fixed}$$

If we consider a fixed temperature then integrate w/ $V = nRT/p$ ideal gas

$$dG = \frac{nRT}{p}dp$$

$$G(\overset{T,}{p_2}) = G(\overset{T,}{p_1}) + nRT\ln(p_2/p_1)$$

If we do this for ONE MOLE

$$\bar{G}(\overset{T,}{p_2}) = \bar{G}(\overset{T,}{p_1}) + RT\ln(p_2/p_1)$$

Then, noting that G is extensive, so $G = n\bar{G}$

$$\frac{\partial G}{\partial n} = \mu = \bar{G}.$$

Thus

$$\mu(\overset{T,}{p_2}) = \mu(\overset{T,}{p_1}) + RT\ln(p_2/p_1) \qquad \text{ideal gas } T \text{ fi}$$

one comp, 1 mol

Now fix $p_1 = 1\,atm$. Then *define*

$$\mu^0(T) = \mu(\overset{T,}{p_1} = 1atm, \cancel{T})$$

Thus $\mu(Tp) = \mu^\circ(T) + RT\ln(p/1\text{atm}) \equiv \mu^\circ(T) + \underbrace{RT\ln(p_i)}_{\text{IMPLICIT IS DIV BY 1 AT.}}$

For an ideal gas mixture, the pressure of a given component is p_i and is the same pressure the gas wou. have if it were alone. Since ideal gas ⇒ molecules don't know others presence, we have

$$\mu_i(Tp) = \mu_i^\circ(T) + RT\ln(p_i) \qquad i = A, B, \ldots \text{ species.}$$

For reaction equilibrium, we have, for the

Example $A \leftrightarrow B$ isomerizat T, p fixed

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$\nu_A = -1 \quad \nu_B = +1$$

Write $dn_A = -d\xi$ then $dn_B = +d\xi$ clearly

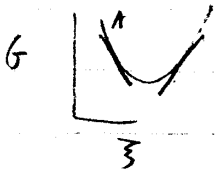
Then

$$dG = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi$$

$$\left.\frac{dG}{d\xi}\right)_{PT} = \mu_B - \mu_A$$

When $\mu_A > \mu_B$ reaction proceeds from A to B

$\mu_A < \mu_B$ " " " B → A



Thus, at equil, $\left.\frac{dG}{d\xi}\right)_{PT} = 0$ and

$\mu_B = \mu_A$ general CONDITION OF MAT EQUI FOR RXN (TA=TB FOR THERMAL) WHY μ SO IMPORTA

Now ideal gas

Then $-(\mu_B^\circ - \mu_A^\circ) = RT\ln(p_B/p_A)_{eq}$ And write

$$\Delta G^\circ_T = \mu^\circ_B - \mu^\circ_A = -RT\ln(P_B/P_A)_{eq}$$

Define $K_p^\circ(T) = (P_B/P_A)_{eq}$ $\boxed{\Delta G^\circ_T = -RT\ln K_p^\circ}$

↳ BECAUSE [ ] is measured as pressure KEY CONNECTION

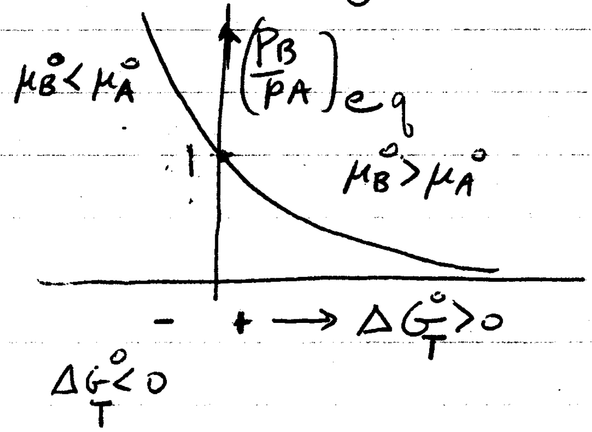
Thus ~~$\Delta G^\circ_T = -RT\ln(P_B/P_A)_{eq}$~~

Or $(P_B/P_A)_{eq} = e^{-\Delta G^\circ_T/RT}$

Thus plotting

As $\Delta G \to -\infty$ partial pressure of B in mixture increases exponentially. Equilibrium lies toward B.

[NOT extent plot, this is equi point versus ΔG°_T, the standard state chem pot. diff.]



In general for

$$aA + bB + .. \to cC + dD + \cdots$$

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

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

OTHER UNITS:

Let us be general for a moment and consider *any* process at fixed T, p. Then, we found that $\Delta G \leq 0$ was condition to determine the direction of change.

But $\Delta G = \Delta H - T\Delta S$ (T, p) fixed. Then

ΔH	ΔS	$-T\Delta S$	Spont.	ΔG
+	−	+	no	>0
−	+	−	yes	<0
−	−	+	maybe	<0 if $\lvert\Delta H\rvert > \lvert T\Delta$
+	+	−	maybe	<0 if $\lvert T\Delta S\rvert > \Delta$

($\Delta H = đq$ at P fixed

$\Delta H < 0 \Rightarrow$ system gives up hea

For chemical reactions, ΔH negative (exothermic reaction) is favored by formation of strong chemical bonds. ΔS positive favored by increase in states available to a system. Example

$$N_2 \rightarrow 2N$$

$\Delta H > 0$ endothermic – must put in energy (add heat) to break N_2 bound. But form 2 molecules from, so $\Delta S > 0$. Then equilibrium is compromise between these two competing tendencies. However, which wins depen on T. We see that increasing T favors formation of N atoms. The T rise is equivalent to an increase of energy content of the system, and this energy increment will be most "randomized" if, in addition to just heating the species, the reaction is displaced to the side of taking up this energy – toward N atoms. Thus T increase causes composition to change in the endothermic direction (Le Chatelier's Principle).

To see this quantitatively, lets return to IDEAL GAS equilibrium and see how it changes with T. From the Gibbs-Helmholtz equation [you prove in problem set]

$$\left[\frac{\partial(\Delta G^\circ/T)}{\partial T}\right]_p = -\frac{\Delta H^\circ}{T^2}$$

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

$$\left.\frac{\partial \ln K_p^\circ}{\partial T}\right)_p = \boxed{\frac{\Delta H^\circ}{RT^2} = \frac{d\ln K_p^\circ}{dT} \quad \text{van't Hoff eq.}}$$

⊛ DO [illegible], NEXT PAGE,
Le CHATELIER, HERE

Note that the ideal gas enthalpy is independent of pressure $\Delta H = \Delta U + \Delta(pV) = \Delta U + nR(\Delta T)$ and this jibes with R.H.S.

Since v. Hoff eq. is ordinary derivative can integrate it.

Also $\dfrac{d\Delta H^\circ}{dT} = \Delta C_p^\circ = \Delta a + (\Delta b)T + (\Delta c)T^2$

$\Delta H(T) - \Delta H_0 = \Delta a\, T + \frac{\Delta b}{2} T^2 + \ldots$ (ΔH_0 is int. const.)

Thus $\dfrac{d\ln K_p^\circ}{dT} = \dfrac{\Delta H_0}{RT^2} + \dfrac{\Delta a\, T}{RT^2} + \dfrac{\Delta b}{2}\dfrac{T^2}{RT^2}$

Int. again

$$R\ln K_p^\circ = C - \frac{\Delta H_0}{T} + \Delta a \ln T + \frac{\Delta b}{2} T + \cdots$$

C is also an integration constant.

If you know ΔH_{298}. Then get ΔH_0 from first integration.

get C from final answer from <u>one</u> value of K_p°.

Returning to van't Hoff

$$\text{If } \Delta H^\circ > 0 \Rightarrow \frac{d\ln K_p^\circ}{dT} > 0 \quad \text{so if } \delta T > 0$$

$\Rightarrow d\ln K_p^\circ > 0$. Verifying our example $N_2 \to 2N$.

<u>Le Chatelier in general</u> [IMPORTANT SINCE MAX YIELD ETC]

From $$\frac{dG}{d\xi} = \left(\sum_i \mu_i \nu_i\right)$$

and define

$$\mathcal{A} = -\sum_i \mu_i \nu_i \qquad \mathcal{A} \equiv \text{Advancement.}$$

$$\frac{\mathcal{A}}{RT} = -\frac{\Delta G^\circ}{RT} - \ln Q \qquad Q \equiv \prod_i p_i^{\nu_i}$$ REACTION QUOTIENT

N.B. pressures of Q are <u>not</u> equilibrium pressure ν

Only when $\mathcal{A}=0$ are the p_i's equil and is

$$Q_{eq} = \prod_i p_{i\,eq}^{\nu_i} \qquad \mathcal{A}=0$$

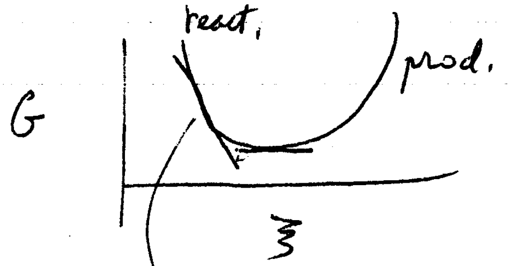
$$\frac{\mathcal{A}}{RT} - 0 = -(\ln Q - \ln Q_{eq}) = \ln Q_{eq}/Q$$

$$\frac{\mathcal{A}}{RT} = \ln Q_{eq}/Q \qquad Q_{eq} = K_p^\circ$$

Le Chatelier's principle is contained above

If . $Q_{eq} > Q$ then $\mathcal{A} > 0$ and reaction goes to the right .

$$\frac{dG}{d\xi} = -\mathcal{A}$$



$\frac{dG}{d\xi} < 0$ $\quad \mathcal{A} > 0$ and react → prod. reac. goes to the right.

All the cases in Levine can be written this way.
Note that since $Q_x = [Q_p^\circ]^{-\Delta|\nu|}$

where Q_x is $\equiv \prod (x_i)^{\nu_i}$ $\quad$ x_i are mole fractions

then and $\Delta|\nu| = \sum \nu_{i,g}$ we have
$$\mathcal{A} = RT \ln (Q_{x\,eq}/Q_x)$$

LEVINE AN. SPEC
CASES Ī YOUR $\mathcal{A}$
EXP., EASY TO UNDERSTAND

Phase Equilibrium

Several phases in thermal and mechanical equilibrium. Index phases with greek superscripts $\alpha, \beta \ldots$ Thus

$$\mu_i^\alpha = \text{chem pot. of species } i \text{ in phase } \alpha.$$

Consider the Gibbs free energy at fixed T and p. We have

$$dG = \sum_i \sum_\alpha \mu_i^\alpha \, dn_i^\alpha \le 0 \qquad (T, P \text{ fixed})$$

Let amount dn_i flow from phase $\beta \to \delta$, then

$-dn_i^\beta = +dn_i^\delta$ with $dn_i^\delta > 0$

Keep all n_j^α fixed $j \neq i$ $\alpha \neq \beta, \delta$. Then

$$dG = \mu_i^\beta \, dn_i^\beta + \mu_i^\delta \, dn_i^\delta \le 0$$

$$= (\mu_i^\delta - \mu_i^\beta) \, dn_i^\delta \le 0$$

Since $dn_i^\delta > 0$

$$\mu_i^\delta - \mu_i^\beta \le 0 \Rightarrow \mu_i^\delta \le \mu_i^\beta$$

And, at equilibrium: $\mu_i^\beta = \mu_i^\delta$

Conclude: Any substance in spontaneous process tends to pass from region of "high chemical potential to region of lower chemical potential — hence name chem pot.

Conclude: The condition of material equi between phases is that each species shall have an equal value of chem pot in all phases ⊕ between which the substance can freely pass ⊛.

⊗ For semi-permeable membrane between phases not true.
- Important for osmosis (Mitchell chemi-osmotic hypothesis)

⊕ Since β, δ arbitrary - holds for all the phases

Exception! If substance initially absent from phase δ.
Now $\mu_j^\delta \neq 0$, we can transfer stuff in $\mu_j^\delta = \frac{\partial G^\delta}{\partial n_j^\delta}\Big)_{T,P,--}$.

If $\mu_j^\beta > \mu_j^\delta$ stuff flows from $\beta \rightarrow \delta$.

If $\mu_j^\delta > \mu_j^\beta$ clearly no flow - no change, stay in equi.
Thus, when component j absent from δ

$\mu_j^\delta \geq \mu_j^\beta$ phase equi j absent from δ.

The phase rule

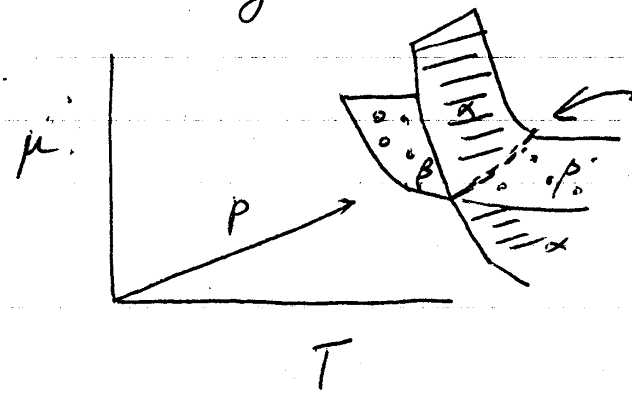
Equilibrium of a pure substance. Consider two phases α, β. Then

$$T_\alpha = T_\beta$$
$$p_\alpha = p_\beta$$
$$\mu_\alpha(T_\alpha p_\alpha) = \mu_\beta(T_\beta p_\beta)$$

In each phase $T_\alpha P_\alpha$ fix all other *intensive* properties. In particular μ_α.

Of the 4 variables $T_\alpha p_\alpha T_\beta p_\beta$ which fix state completely, only one independent: *One Degree of Freedom*. So if we fix T_α, other phase has same temperature, the phase pressures will be the same and be fixed by the eq. of state.

Consider Figure 1



along this line 3 equations are satisfied.

Consider now *3* phases in equilibrium. Then

$$T_\alpha = T_\beta = T_\gamma \quad , \quad p_\alpha = p_\beta = p_\gamma \quad , \quad \mu_\alpha = \mu_\beta = \mu_\gamma$$

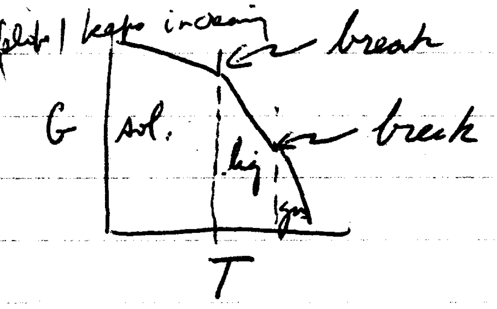
Of the 3 $T_\alpha p_\alpha$ pairs = 6, 6 relations so NO DEGREES OF FREEDOM.

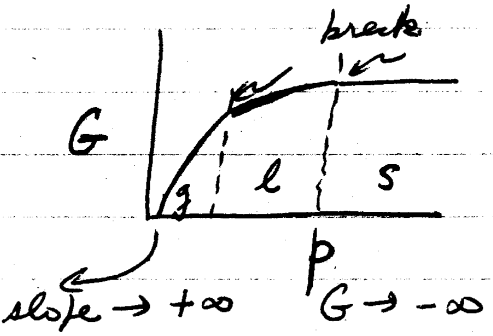
Third surface. Gives intersection at a *point*.

Phase diagram (one component), $\overset{\circ}{S}(T) = \int_0^T \frac{\overset{\circ}{C_p}(T)}{T}\,dT + \frac{\Delta H_m}{T} + \int \ldots$

From $\left.\frac{\partial G}{\partial T}\right)_p = -S$ $\left.\frac{\partial G}{\partial p}\right)_T = V$ for a given phas

we know that as $T \uparrow G \downarrow$, as $p \uparrow G \uparrow$ (S, V pos





$p \to 0$ gas = id

$dG = \int V\,dp \sim \int \frac{d}{p}$

$G \sim \ln p \to -\infty$

At sol-liq trans. $G_s = G_\ell$ but $S_s < S_\ell$, so G continuous but slope has abrupt change.

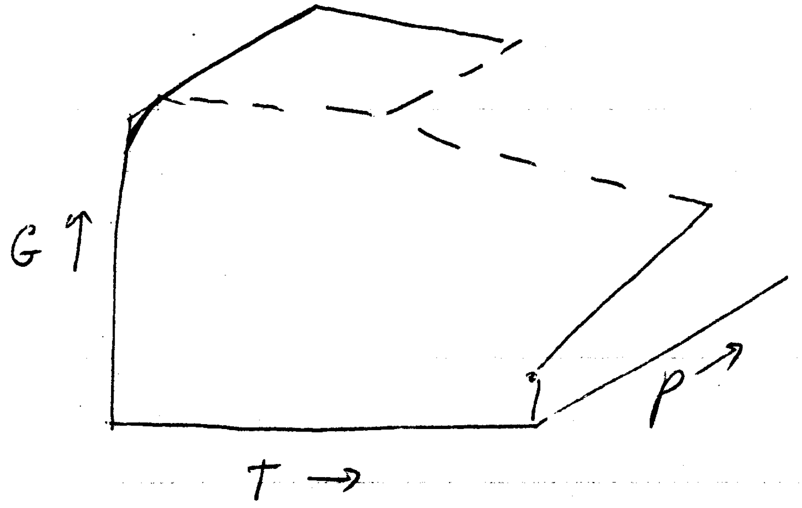


Fig 6-2 pg 23~~5~~
Dye

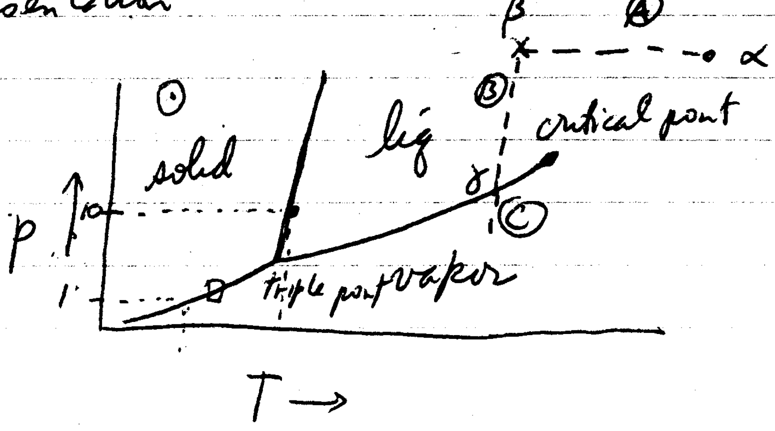
See last page

Lines of intersection are for phase coexistence
3 phases meet at triple point

As p increases molar volume of gas decreases faster than molar volume of liquid. So, reach a point where $\left.\frac{\partial G}{\partial p}\right)_T(\ell) = \left.\frac{\partial G}{\partial p}\right)_T(g)$, where

$V(\ell) = V(g)$. Thus "crease" in surface disappears at this and all points of higher pressure (for a fixed T). The point – pVT where this occurs is the critical point – $p_c T_c$. Here, can't tell difference between gas and liquid.

From projection onto plane of pT get conventional representation



① 2 degrees of freedom need to fixed pT to fixed the
□ 1 degree of freedom. Fix T so then p_1 – fixed
triple pT

for CO_2 at p = 1atm T = −78 °C solid + gas coexist. Thus, solid CO_2 sublimes when it is warmed up to −78° (Dry ice)
At p = 10 atm, T = −56.6°C solid CO_2 will melt to liquid CO_2.

Above $p_c T_c$ we start from point α say. Only one fluid phase exists. If we reduce the T to β we have a fluid, but is it ~~not~~ a gas. How do we know? Reduce p to γ. Then gas + liq in equi with gas. Can't reduce p further until all of liquid phase disappears. Drop further, all gas.

[CRITICAL OPALESCENCE / GROWTH OF CORRELATIONS / LARGE FLUC / MACROSCOPIC ORDER

The phase rule

Degrees of Freedom: Number of independent intensive variables required to specify system state,

Consider c species and p phases. Equi given by $PT\{x_i\}$. No chem reac. All species each phases

Each phase composition given by c-1 relation $\sum_{i=1}^{c} x_i = 1$, Also T, =C+

p phases. Also T, P

number of variable = $p(C+1)$

at equi $(P-1)$ eq. of T $T_\alpha = T_\beta = \cdots$

$p-1)$ eq of P $P_\alpha = P_\beta = \cdots$

c relations

$(p-1)$ eq of μ_1 $\mu_{1\alpha} = \mu_{1\beta} = \cdots$

$(P-1)$ eq of μ_2 $\mu_{2\alpha} = \mu_{2\beta} = \cdots$

$\vdots$

$(p-1)$ eq of μ_C $\mu \cdots$

number of eqs. between variables. $p-1)(C+2)$

Thus f = deg. of freedom = number of variable − number of eqs betw

$$f = p(C+1) - p-1)(C+2) = C+2-p$$

$$\boxed{f = C+2-p}$$ Gibbs' phase rule

If a given component j is absent from a certain phase δ then we reduce by one the number of composition variables required to fix the state. But, also one of the relations is gone

$$\mu_j^{\delta} \overset{?}{=} \mu_j^{\alpha} = \mu_j^{\beta} \ldots$$

Thus no change.

Now, reactive components. If r independent reactions, then reduce f by r. (not pr, since if in equi in one phase, then equi in all)

If other constraints such as electroneutrality of ionic solution subtract: then

$$f = c - p + 2 - r - a$$

or, defining $c_{ind} = c - r - a$

$$\boxed{f = c_{ind} - p + 2}$$

Deciding c_{ind} can be tricky!

An example

Acetic acid in water : 5 species H_2O, HAc, H^+, OH^-, Ac^-

Two dissociation reactions

$$H_2O \rightarrow H^+ + OH^-$$
$$HAc \rightarrow H^+ + Ac^-$$

Electroneutrality $x(H^+) = x(OH^-) + x(Ac^-)$ $\quad$ x = mole fraction

$c = 5$, $r = 2$, $a = 1$ $\qquad c_{ind} = 5-2-1 = 2$

$f = 4 - p = 3$, here.

So T, P, $x(HAc)$ specify the system.

If we would consider 6 species $H_2O, HAc, H^+, OH^-, Ac^-, O^=$ then add other reaction

$$H_2O \rightarrow 2H^+ + O^=$$

So $c = 6$ $\quad r = 3$ $\quad a = 1$ $\quad$. $x(H^+) = x(OH^-) + x(O^=) + x(Ac^-)$]

$c_{ind} = 6-3-1 = 2$ again.

[why not $OH^- = O^= + H^+$
$= [H_2O = 2H^+ + O^=] - [H_2O = H^+$
not ind.

One component system. What is slope dP/dT of the two phase equi line on pT diagram: Clapeyron Equation

Return to picture of line of intersection of the α and β phases. If μ_α' and μ_β' are particular values, then

$$\mu_\alpha' = \mu_\beta'$$

At a close by point, we have

$$\mu_\alpha' + d\mu_\alpha = \mu_\beta' + d\mu_\beta$$

(since still at equi). And, since $\mu_\alpha' = \mu_\beta'$,

$$d\mu_\alpha = d\mu_\beta$$

Now

$$d\mu_\alpha = \left.\frac{\partial \mu_\alpha}{\partial T_\alpha}\right)_{p_\alpha} dT_\alpha + \left.\frac{\partial \mu_\alpha}{\partial p_\alpha}\right)_{T_\alpha} dp_\alpha$$

L22

22

L21

and $$d\mu_\beta = \left.\frac{\partial \mu_\beta}{\partial T_\beta}\right)_{p_\beta} dT_\beta + \left.\frac{\partial \mu_\beta}{\partial p_\beta}\right)_{T_\beta} dp_\beta$$

But since $p_\alpha' = p_\beta'$, $T_\alpha' = T_\beta'$, $dp_\alpha = dp_\beta$, $dT_\alpha = dT_\beta$

so

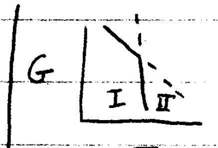
$$\left.\frac{\partial \mu_\alpha}{\partial T}\right)_p dT + \left.\frac{\partial \mu_\alpha}{\partial p}\right)_T dp = \left.\frac{\partial \mu_\beta}{\partial T}\right)_p dT + \left.\frac{\partial \mu_\beta}{\partial p}\right)_T dp$$

For a pure substance $\mu_\alpha = \bar{G}_\alpha$ $\mu_\beta = \bar{G}_\beta$, so

noting $\bar{S}_\alpha = -\left.\frac{\partial \mu_\alpha}{\partial T}\right)_p$ $\bar{V}_\alpha = \left.\frac{\partial \mu_\alpha}{\partial p}\right)_T$,

$$-\bar{S}_\alpha\, dT + \bar{V}_\alpha\, dp = -\bar{S}_\beta\, dT + \bar{V}_\beta\, dp$$, or

$$\frac{dp}{dT} = \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta}$$



$T < T_c$ $\frac{\partial G^{II}}{\partial T} < \frac{\partial G}{\partial T}$

$T > T_c$ $\frac{\partial G^{II}}{\partial T} < \frac{\partial G}{\partial T}$

$S^{II} > S^{I}$ all $T \Rightarrow \Delta$

Furthermore $\bar{S}_\alpha - \bar{S}_\beta = \Delta\bar{H}/T$ where $\Delta\bar{H}$ is the latent of the transition. Thus

$$\frac{dp}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}} = \frac{\Delta H}{T\Delta V}$$ (the extensive ratio cancels n value

Clapeyron Eq.

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$ Clausius - Clapeyron equation

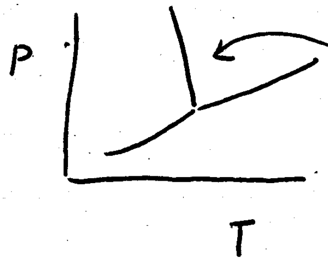
Must have single phase - so μ_α μ_β are only f^ns of $T_\alpha p_\alpha$, T_β

(Note that for H_2O, say, we can still consider dissociation
since, at the end, cond = 1 still.)

Thus $f = 1$. And a ΔT will fix the Δp. Thus ordinary der dp

L22

23



H_2O

$\left.\begin{array}{l}\Delta H_{vap}\\ \Delta H_{melt}\\ \Delta H_{sub}\end{array}\right\} > 0$ $\Delta V > 0$ (almost)

for H_2O $\Delta V < 0$

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$ Clapeyron

---

for gas liq or gas solid:

① $V_g >> V_{l,s}$

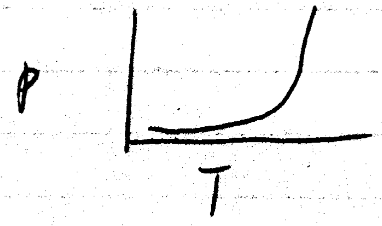
② $V_g = \frac{RT}{p}$ ideal

} away from crit point

③ $\Delta \bar{H}$ const.

$$\ln \frac{p_2}{p_1} = -\frac{\Delta \bar{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ Clausius - Clapeyron

Exponential increase of pressure with temperature.
(Don't heat things in sealed containers)



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32''

Phase Rule Example.

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

start with all $CaCO_3(s)$.

$c = 3 \quad r = 1 \quad$ i.e. $\mu[CaCO_3] = \mu[CaO] + \mu[CO_2]$

are there other restrictions among intensive variables?

Since we start w̄ all $CaCO_3(s)$ we do produce a known amount of product so possible mole fraction restrictio

But need more info for this problem. How many phases.
If $CaCO_3(s)$ + $CaO(s)$ are two solid phases, then

$$x[CaCO_3(s)] = 1 \text{ in phase } CaCO_3(s)$$

$$x[CaO(s)] = \left.\begin{array}{l} 1 \\ 0 \end{array}\right\} \begin{array}{l} \text{phase } CaO(s) \\ \text{phase } CaCO_3(s) \end{array}$$

Since these mole fraction are fixed, not variables, no further restriction, then

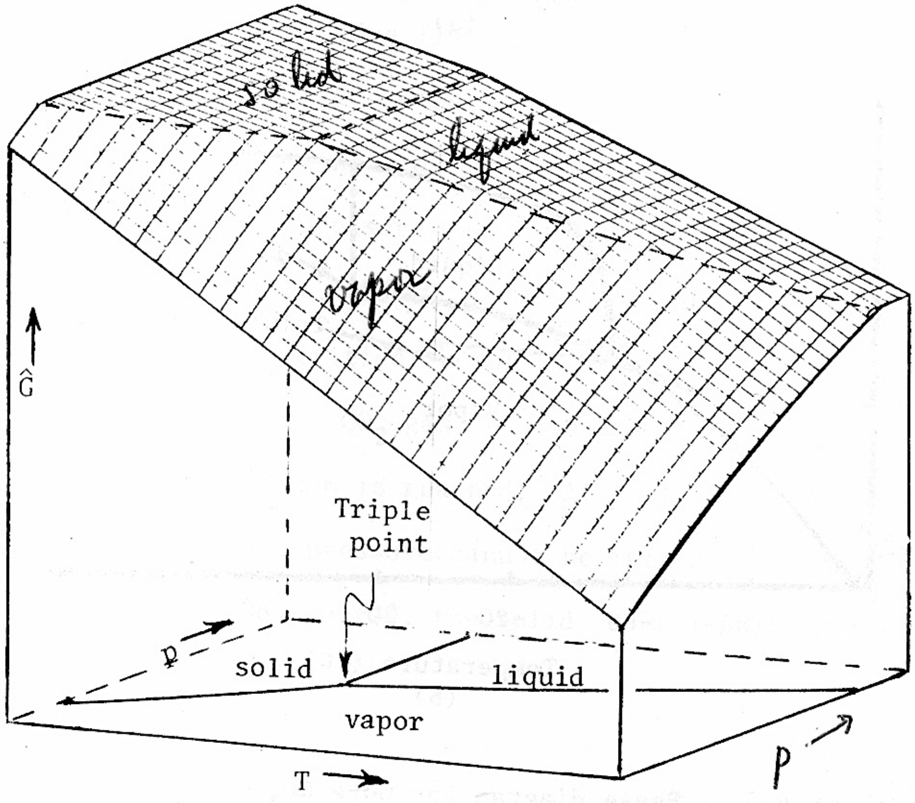
$$c_i = c - r - a = 3 - 1 - 0 = 2$$

And $\quad f = c_i + 2 - p = 2 + 2 - 3 = 1$

On the other hand, suppose $CaCO_3(s)$ + $CaO(s)$ formed a solid solution. Then, since each $CaO(s)$ is formed from a $CaCO_3(s)$, $x[CaCO_3(s)] + x[CaO(s)] = 1$. And, since they are in the same phase, this is a new restriction.

Then $\quad c_i = c - r - a = 3 - 1 - 1 = 1$

but $\quad f = c_i + 2 - p = 1 + 2 - \underline{\underline{2}} = 1 \quad$ again


solid
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