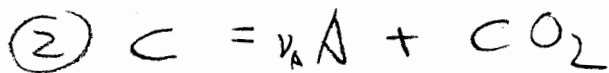


mixed volatiles

(1)



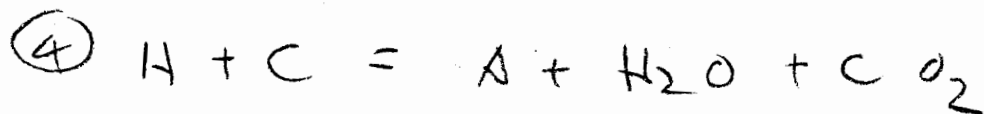
A, B volatile
absent



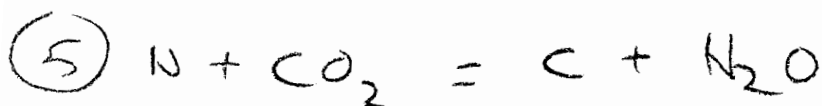
H contains H_2O high pressure



C contains CO_2 carbon



ν 's are
stoichiometric
coeffs.



on a T-X diagram wrt T

direction of a reaction is such that

the high entropy assemblage is always
produced with increasing T.

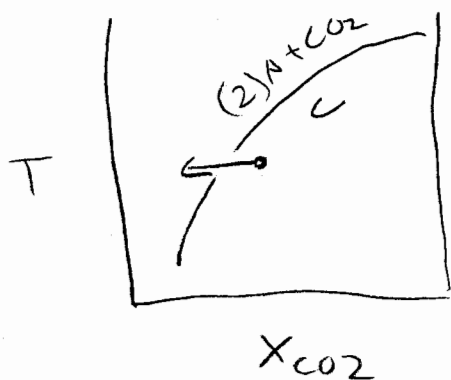
$$\left. \frac{\partial \Delta G_{rxn}}{\partial T} \right|_P = -\Delta S_{rxn}$$

① product assemblage has higher entropy
than the reactant.

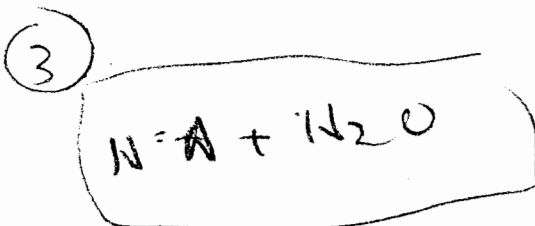
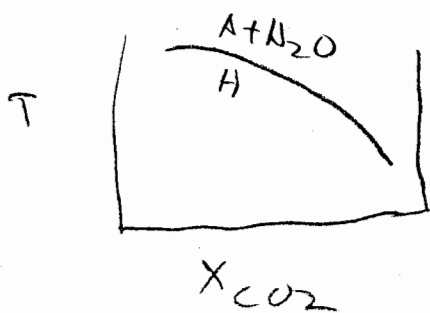
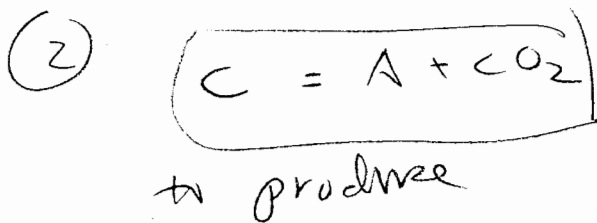
volatile species is always on the high
entropy side.

② Le Chatelier's principle
 perturb system by changing comp. of fluid
 at const. T. reaction will proceed to
 bring fluid back into equilib.

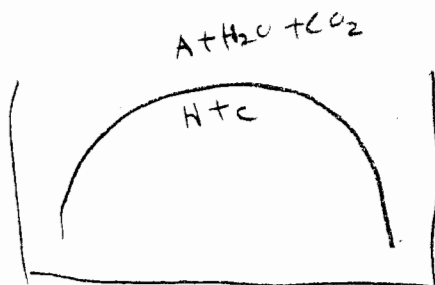
②



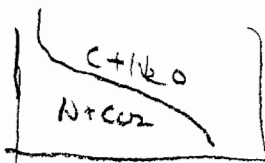
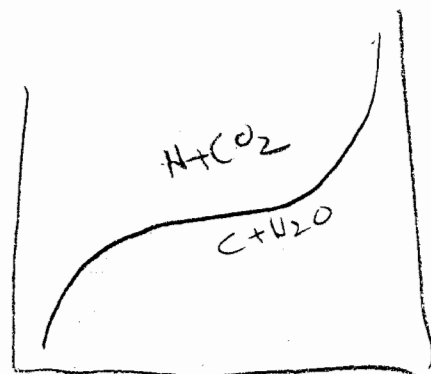
e.g. add H_2O to fluid
 reaction will proceed to right



④



⑤

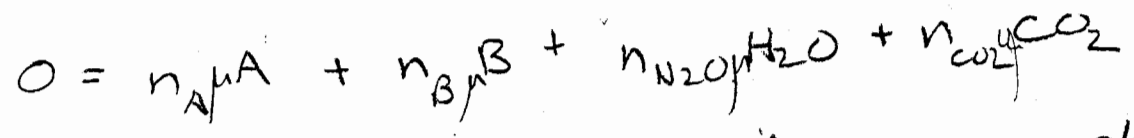


depends on what is
 on high T side

configuration of T-X_{CO2} curves

reaction is generally

Greenwood
(1975) AJSci.
275, 573-
599



at equilib. if all of the solids are pure phases $a_B = 1$
 $a_A = 1$

$$d\Delta G_{rxn} = 0 = -\Delta S_{rxn} dT + \Delta V_{reactive} dP + d(RT \ln [a_{H_2O}^{n_{H_2O}} a_{CO_2}^{n_{CO_2}}])$$

at P constant

$$0 = -\Delta S_{rxn} dT + d(RT \ln [a_{H_2O}^{n_{H_2O}} a_{CO_2}^{n_{CO_2}}])$$

assume that H₂O & CO₂ mix ideally

- OK at high T's and P's.

- so substitute x for activity

$$0 = \Delta S_{rxn} dT + \frac{n_{H_2O}}{X_{H_2O}} RT dX_{H_2O} + n_{H_2O} R \ln X_{H_2O} dT$$

$$+ \frac{n_{CO_2}}{X_{CO_2}} RT dX_{CO_2} + n_{CO_2} R \ln X_{CO_2} dT$$

because $X_{H_2O} + X_{CO_2} = 1$

$$- dX_{H_2O} + dX_{CO_2} = 0$$

$$\text{and } dX_{H_2O} = -dX_{CO_2}$$

→ ΔS_{rxn} step needs to be added

$$0 = \Delta S_{rxn} dT - \frac{n_{H_2O}}{X_{H_2O}} RT dX_{CO_2} + \frac{n_{CO_2}}{X_{CO_2}} RT dX_{CO_2}$$

$$\frac{\partial T}{\partial X} = \frac{RT}{\Delta S_{rxn}} \left(\frac{n_{CO_2}}{X_{CO_2}} - \frac{n_{H_2O}}{X_{H_2O}} \right)$$

can tell slopes of curves on $T-X_{CO_2}$ diagrams with this expression (2)

decarbonation reaction

$$\frac{\partial T}{\partial X_{CO_2}} = \frac{n_{CO_2}}{X_{CO_2}} \frac{RT}{\Delta S_{rxn}}$$

because $\Delta S_{rxn} +$
usually $+$

dehydration reaction

$$\frac{\partial T}{\partial X_{CO_2}} = - \frac{n_{H_2O}}{X_{H_2O}} \frac{RT}{\Delta S_{rxn}}$$

usually $-$

reaction type (4)
ma

$$n_{CO_2} > 0$$

$$n_{H_2O} > 0$$

so slope depends on magnitude

reaction type (5) n_{CO_2} and n_{H_2O} have opposite signs.

when n_{CO_2} is $+$ and n_{H_2O} is $-$ slope is pos.

when n_{CO_2} is $-$ and n_{H_2O} is $+$ slope is neg.

Variance - take system $CaO - MgO - SiO_2$
 $H_2O - CO_2$

$$C = 5$$

$$F = 5 + 2 - \phi$$

6 phases = univariant

but because $T-x_{CO_2}$ diagrams are drawn (3)
at constant P , the univariant 6-phase
lines degenerate to points - isobarically
since fluid is present 5 solids invariant
coexist at
these points.

and the number of phases that coexist
along a univariant curve in $T-x_{CO_2}$ is

4.

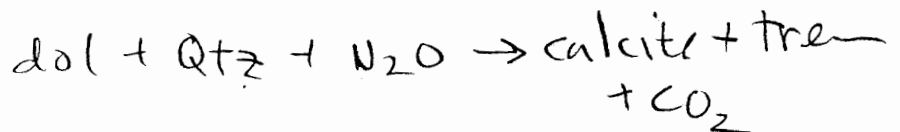
types of reactions

- constant fluid comp. - phase assembl.
changes as T increases - not realistic
- infiltration \rightarrow by H_2O at const. T .

closed system -

rock has fluid = $x_{CO_2} = 0.4$

increase T - hit rxn (1c)



So - consume dol + Qtz - create trm.

hits the invariant point

fluid comp. changes $\hat{=}$ amt. of ④
reaction depend on porosity

progress variable $\hat{=}$ ξ

progress related to both bulk comp.

\rightarrow rock $\hat{=}$ amt. of initial fluid

when there is little porosity - rock evolves along
curve with little reaction occurring.

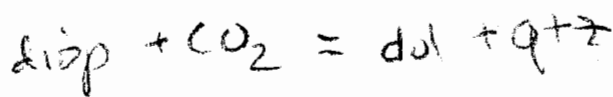
rock arrives at invariant point - an
additional phase joins assemblage

- diapside - two reactions proceed $\hat{=}$

comp. of fluid must be buffered.

can choose any two -

16 $\hat{=}$ 5



reaction take place until one of the
solids disappears.

(5)
metamorphosed siliceous carb. rocks

- long attracted attention because of
larger number of minerals that form in

- chemically simple system



chert nod. in limestone

siliceous limestones

Bowen (1940) suggested a definite reaction
sequence.

serpentine - talc - diop - periclase - Wo - monticellite

- akimotoite - spinel - merwinite - kyanite

Tremble for dire peril walks

monstrous acrimony's spurning mercy's
kams.

Tilley '48 added a stutter to this
law (talk at the row Trend)

beginnings of P-T
ta -
quads -

fluid comp is important

classic papers by

Greenwood (1975) *AJS*

275, 573-579

1

Ferry (1976) *AJSci.* 276

841-882

Rice (1977) *AJSci.* 277, 1-24.