Geothermodynamics

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Class notes

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R$\rightleftharpoons$ P

$[\frac{^{34}S}{^{32}S}]_{reactant}/[\frac{^{34}S}{^{32}S}]_{product} =^{34} \alpha_{R,P}$ aka the fractionation factor

$^{34}\alpha_{R,P} = (^{34}\alpha^{EQ}_{R,P} -^{34} \alpha^{Kin}_{R,P})\frac{\phi_{P,R}}{\phi_{R,P}} +^{34} \alpha^{Kin}_{R,P}$

Where $\frac{\phi_{P,R}}{\phi_{R,P}}$ represents the back reaction (numerator) divided by the forward reaction (denominator). It is also true that $\frac{\phi_{P,R}}{\phi_{R,P}} = e^{\frac{\Delta G_r}{RT}}$.

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Thermodynamics terms:

System:

i) observer defined, separate from the rest of the universe (ROU)
ii) nature of the boundary between the system and the ROU defines the system type
    a. open: mass and energy can cross the boundary. Example: hydrothermal ore system
    b. closed: energy may cross but not mass
    c. adiabatic: no heat energy may cross. Example: developing clouds or ascending magma
    d. isolated: neither heat nor mass may cross

Can think of a system as a collection of phases (see below)

Phase:

substance with uniform chemical and physical properties or properties that smoothly vary

i) minerals: each type is a potential phase
ii) liquids: silicate melts, aqueous solutions, glasses
iii) gases:
iv) fluids: gas/liquid above a “critical” point

most phases we encounter are solutions with varying chemical compositions, not pure solutions.

example: plagioclase feldspar: imagine that the green in the image is anorithite (Ca-rich feldspar) and the red is albite (Na-rich feldspar)

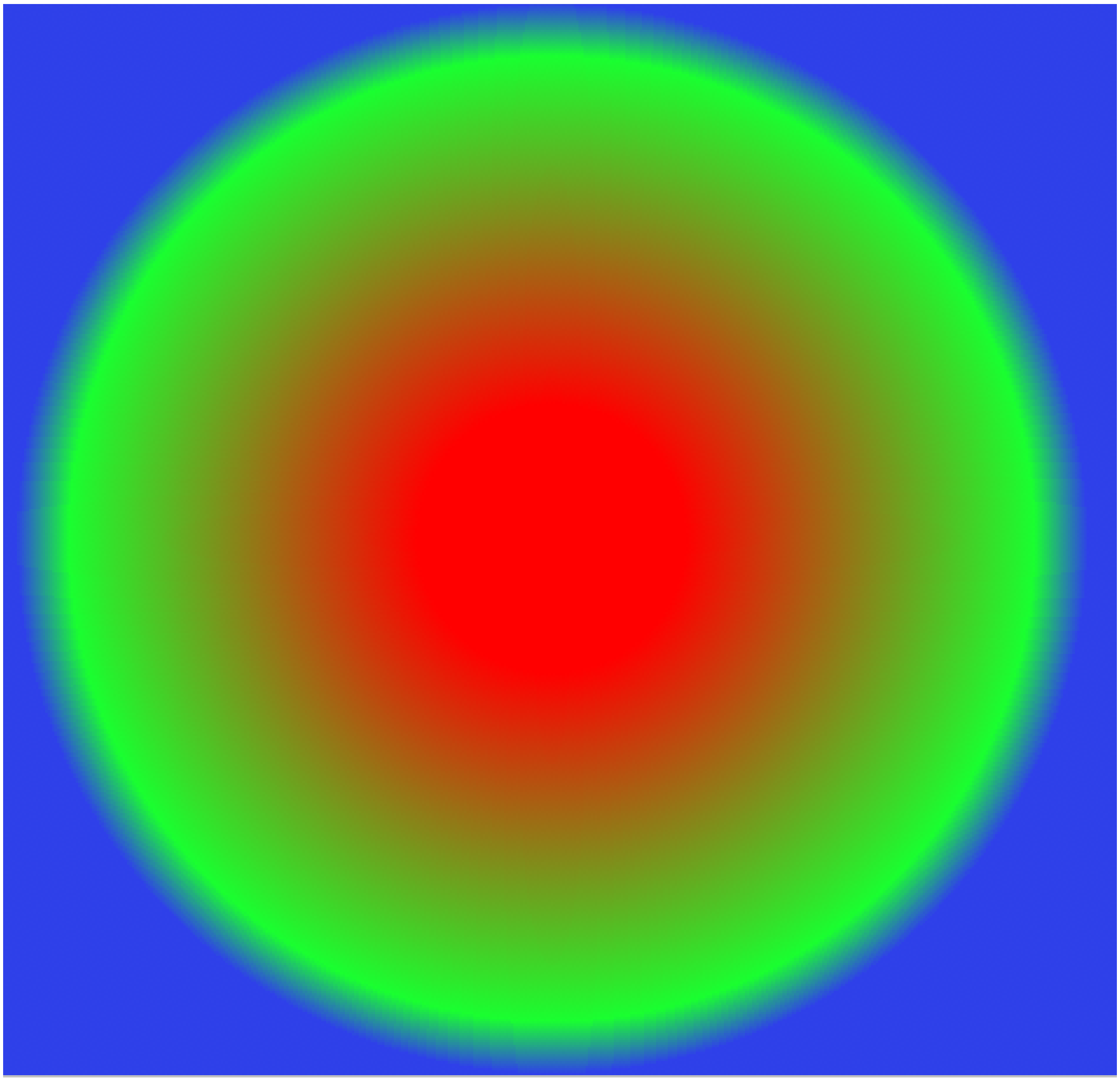

Figure 1: Gradient of phases

Components

chemical formula used to describe the composition of a phase

example: alkaline feldspar (f_{sp})

Composition: $Na_{0.5}K_{0.5}AlSi_3O_8$

Components: can use different units, below are three versions of the same information, typically we choose the option with the smallest number of components (aka the last option here)

Element	Atom %
Na	3.85
K	3.85
Al	7.70
Si	23.08
O	61.54

Oxides	Mol %
K_2O	6.25
Na_2O	6.25
Al_2O_2	12.50
SiO_2	75.00

f_{sp} molecules	mol %
$KAlSi_3O_8$	50
$NaAlSi_3O_8$	50

Aside: Why do we care about feldspar? It makes white rocks white (with quartz), but Peter says green rocks are the most important

Variables

refers to the chemical or physical characteristics of a phase or system

examples: temperature (T), pressure (P), composition, density (ρ), chemical potential (μ), fugacity, activity

variables come in two flavors: 1. intensive: independent of the amount of material present i) examples: T, P, μ 2. extensive: dependent on the amount of material present i) examples: mass, volume, total heat capacity ii) typically 1st order dependencies

The ratio of two extensive variables is an intensive variable because the 1st order dependencies cancel. Example: $\rho = m/v$

State

Ensemble of values for all relevant variables describing a phase or a system

relevant variables = state variables

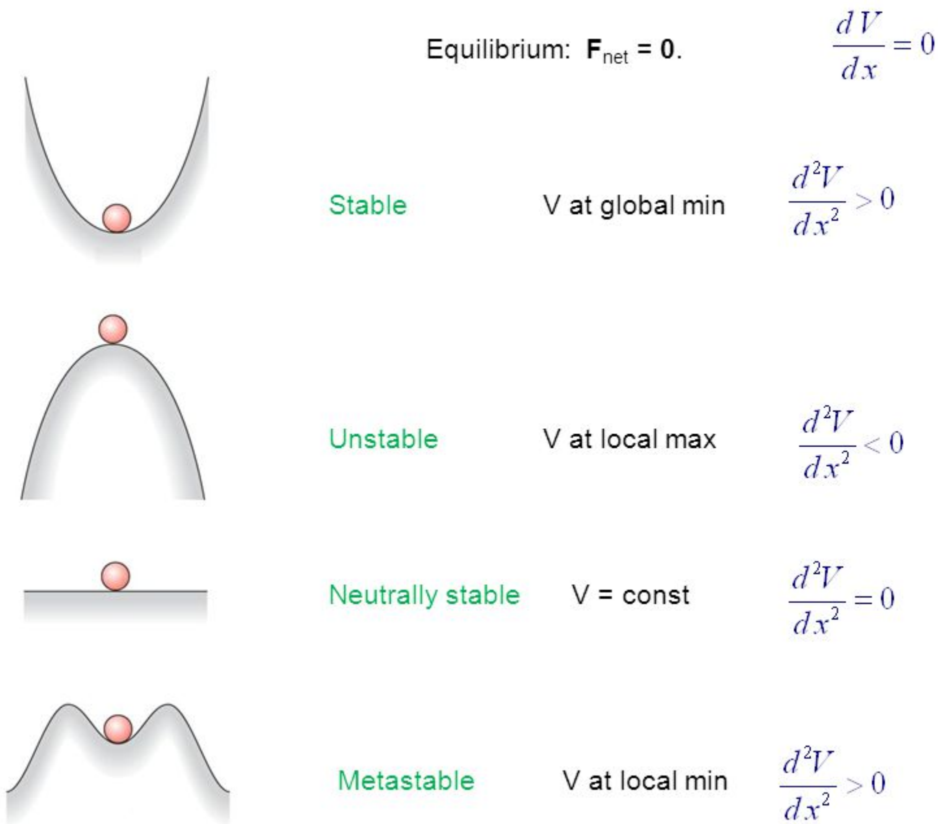

Figure 2: Mechanical Analogy for Equilibrium States

Equation of State is the explicit representation of the mathematical relationship between the variables of a particular phase or system

Example: ideal gas law $PV = nRT$

Equilibrium

a system is at equilibrium if all the variables that describe its state do not change with time (scale depends on the question)

Types of equilibrium (essentially defined by its response to a small pertubation): 1. stable equilibrium: returns to initial state after small pertubation 2. unstable equilibrium: does not return to initial state after small pertubation (not very relevant to real world) 3. metastable equilibrium: returns to initial state after a sufficiently small pertubation 4. conditional equilibrium (neutrally stable): doesn't care about pertubations (not very relevant to real world)

First order derivative for all of these states is the same (0)

Definitions

Component:

Equilibrium:

Fractionation Factor: ${}^{x}\alpha_{A/B} = R_A^x/R_B^x = ({}^{x}\alpha_{A/B}^{Eq} - {}^{x}\alpha_{A/B}^{Kin})\frac{\phi_{B/A}}{\phi_{A/B}} + {}^{x}\alpha_{A/B}^{Kin}$ where A and B are two compounds (reactant/product etc)

Isotope Ratio: $R^x = \frac{{}^{x}A}{{}^{y}A}$ where x is the rare isotope of the element A and y is the common isotope

Phase:

State: Ensemble of values for all relevant variables describing a phase or a system

State variable: relevant variables for describing a phase or system

System:

Variable: refers to the chemical or physical characteristics of a phase or system

$\frac{\phi_{B/A}}{\phi_{A/B}} = e^{\frac{\Delta G_r}{RT}}$