

Geothermodynamics

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Class notes

Aug 27 2018

$R \rightleftharpoons P$

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

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

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

Aug 29 2018

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 anorthite (Ca-rich feldspar) and the red is albite (Na-rich feldspar)

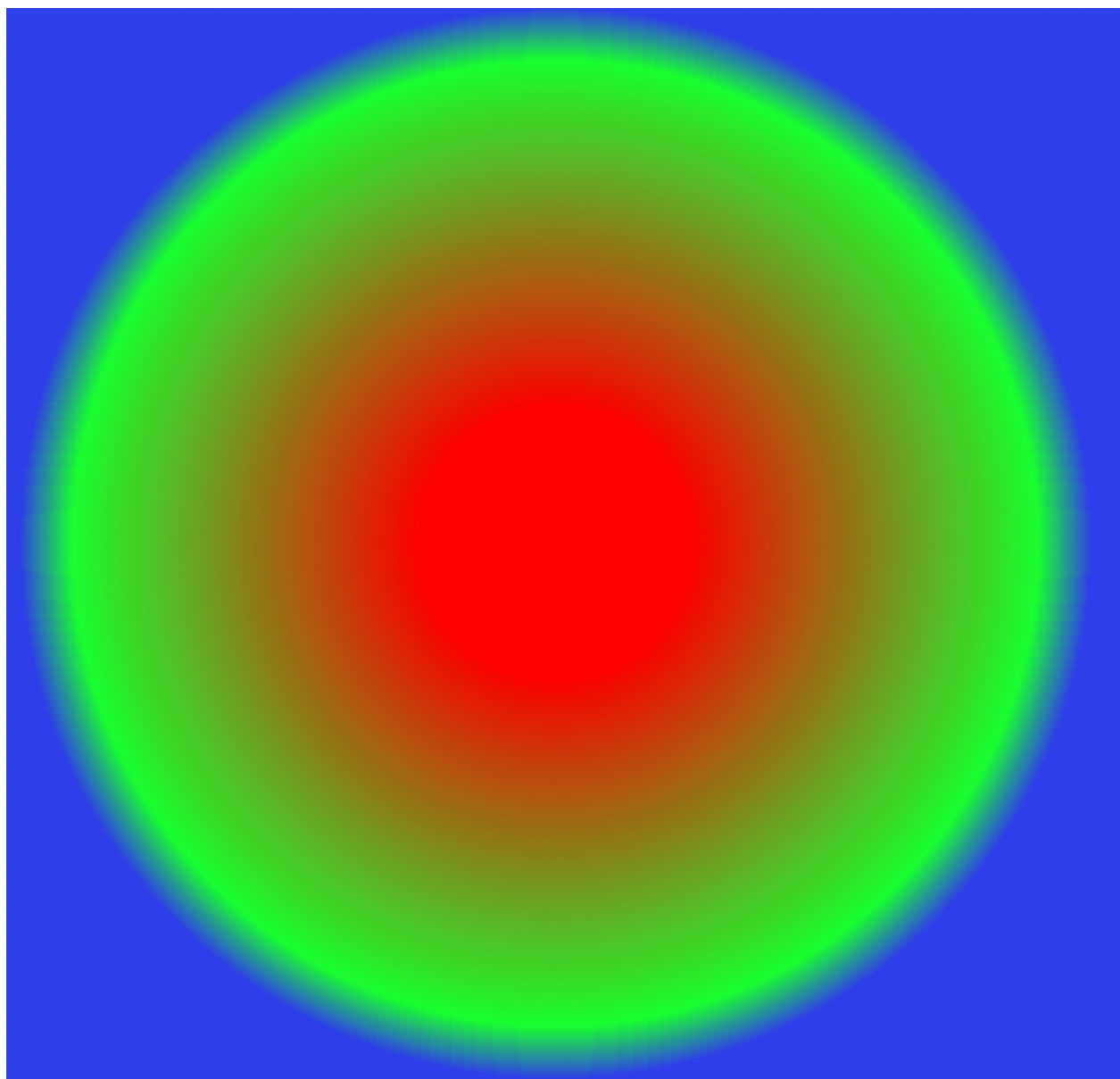


Figure 1: Gradient of phases

Components

chemical formula used to describe the composition of a phase

example: alkaline feldspar (f_{sp})

Composition: $\text{Na}_{0.5}\text{K}_{0.5}\text{AlSi}_3\text{O}_8$

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_3	12.50
SiO_2	75.00

f_{sp} molecules	mol %
KAlSi_3O_8	50
$\text{NaAlSi}_3\text{O}_8$	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

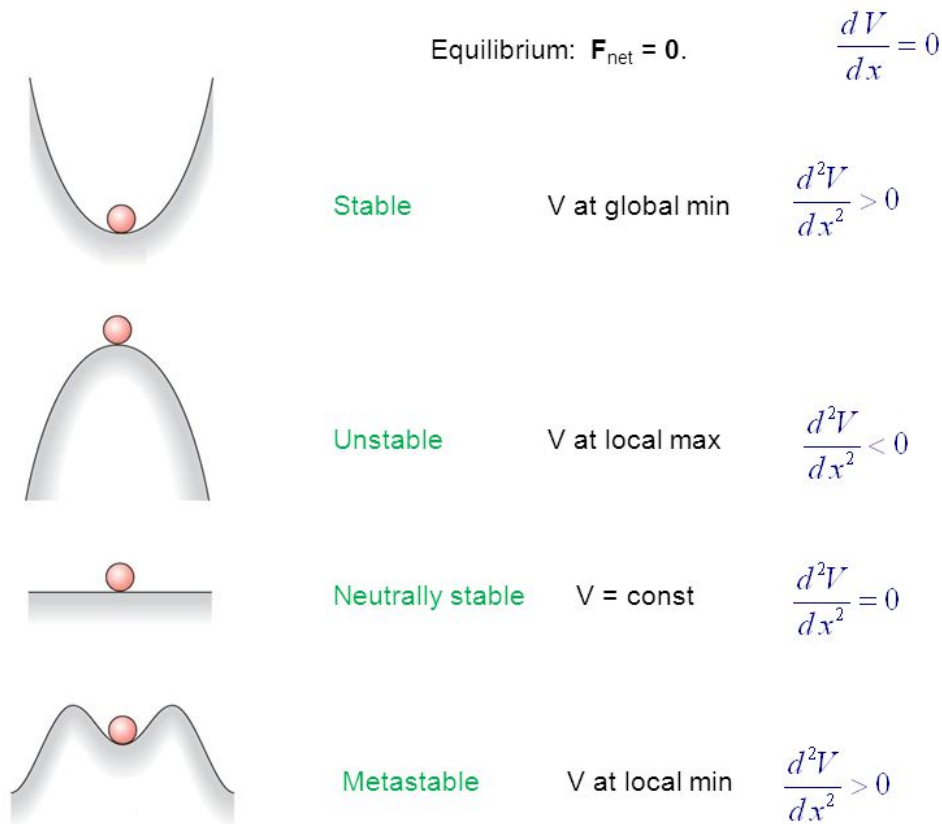


Figure 2: Mechanical Analogy for Equilibrium States

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 perturbation): 1. stable equilibrium: returns to initial state after small perturbation 2. unstable equilibrium: does not return to initial state after small perturbation (not very relevant to real world) 3. metastable equilibrium: returns to initial state after a sufficiently small perturbation 4. conditional equilibrium (neutrally stable): doesn't care about perturbations (not very relevant to real world)

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

Aug 31 2018:

Thermodynamics doesn't care how you get there, just where you start and where you end

Thermodynamics thought experiment: Flagstaff to Benson

What is the system: you! on top of Flagstaff Mountain (elevation 7000 ft)

There is a lot of wind, so T is constant

And we are carrying around bananas to replenish our energy, so don't worry about that

Pick a path from Flagstaff Mountain to Benson Earth Sciences Building and figure out the change in energy!

We care about potential energy in this scenario: $E_p \sim \rho gh$

Density (ρ) is constant (we aren't gaining/losing weight) and gravity (g) is constant as far as we care. So the change in energy is dependent on the change in elevation (h): $\Delta E_p = \Delta h = h_{Benson} - h_{Flagstaff} = 5366 - 7000 = -1634 \text{ ft}$

It doesn't matter if you go other places on the way from Flagstaff to Benson, or if you have to cross a ridge to get down to Benson, all of these intermediate stops will cancel out.

This is a state function.

State functions

State functions only depend on the initial and final state (1st characterization of state function)

$\int_{z_0}^{z_1} dz = z_1 - z_0$ (2nd characterization of state function)

We are taking the definite integral $\int_{z_0}^{z_1}$ of a total or exact differential dz

The definition of a total or exact differential is that when you integrate it the answer is path independent

Path independence: doesn't matter how you get from initial state to final state

State functions are cyclic, if you go from A to B and then B to A there is no net change: $\int_{z_0}^{z_1} dz + \int_{z_1}^{z_0} dz = 0$

State function: $z(x, y)$ so what's the differential? $dz = f(dx, dy) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$ where $\left(\frac{\partial z}{\partial x}\right)_y$ is the partial differential, meaning that you are looking at the change in z given a change in x while holding y constant.

Example: Ideal gas law

$PV = nRT$ ideal gas law aka the equation of state you didn't know you knew

Let's find the equation for the volume and find the total differential: $V = \frac{nRT}{P}$

Volume is an extensive variable (it depends on the amount of stuff, if you add more stuff you add more volume) so we have 3 variables in this function: n , T , and P and R is always a constant (by definition)

Using our simplified differential function above: $dV = \left(\frac{\partial V}{\partial n}\right)_{T,P} dn + \left(\frac{\partial V}{\partial T}\right)_{n,P} dT + \left(\frac{\partial V}{\partial P}\right)_{n,T} dP$

Let's break it down a little more: if we take the partial differential of the volume with respect to the number of moles holding temperature and pressure constant (first term from above), we can replace the partial of volume with our definition of volume, $V = \frac{nRT}{P}$, and then remove the constants from the partial of this equation. This leaves us with the partial differential of the number of moles, divided by the partial differential of the number of moles, which is 1. Thus the partial differential of volume with respect to the number of moles holding temperature and pressure constant is simply equal to $\frac{RT}{P}$

$$\left(\frac{\partial V}{\partial n}\right)_{T,P} = \left(\frac{\partial \left[\frac{nRT}{P}\right]}{\partial n}\right)_{T,P} = \frac{RT}{P} \left(\frac{\partial n}{\partial n}\right) = \frac{RT}{P}$$

Let's repeat for the other two (without the long version):

$$\left(\frac{\partial V}{\partial T}\right)_{n,P} = \left(\frac{\partial \left[\frac{nRT}{P}\right]}{\partial T}\right)_{n,P} = \frac{nR}{P} \left(\frac{\partial T}{\partial T}\right) = \frac{nR}{P}$$

And the tricky one:

$$\left(\frac{\partial V}{\partial P}\right)_{n,T} = \left(\frac{\partial \left[\frac{nRT}{P}\right]}{\partial P}\right)_{n,T} = nRT \left(\frac{\partial \frac{1}{P}}{\partial P}\right) = nRT(-P^{-2})$$

Remembering differential rule: $\frac{\partial x^n}{\partial x} = nx^{n-1}$

The definition of volume we've been using, $V = \frac{nRT}{P}$ is extensive. If we increase n by k , T by k and P by k we get: $V_k = \frac{knRkT}{kP} = \frac{k^2}{k} \frac{nRT}{P} = k \frac{nRT}{P} = kV_0$

If we define $\bar{V} = \frac{V}{n} = \frac{RT}{P}$ then we have an intensive variable (the ratio of two extensive variables is an intensive variable), so now if we increase all of the variables (T and P) by k we get: $\bar{V}_k = \frac{RkT}{kP} = \frac{k}{k} \frac{RT}{P} = \frac{RT}{P}$

This leads to the second test for exactness: the differential should be commutative (the order of differentiation shouldn't matter)

$$\frac{\partial \left(\frac{\partial \bar{V}}{\partial T}\right)}{\partial P} = \frac{\partial \left(\frac{\partial \bar{V}}{\partial P}\right)}{\partial T}$$

And now we get the fourth characterization of state functions.

If any of the characterizations of a state function is true, all of them are true, so you only need to prove it once.

Sep 5 2018

We are going to take the concepts and properties and start to develop laws of thermodynamics, with the intention of getting to the point where we can isolate the effects of chemical work on a system.

Mathematical criterion for equilibrium using a mechanical analogy: Gravitational potential energy (GPE)

Again the slope for all of these cases is 0. The definition of equilibrium is $\frac{dh}{dx} = 0$ at equilibrium.

$GPE \sim \rho gh$ so $\frac{d(GPE)}{dx} = \frac{d(\rho gh)}{dx}$ but ρg is constant so $\frac{d(\rho gh)}{dx} = \rho g \frac{dh}{dx} = 0$ at equilibrium. So $d(GPE) = 0$

Thermodynamics is based on a single assumption that can be expressed several ways:

1. energy can neither be created nor destroyed
2. all forms of energy are interconvertible
3. each definite state of a definite system is characterized by a definite energy
4. can't get something for nothing

Sep 7 2018

Sep 10 2018

Sep 12 2018

Definitions

Component: chemical formula used to describe the composition of a phase

Equilibrium: a system is at equilibrium if all the variables that describe its state do not change with time

Exact differential (aka total differential): a differential that when integrated is path independent

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


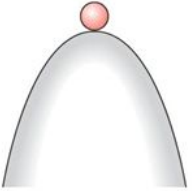
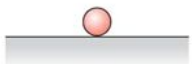
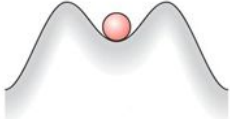
Equilibrium: $\mathbf{F}_{\text{net}} = \mathbf{0}$.				$\frac{dV}{dx} = 0$
	Stable	V at global min	$\frac{d^2V}{dx^2} > 0$	
	Unstable	V at local max	$\frac{d^2V}{dx^2} < 0$	
	Neutrally stable	V = const	$\frac{d^2V}{dx^2} = 0$	
	Metastable	V at local min	$\frac{d^2V}{dx^2} > 0$	

Figure 3: Mechanical Analogy for Equilibrium States

Path independence: it doesn't matter how you get from the initial to the final state, only the difference between these states

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

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

State function: function depending only on the initial and final states, it is path independent and cyclic

State variable: relevant variables for describing a phase or system

System: A defined set of area/mass/energy separate from the rest of the universe, can be considered a collection of phases

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

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