

# Geothermodynamics

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## Class notes

### Aug 27 2018

$R \rightleftharpoons P$

$\left[ \frac{{}^{34}S}{{}^{32}S} \right]_{\text{reactant}} / \left[ \frac{{}^{34}S}{{}^{32}S} \right]_{\text{product}} = {}^{34}\alpha_{R,P}$  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)

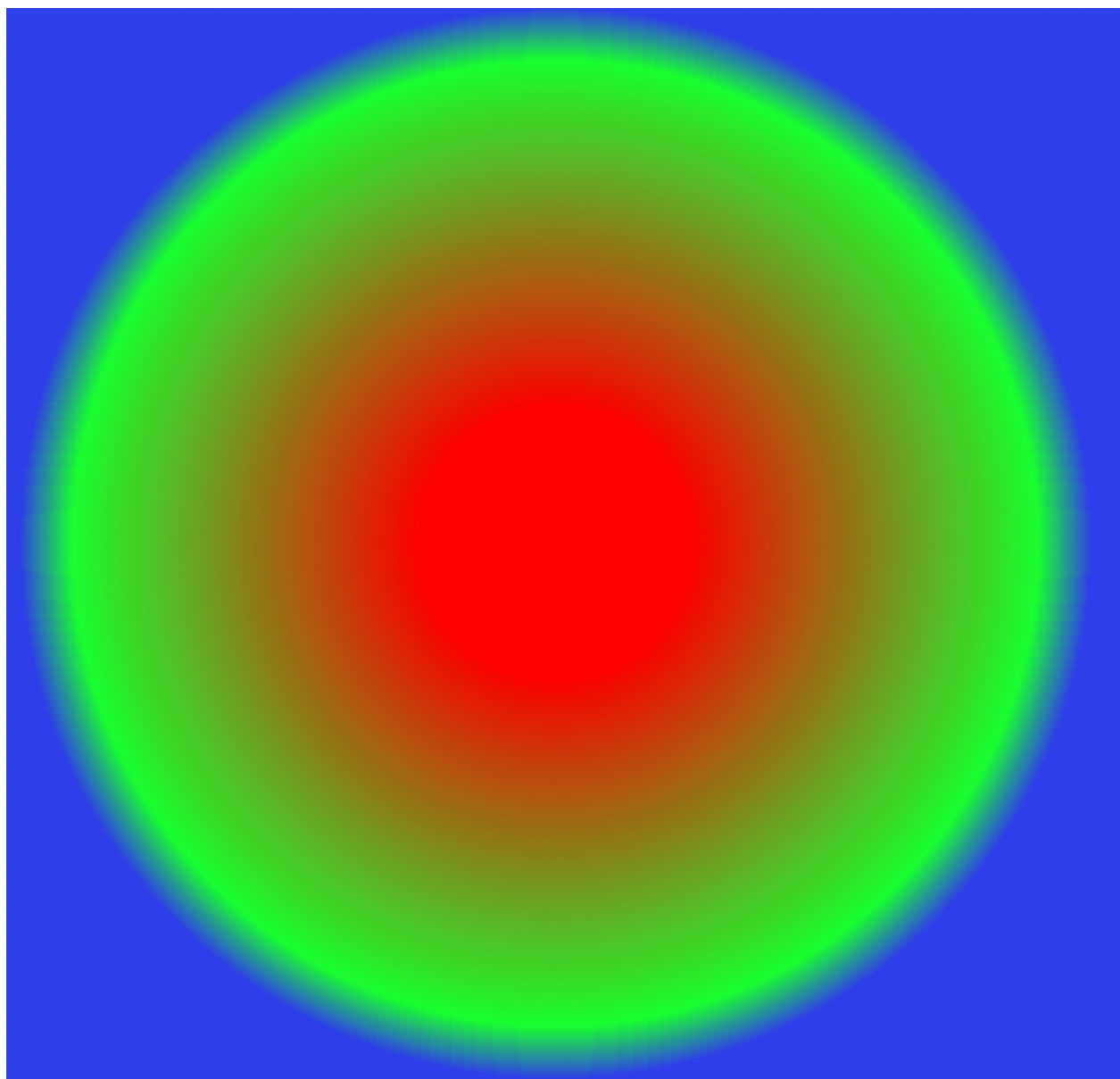


Figure 1: Gradient of phases

## 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 %
$\text{K}_2\text{O}$	6.25
$\text{Na}_2\text{O}$	6.25
$\text{Al}_2\text{O}_3$	12.50
$\text{SiO}_2$	75.00

$f_{sp}$ molecules	mol %
$\text{KAlSi}_3\text{O}_8$	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 ( $\rho$ ), chemical potential ( $\mu$ ), fugacity, activity

variables come in two flavors: 1. intensive: independent of the amount of material present i) examples: T, P,  $\mu$  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

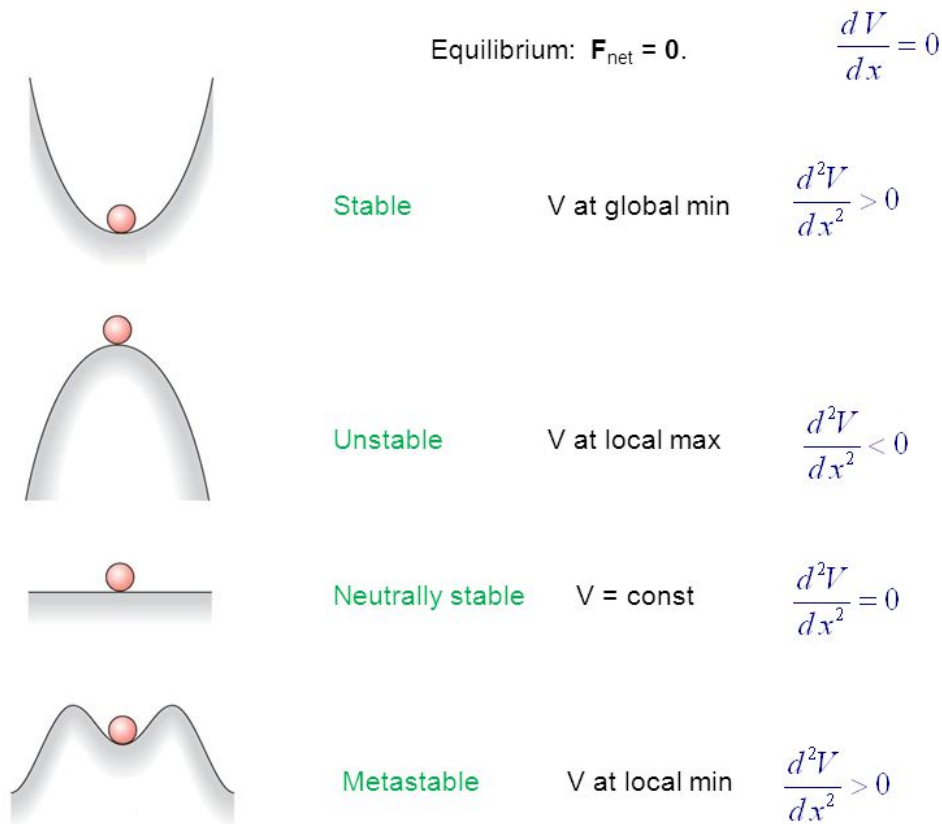


Figure 2: Mechanical Analogy for Equilibrium States

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 ( $\rho$ ) 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  $\rho g$  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

Gibbs' contribution was taking this and converting into a mathematical statement

relationships implied by these statements, to illustrate let's say: let there be a property of a system called the internal energy ( $U$ ). Let  $U$  of the system under consideration be a function of the state variables ( $x, y, z, \dots$ ) such that  $U(x, y, z, \dots)$

1.  $U(x, y, z, \dots)$  is fully characterized by the state of the system. This means if we can know  $x, y, z, \dots$  we can then know  $U$
2.  $U_{system} = \sum U_{parts}$
3.  $\int_{U_1}^{U_2} dU = U_2 - U_1$
4.  $\int_{U_1}^{U_2} dU + \int_{U_2}^{U_1} dU = 0$
5.  $\int_{U_1}^{U_2} dU$  is path independent

Violation of any of these implies perpetual motion.

The essential contribution of Gibbs to thermodynamics:  $U(x, y, z, \dots)$  has an exact differential.

Now let's take advantage of this:

$$dU = \left(\frac{\partial U}{\partial x}\right)_{y,z,\dots} dx + \left(\frac{\partial U}{\partial y}\right)_{x,z,\dots} dy + \left(\frac{\partial U}{\partial z}\right)_{x,y,\dots} dz + \left(\frac{\partial U}{\partial \dots}\right)_{x,y,z,\dots} d\dots$$


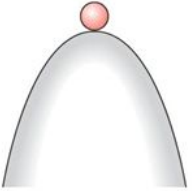
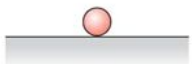
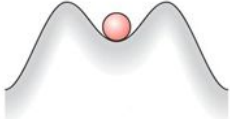
Equilibrium: $\mathbf{F}_{\text{net}} = \mathbf{0}$ .				$\frac{dV}{dx} = 0$
	Stable	V at global min	$\frac{d^2V}{dx^2} > 0$	
	Unstable	V at local max	$\frac{d^2V}{dx^2} < 0$	
	Neutrally stable	V = const	$\frac{d^2V}{dx^2} = 0$	
	Metastable	V at local min	$\frac{d^2V}{dx^2} > 0$	

Figure 3: Mechanical Analogy for Equilibrium States

In the lingo: a function with this property is known as a state function

How do we change internal energy? We add or subtract something.

[Energy|Cognate intensive thermo variable| |<—|<—————| |Heat (Q)| Temperature (T)|  
|PV (mechanical work)|Pressure (P)| |Electrical work|Electrical potential| |Gravitational work|Gravitational  
potential| |Chemical work (object of our affection)|Chemical potential ( $\mu$ )|

Think of the cognate variables as the thing that lets you investigate the directionality of the change in energy.

Chemical work has two types:

1. change in composition of a phase: exchanging between garnet and biotite (exchange reaction)
2. change in abundance of a phase: exchanging between liquid water and water vapor (net transfer reaction)

Consider a system in which chemical work is impossible. The system is fixed in composition (pure substance). System has one phase only that is fixed in abundance or amount.

In this system we allow PV work and heat only.

$U$  can be changed by adding or extracting heat, by performing PV work, or by allowing system to perform PV work on its surroundings.

$$dU = \delta Q + \delta W$$

We can't know a priori how to integrate  $\delta Q$  or  $\delta W$ . a priori don't know if these are exact differentials.

Need to transform these into integrateable forms (alternatively we need to transform energetic changes into a form that relies on easily measured variables).

## Sep 7 2018

Thought experiment: assume that the system is at the same temperature for all time.  $dl$  here is small enough that the pressure remains constant. We can move the piston by  $dl$  by applying a force to the piston.

$\delta W = -P * A * dl$  where  $A * dl = dV$  so  $\delta W = -PdV$  which we can rearrange to  $\frac{\delta W}{P} = d(-V)$  normalizing by  $P$  makes this into an exact differential that we can integrate.

Scientific thermodynamic convention:  $\delta W$  has a positive value when work is done on a (actually to) the system.  $P$  always takes on a positive value, work done on the system decreases volume and our sign convention accounts for this.

Process: the act of adding or extracting energy from its system

Reversible: (cylinder thought experiment) if the process is stopped at any time, the state of the system does not change. Reversible processes are series of equilibrium states

Irreversible: when the process is stopped, further changes to the state of the system occur.

[Reversible|Irreversible| |<—|<—————| |idealization|reality| |well developed coherent theory|complicated and splintered theory| |theory applicable b/c relevant lab data exists|lab data doesn't yet exist| |good for geologic time. rocks tend to act like a state| |

$$\frac{\delta W}{P} = d(-V) \text{ is only for a reversible process}$$

In general, the work done on a system will be greater than in our thought experiment. (throw a big rock onto a piston vs tiny particles).  $\therefore \delta W \geq -PdV$

During a reversible process:

$$\frac{\delta[\text{energy}]}{\text{cognateintensivevariable}} = d(\text{newvariable})$$



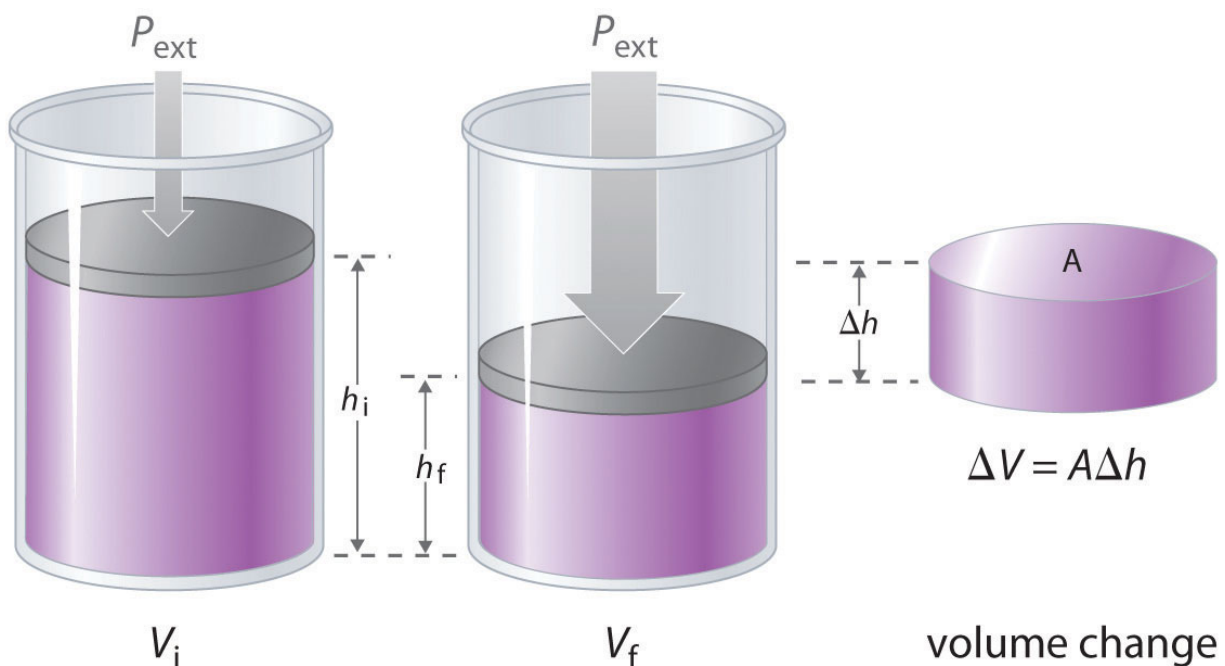


Figure 4: Mechanical Piston Example

Now we can consider heat:  $\frac{\delta Q}{T} = dS$  where  $T$  is the potential that monitors heat flow and  $S$  is the thermal displacement.

Forget about the definition of entropy right now, none of this disorder shit. Entropy isn't that special. Just a variable.

$\frac{\delta Q}{T} \leq dS$  For a reversible process, it's equal. In reality, it's an inequality. Entropy is always greater than the heat.

2nd law of thermodynamics

$dU = TdS - PdV$  now measurable (for a pure substance)

**Sep 10 2018**

Pursue the definition at equilibrium, specifically the definition of  $U$ . Start releasing restraints.

$d = \delta Q + \delta W = TdS - PdV = 0$  when you do thermal work you add or subtract heat at constant temperature.

$U$  is a function of  $S$  and  $V$  for a fixed amount of substance:  $U(S, V)$

New definition for  $T$  and  $P$ :

$T = \left(\frac{\partial U}{\partial S}\right)_{n, P, V} ds$  intensive

$-P = \left(\frac{\partial U}{\partial V}\right)_{S, n, T} dV$  intensive

Expand this to allow for possibility of chemical work: ie phase composition might change or abundances of phases in your system might change

1. Define a phase or system (collection of phases) described by  $c$  components ( $c$  = number of components  $\rightarrow 1, 2, 3, \dots, c$ )
2. each component will be present in an amount  $n_1, n_2, n_3, \dots, n_c$

This releases the pure substance restraints

$U$  is now:  $U(S, V, n_1, n_2, n_3, \dots, n_c)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n \neq n_1} dn_1 + \dots$$

Define a new intensive variable of chemical potential of component:  $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n \neq n_i}$

$$dU = Tds - PdV + \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots + \mu_c dn_c = TdS - PdV + \sum_{i=1}^c \mu_i dn_i$$

Euler's theorem tells us for homogeneous function of degree 1 (if you double stuff and you double other variables then you double internal energy)

$$U(S, V, n_i) = TS - PV + \sum_{i=1}^c \mu_i n_i$$

for 1 component (pure substance) varies in abundance not composition:  $U = TS - PV + \sum \mu_i n_i$

$$\text{Divide by } n_i: \frac{U}{n_i} = \frac{TS}{n_i} - \frac{PV}{n_i} + \frac{\mu_i n_i}{n_i}$$

$$\bar{U} = T\bar{S} - P\bar{V} + \mu_i$$

$$\mu_i = \bar{U} - T\bar{S} + P\bar{V}$$

$\bar{U}$  is the internal energy per mole of component 1

Solution phase of multicomponent system: divide by  $\sum_{i=1}^c n_i$

$$\bar{U} = T\bar{S} - P\bar{V} + \sum_{i=1}^c \mu_i x_i$$

$X_i$  is the mole fraction of component i aka the moles of component i divided by the total number of moles in the system

examples:

Plagioclase crystal:

Component 1:  $\text{NaAlSi}_3\text{O}_8$  (Ab)

Component 2:  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (An)

$$X_{ab} = \frac{n_{ab}}{n_{plagioclase}} = \frac{n_{ab}}{n_{ab} + n_{an}}$$

consider a solution phase  $j$  (way of indicating which phase you are talking about)

$$\bar{U}_j = T\bar{S}_j - P\bar{V}_j + \sum_{i=1}^c \mu_{i,j} X_i \quad (\text{Component } i \text{ may be present in multiple phases})$$

example:  $\mu_{H_2O}$  the numerical value will be different for steam versus ice

$\mu_{SiO_2}$  numeric value will be different for  $\alpha$ -quartz,  $\beta$ -quartz, stishovite, tridymite

$\mu_{Al_2SiO_5}$  different for andalusite, byomite, sillimanite

$\mu_{i,j}$  where  $i$  is the component and  $j$  is the phase

ex:  $\mu_{i,j}^{P,T}$  as  $\mu_{Al_2SiO_5,kyamite}^{3kbar,500C}$

Sep 12 2018

Homogeneous equilibrium: refers to processes internal to a phase ( $\Delta T, \Delta P, \Delta n_i$ )

known volume of a single phase

example: plagioclase feldspar: here we refer to the state of the internal distribution of components within a phase

Internal distribution is time invariant:

$$\bar{U}_j = T\bar{S}_j - P\bar{V}_j + \sum_{i=1}^c \mu_{i,j} X_j \text{ molar internal energy}$$

1. take the total differential (use the product rule)

$$d\bar{U}_j = Td\bar{S}_j + \bar{S}_j dT - Pd\bar{V}_j - \bar{V}_j dP + \sum_{i=1}^c \mu_{i,j} dX_j + \sum_{i=1}^c X_j d\mu_{i,j} = 0 \text{ at equilibrium}$$

2. compare to alternate form of  $d\bar{U}_j$

$$d\bar{U}_j = Td\bar{S}_j - Pd\bar{V}_j + \sum_{i=1}^c \mu_{i,j} dX_j = 0 \text{ at equilibrium}$$

3. at equilibrium these expressions are the same, so we can set them equal and eliminate common terms

$$\bar{S}_j dT - \bar{V}_j dP + \sum_{i=1}^c X_j d\mu_{i,j} = 0$$

now we can multiply by the total amount of material in the system to get the extensive version:

$$S_j dT - V_j dP + \sum_{i=1}^c n_i d\mu_{i,j} = 0$$

This allows us to define the Gibbs-Duhem equation which applies under conditions of homogeneous equilibrium (that is that it refers to a single phase ignoring for the time what else might be present)

What good is it? shows how at equilibrium cation ordering (chemical zoning) in a crystal responds to  $dP, dT$ . We can use this to back out the changes in  $T$  and  $P$  experienced by a crystal using the final cation ordering in a crystal. It allows for the construction of phase diagrams without any knowledge of thermodynamics.

Its most famous application is in the derivation of the phase rule:

Consider a system of  $p$  phases and  $c$  components. The number of variables (degrees of freedom,  $f$ ) that define this system will be  $c + 2$  in number.  $f = c + 2 - p$

example: metamorphosed bauxite with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in 1:1 molar proportions ( $\text{Al}_2\text{SiO}_5$ ). You can find this in NM and NH in three different minerals: kyanite, andalucite and sillimanite

$$c = 1, p = 3 \text{ so } f = 1 + 2 - 3 = 0$$

This tells us that temperature and pressure can't be changed independently. Don't apply this willynilly.

Let's get away from homogeneous equilibrium and into

Heterogeneous equilibrium: defined by relations among variables in a system with 2 or more phases at equilibrium.

Consider a 2 phase system: - phases are pure substances defined by the same composition and described by one component - the outer boundary is rigid, impermeable and insulating

Each phase ( $\alpha$  and  $\beta$  have variables  $V, n, S, P, T, \mu$  specific to the phase)

Because the boundary is rigid, we can say:  $V_{system} = V_{\alpha} + V_{\beta} = constant$  so  $dV_{system} = 0 = dV_{\alpha} + dV_{\beta}$  so  $dV_{\alpha} = -dV_{\beta}$

Because the boundary is impermeable, we can say:  $n_{system} = n_{\alpha} + n_{\beta} = constant$  so  $dn_{\alpha} = -dn_{\beta}$

Because the boundary is insulating we can say:  $dQ_{system} = 0$  so  $dS_{system} = \frac{dQ_{system}}{T} = 0$  at equilibrium and  $S_{system} = S_{\alpha} + S_{\beta}$  so  $dS_{\alpha} = -dS_{\beta}$

Because the system is at equilibrium  $U_{system}$  is at a local minimum so  $dU_{system} = 0$

next we will apply these constraints to come up with 3 conditions of heterogeneous equilibrium.

## 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

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

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