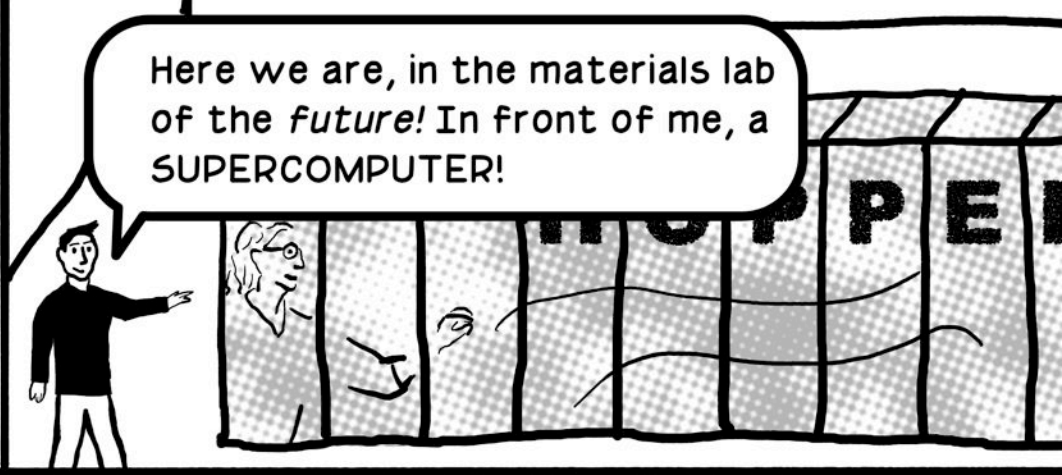


Materials stability & Nature's bike shop

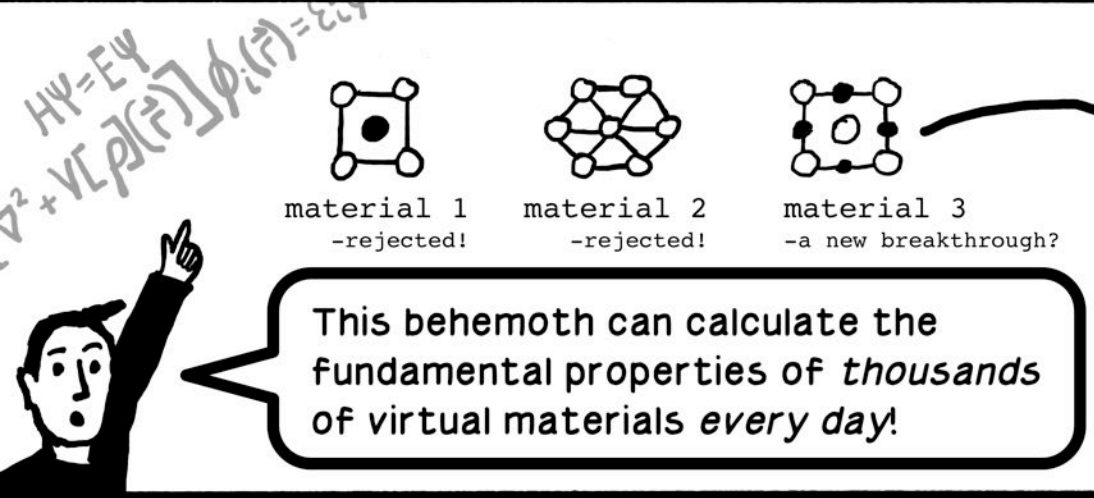
A comics guide* to predicting new materials!



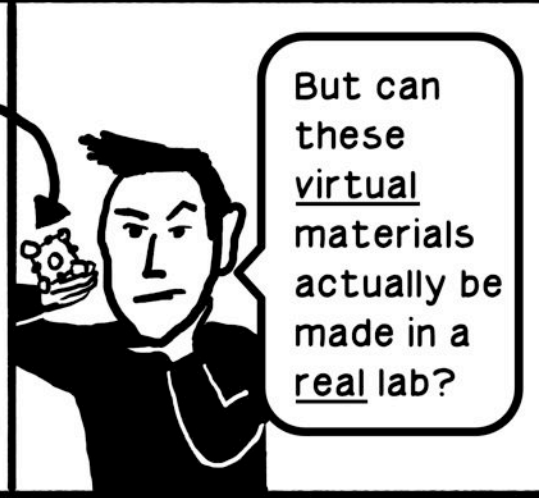
by Anubhav Jain



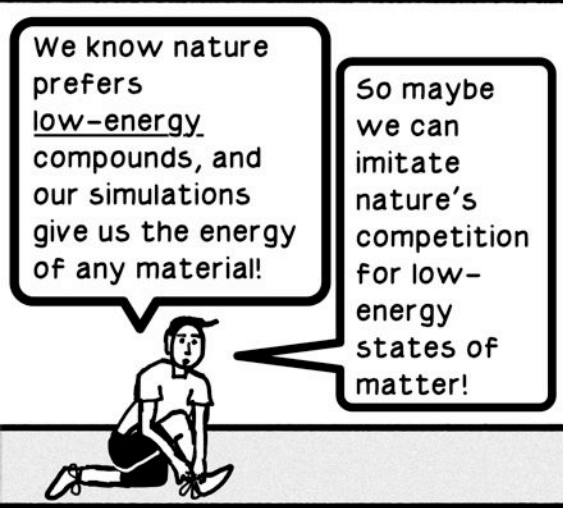
Here we are, in the materials lab of the *future*! In front of me, a SUPERCOMPUTER!



This behemoth can calculate the fundamental properties of *thousands* of virtual materials *every day*!

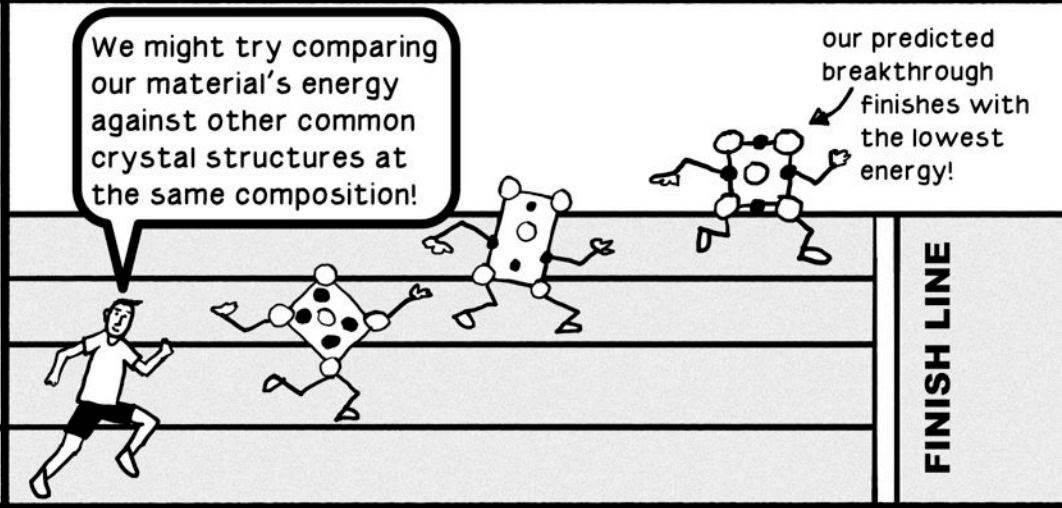


But can these virtual materials actually be made in a real lab?



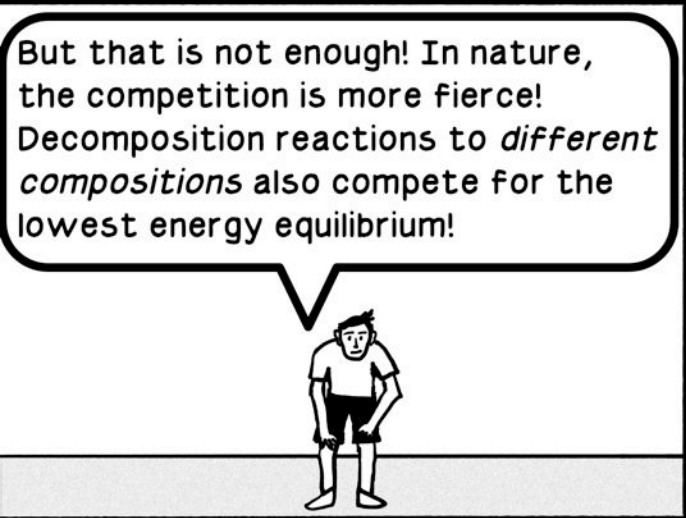
We know nature prefers low-energy compounds, and our simulations give us the energy of any material!

So maybe we can imitate nature's competition for low-energy states of matter!

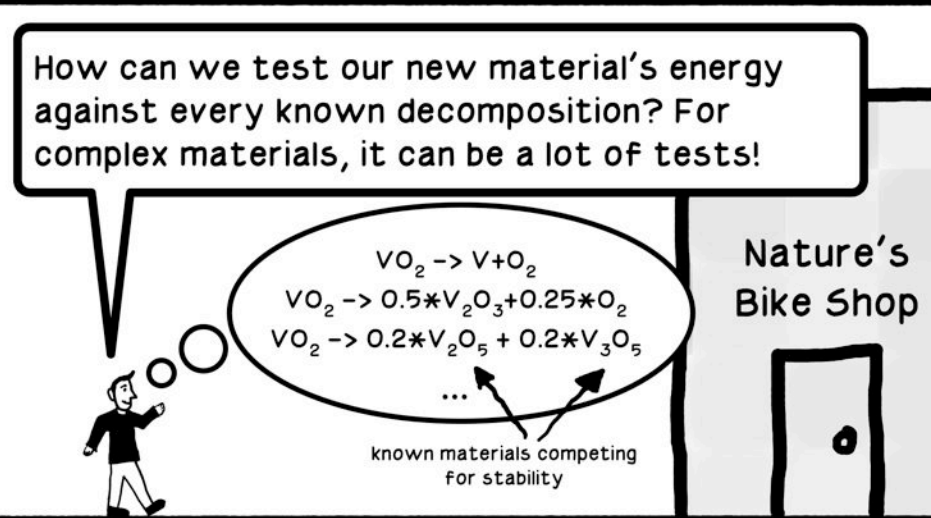


We might try comparing our material's energy against other common crystal structures at the same composition!

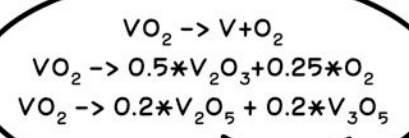
our predicted breakthrough finishes with the lowest energy!



But that is not enough! In nature, the competition is more fierce! Decomposition reactions to *different compositions* also compete for the lowest energy equilibrium!



How can we test our new material's energy against every known decomposition? For complex materials, it can be a lot of tests!



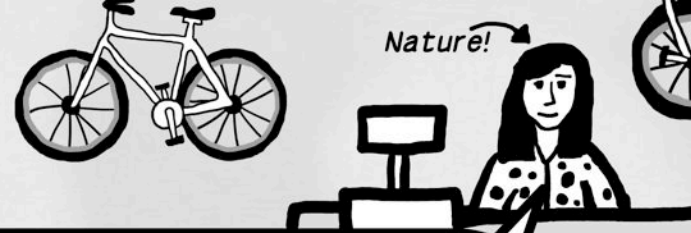
known materials competing for stability

Nature's Bike Shop

*Inspired by Scott McCloud's *Understanding Comics*
Comic font: Basic Comical NC by Jayvee Enaguas

Here we are in Nature's bike shop! Nature, perhaps you can tell us about how your business operates!

Sure! We have a stockroom containing wheels and bike frames. Depending on how many of each we have, we assemble unicycles or bicycles to sell at a profit!

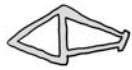


Here's our profit sheet!

Our goal is to maximize profit based on stockroom composition!



wheels
no profit [\$0/part]



frames
no profit [\$0/part]



unicycles [wheel+frame]
\$20 profit [\$10/part]



bicycles [2 wheels+frame]
\$30 profit [\$10/part]

If stockroom contains...

We will make/earn:

2 wheels + 1 frame

bicycle [\$30=\$10/part]



2 wheels + 2 frames

2 unicycles [\$40=\$10/part]



3 wheels + 1 frame

bicycle+wheel [\$30 = \$7.5/part]



So Nature's products and her profit depends on the starting ratio of wheels to frames! What's her strategy?

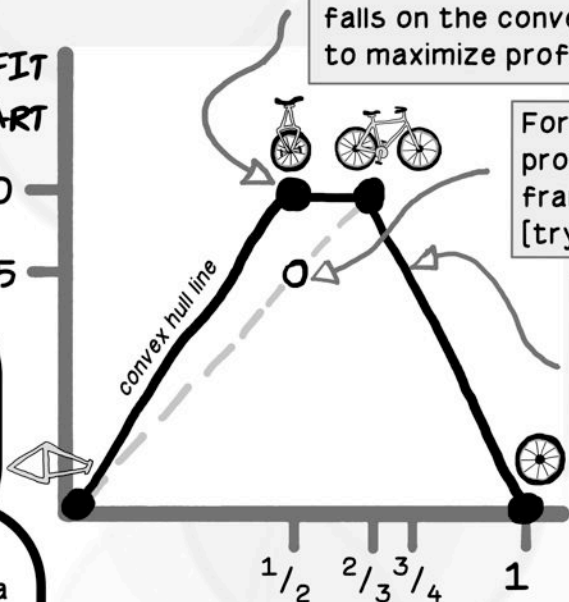
Let's plot the profit for all known products versus the fraction of wheels they contain as solid black dots!

Next, connect those profits via a black convex hull line, like a rubber band snapping over pushpins!

The final plot tells us the most profitable products for different stockroom compositions - we just need to follow the convex hull!

PROFIT PER PART

\$10
\$7.5



COMPOSITION OF STOCKROOM (FRACTION WHEELS)

At a wheel fraction of 0.5 [example #2 above], the unicycle falls on the convex hull. So that's what Nature should make to maximize profit, giving \$10/part as found earlier!

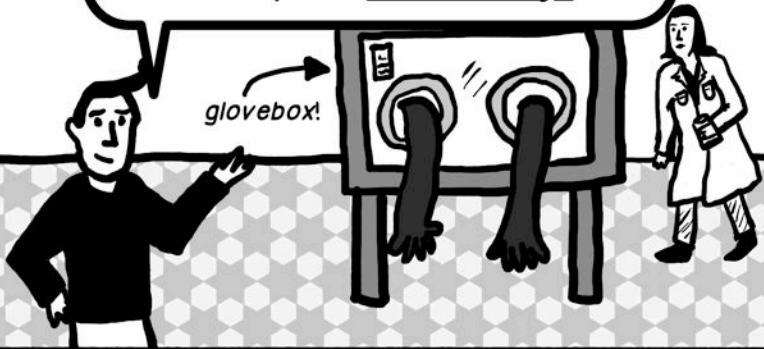
For comparison, at that same fraction of 0.5, producing a mixture of bicycles and leftover frames would earn only \$7.5/part! [try the math with 2 frames and 2 wheels]

For a wheel fraction of 0.75 [example #3 above], the convex hull connects bicycles and wheels. The profit from this mixture is \$7.5/part. So a new product at this ratio [like a tricycle!] must earn over \$7.5/part in order to be sold at Nature's bike shop!

Okay ... but what does all this have to do with chemistry?



Here we are in an experimental lab, trying to apply lessons from Nature's bike shop to chemistry!



Looks like a PhD candidate is mixing Fe and P in a sealed glovebox can we *predict* the result?



Bike shop convex hull



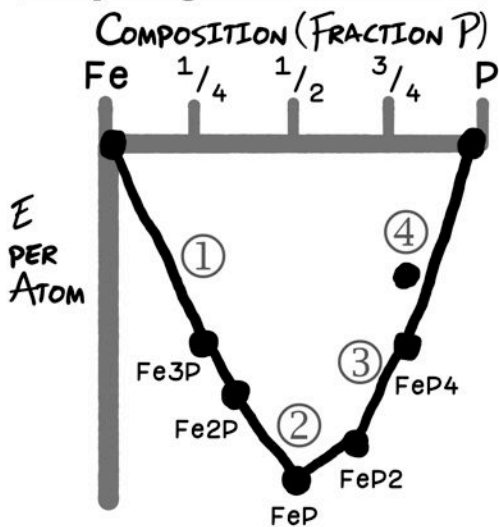
Fe-P convex hull



Yes!
But first we need to turn our convex hull upside-down!



"Interpreting the Fe-P convex hull"

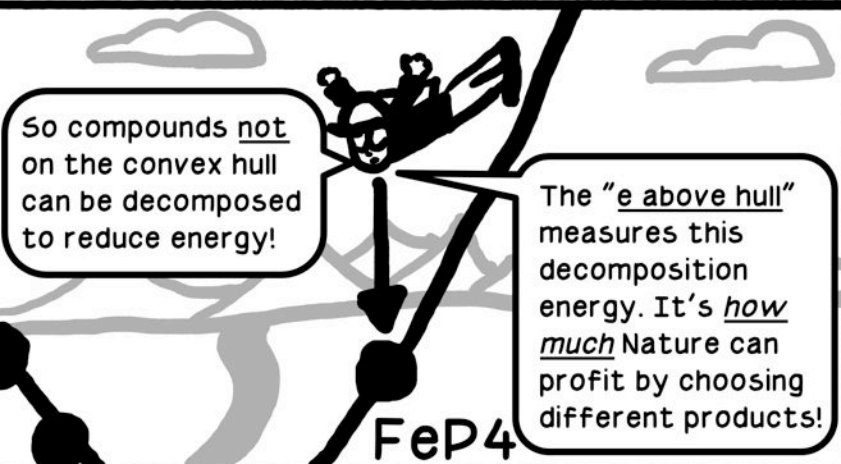


① Like in the bike shop, each point represents a product that Nature can make. Once again, the convex hull connects points like a rubber band over pushpins. On the y-axis, we plot the [computed] energy per atom.

② FeP - with a single Fe and a single P - is like Nature's unicycle! FeP2 is like a "bicycle". Points on the convex hull cannot be decomposed to other products to reduce energy; they are thermodynamically stable!

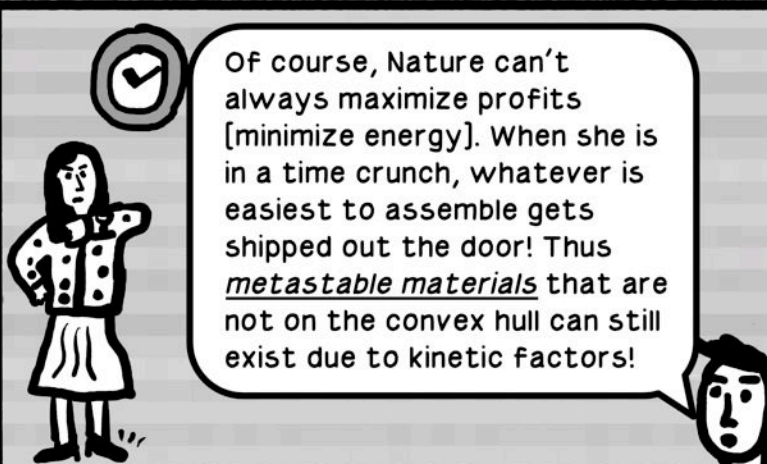
③ At a ratio of Fe:P = 1:3, there exists no stable FeP3 phase ["tricycle"]. Energy is minimized by forming a mixture of FeP2 and FeP4. To predict a new FeP3 phase, we should find a structure with energy below the convex hull [not just the lowest-energy FeP3 structure!]

④ Multiple crystal structures - with different energies - can be compared at the same composition. The two FeP4 points are like two models of a 4-wheeled bike! [one is stable, the other metastable]

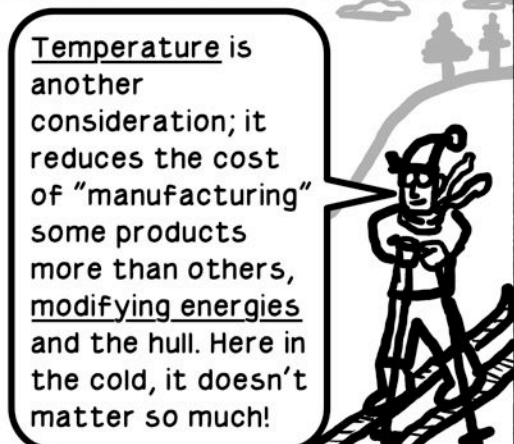


So compounds not on the convex hull can be decomposed to reduce energy!

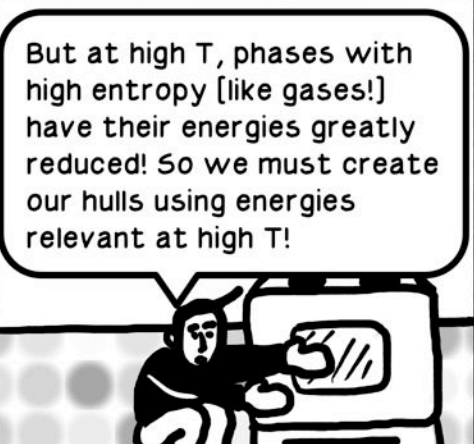
The "e above hull" measures this decomposition energy. It's how much Nature can profit by choosing different products!



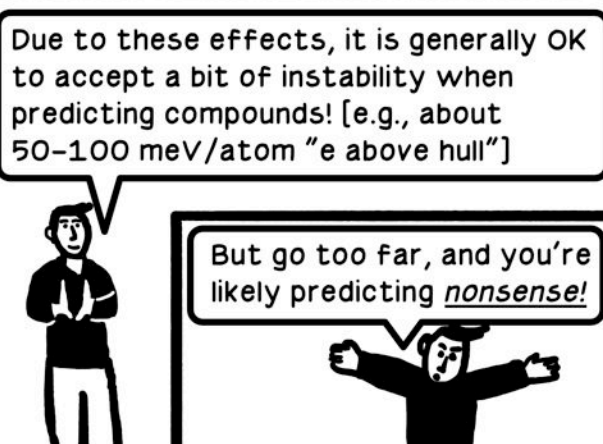
Of course, Nature can't always maximize profits [minimize energy]. When she is in a time crunch, whatever is easiest to assemble gets shipped out the door! Thus metastable materials that are not on the convex hull can still exist due to kinetic factors!



Temperature is another consideration; it reduces the cost of "manufacturing" some products more than others, modifying energies and the hull. Here in the cold, it doesn't matter so much!



But at high T, phases with high entropy [like gases!] have their energies greatly reduced! So we must create our hulls using energies relevant at high T!



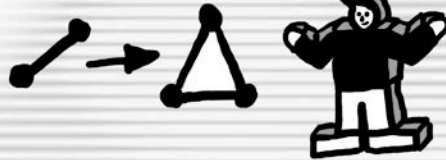
Due to these effects, it is generally OK to accept a bit of instability when predicting compounds! [e.g., about 50-100 meV/atom "e above hull"]

But go too far, and you're likely predicting nonsense!

Perhaps you're wondering what to do with more than 2 components?



Fortunately, convex hulls can be applied to systems with any number of components - we just need to add another dimension!



For example, let's say Nature adds another part for building products - the basket!



Now Nature also sells...

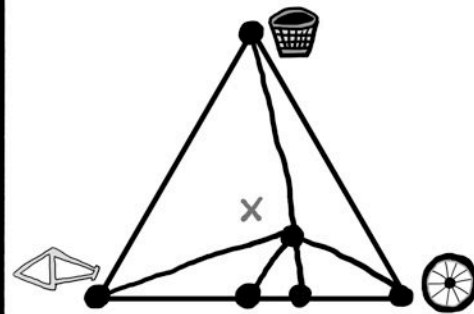


First, we plot Nature's products on a triangle: the closeness to a vertex is the fraction of that component!

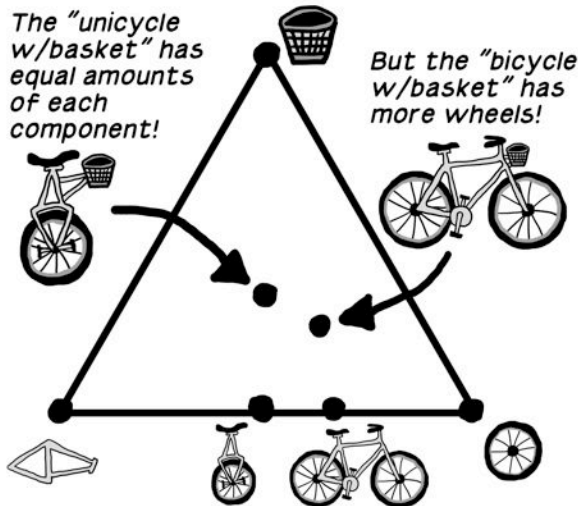
We can't see the profits on this 2D plot, so pretend we stick up *tent poles* at each product. The height of the pole is the profit per part.

A 2D plot only shows the "outline" of the tent from above as lines. Unstable points that do not touch the tent are indicated by a different symbol or color [in this case, a gray 'X']

The convex hull is like stretching a tent over the poles - only the stable materials will touch the tent!



The unicycle with a basket is unstable because with equal amounts of all parts, the bicycle with basket along with a leftover frame and basket is the most profitable combination! Try the math with 2 of each part...



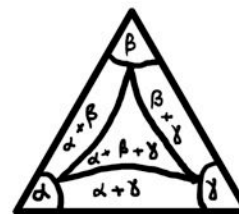
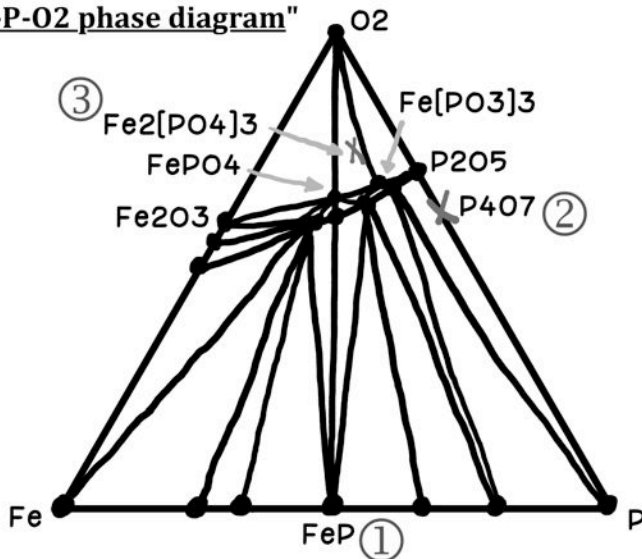
The bottom edge is like our first convex hull!



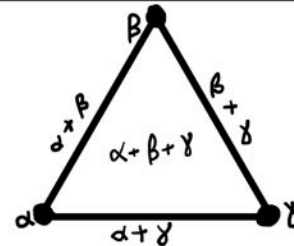
Going back to chemistry, we can use the same idea to create phase stability diagrams for *ternary* systems!

Note that these phase stability diagrams can appear different than experimental diagrams because no solubility is taken into account. Single-phase regions are always points, two-phase regions are always infinitesimal lines, and all finite areas are 3-phase regions!

"Fe-P-O2 phase diagram"



Experimental



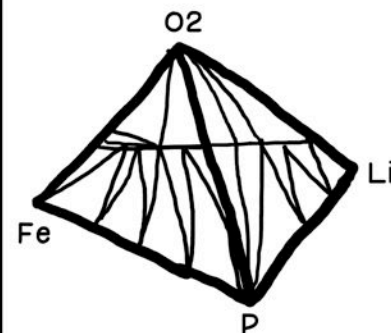
Computational

① Like always, stable compounds like FeP are marked by circles and intersect the lines [the convex hull surface]

② Unstable compounds on a line segment decompose to its two endpoints, like P4O7 -> P + P2O5

③ Compounds inside a triangle decompose to its three vertices, like 4Fe2[PO4]3 -> 6FePO4 + 2Fe[PO3]3 + 3O2

One can even add *more* components. For example, a 4-element phase diagram is plotted as a 3D tetrahedron with elements at each corner and energy in a hidden 4th dimension! This is difficult to read but the analysis is straightforward.



The convex hull algorithm computes the most stable decomposition, regardless of number of elements!

So there you have it!
Computational phase diagrams in a nutshell!

Yes?!

But everything you've told us is for fixed starting compositions! Sometimes, the element ratios depend on the environment!

Oxygen sneaks in from the air! Chemicals come from a concentrated solution! How can we take this into account?

I see your point...
but it's still like the bike shop!

However, let's imagine some of Nature's parts aren't in her supply room. Instead, she must buy parts from an open market!

If Nature no longer starts with wheels, she must subtract from her profit the total cost of buying wheels when deciding what products to sell!

$$P = R - cN$$

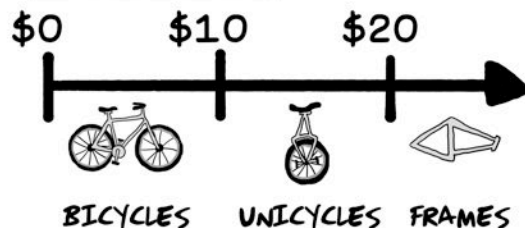
PROFIT REVENUE NUMBER OF WHEELS
COST PER WHEEL

WHEELS FOR SALE!

Let's see what Nature produces from a frame depending on the cost of wheels!

Thus, whomever controls the price of wheels controls Nature's products!

"Price of wheels"



CASE 1:
\$1 WHEELS!

CASE 2:
\$15 WHEELS!



unicycle
\$20 - [1*\$1]
= \$19 profit



unicycle
\$20 - [1*\$15]
= \$5 profit



bicycle
\$30 - [2*\$1]
= \$28 profit



bicycle
\$30 - [2*\$15]
= \$0 profit

Things are similar in chemistry! When an element is open to the environment, we need to minimize the grand potential [energy "cost" when "purchasing" open elements!]

$$\Phi_G = G - \mu N$$

GRAND POTENTIAL GIBBS FREE ENERGY CHEMICAL POTENTIAL AMOUNT OF ELEMENT IN PRODUCT

When wheels are cheap, make bicycles!

But if wheels are expensive, unicycles are better!

The chemical potential of an open element is like its "cheapness" on the free market!

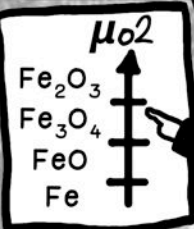
A good experimentalist is like a corrupt tycoon, fixing the price of these elements to get what they want!

CASE 1:
HIGH μ_{O_2}

CASE 2:
LOW μ_{O_2}

I'm synthesizing in air at low temperatures - oxygen is cheap! Metals will absorb lots of O₂!

I'm synthesizing under an inert gas atmosphere at high temperature! Oxygen is expensive to obtain! Less O₂ will be absorbed! Muahahaha!

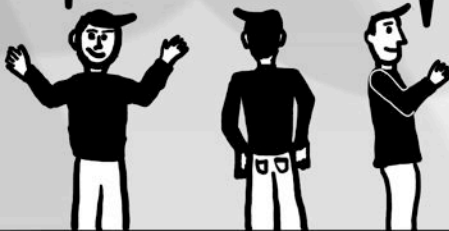


crucible containing Fe₂O₃

sealed tube containing FeO

Open phase diagrams look like regular phase diagrams with the same number of closed elements!

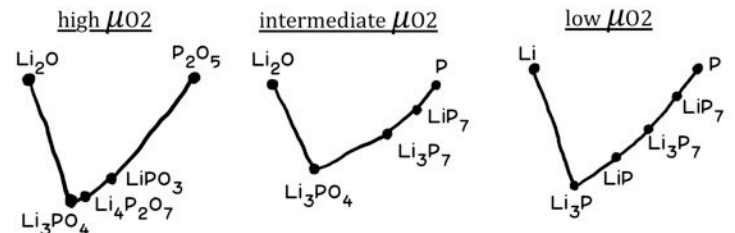
A series of these diagrams is shown at different chemical potentials of the open elements to give a full view of the system!



V closed, O2 open* – a series of points!

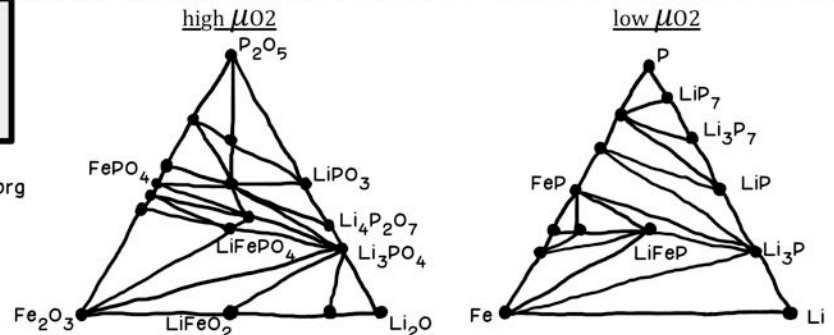
- $\mu_{O_2} > -0.9$ • V_2O_5
- $-1.4 < \mu_{O_2} < -0.9$ • V_3O_7
- $-2.2 < \mu_{O_2} < -1.4$ • VO_2
- $-2.4 < \mu_{O_2} < -2.2$ • V_3O_5
- $-4.2 < \mu_{O_2} < -2.4$ • V_2O_3
- $\mu_{O_2} < -4.2$ • V

Li & P closed, O2 open* – a series of 1-dimensional lines! As oxygen becomes less cheap, oxides disappear!



Li & P & Fe closed, O2 open* – a series of 2D ternary plots!

* Data from www.materialsproject.org (May 2014)



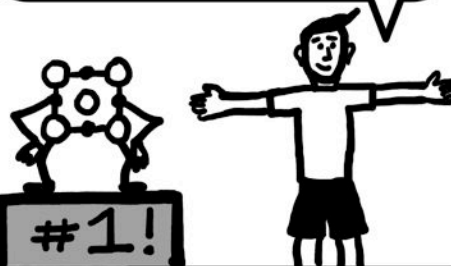
Note that if a compound is stable on a closed phase diagram, opening an element to the environment can make that compound unstable!

But the reverse is not possible! An unstable compound cannot be made stable by opening one of the elements!



Whether your environment is open or closed, or you have two elements or four, remember that the race for stability involves more than just structure polymorphs!

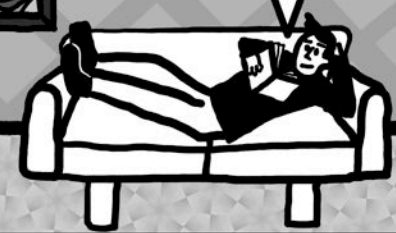
With convex hulls, we simultaneously evaluate all decompositions!



And there's plenty more to learn!

For example, Ellingham Diagrams are another way to visualize stability under temperature and pressure.

And Pourbaix Diagrams are essentially phase diagrams with electrons and protons as "open" components!



Nature's Bike Shop



Bye!
Good luck!



Hope you enjoyed touring Nature's bike shop and our phase diagram explorations!

For more information, including how to test your own compounds for stability, check out:

www.hackingmaterials.com/pdcomic

See you next time!

