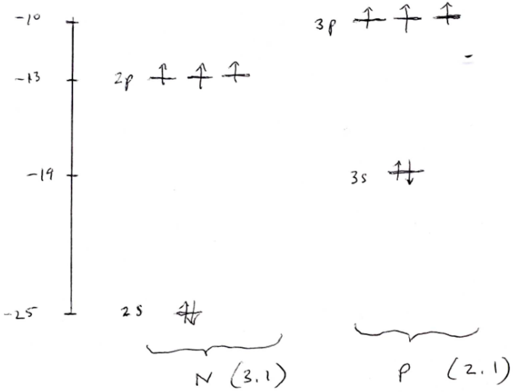
Nitrogen

vs.

Phosphorus

The Free Atom

Atomic energy levels, valence orbital ionization energies (VOIE)



- Electronegativity for carbon: 2.5
- Electronegativity for hydrogen: 2.2

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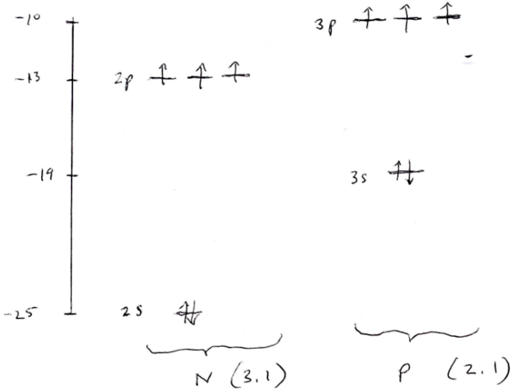

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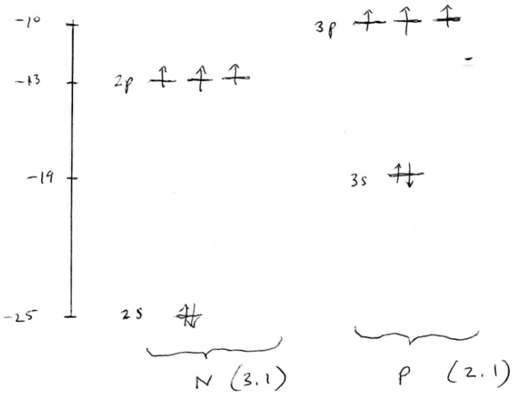

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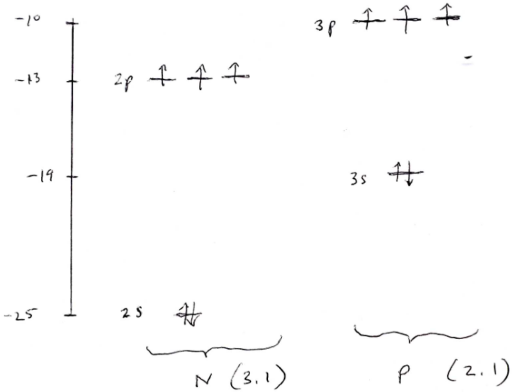

- Quartet ground state, spin multiplicity given by $2S + 1 = 2(\frac{3}{2}) + 1 = 4$
- Four possible values for the spin: $+\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

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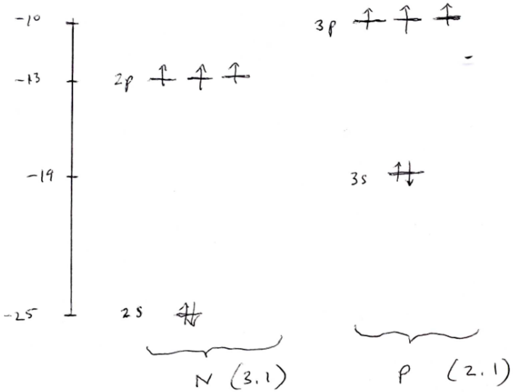

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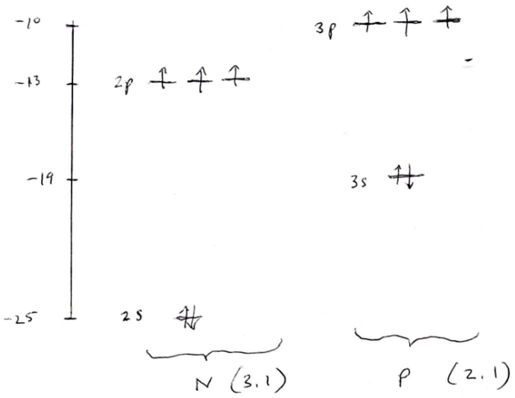

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Single versus Triple Bonds

Atomic energy levels, valence orbital ionization energies (VOIE)

	kJ/mol
N–N	159
N≡N	946
P–P	200
P≡P	490

P_2

P≡N

N≡N >> 3(N–N)

P≡P << 3(P–P)

weak N–N due to LP repulsion
(similar for O–O, F–F)

- ΔH_f° for P_2 is +144 kJ/mol
- ΔH_f° for P≡N is +104 kJ/mol

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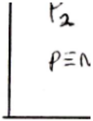

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- The higher the sum of electronegativities of the two atoms involved in bonding, the higher the probability for formation of a double bond
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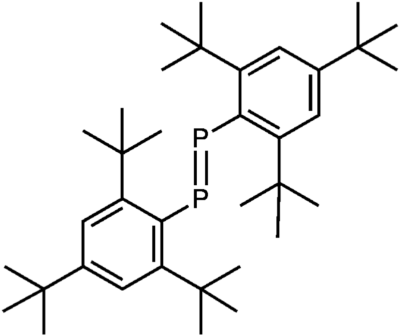
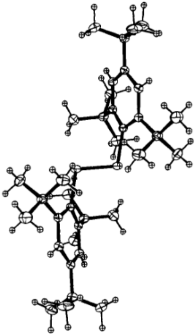
Yoshifuji's Example of a Phosphobenzene

Isolated and characterized in 1981, DOI: 10.1021/ja00405a054





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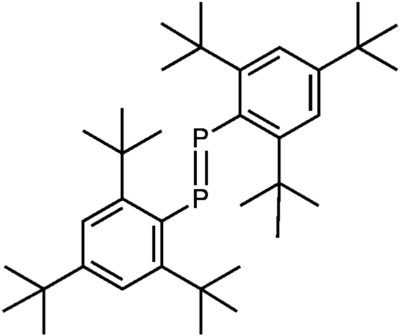

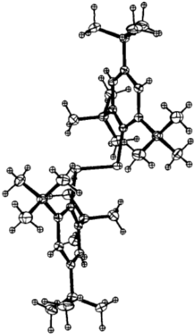

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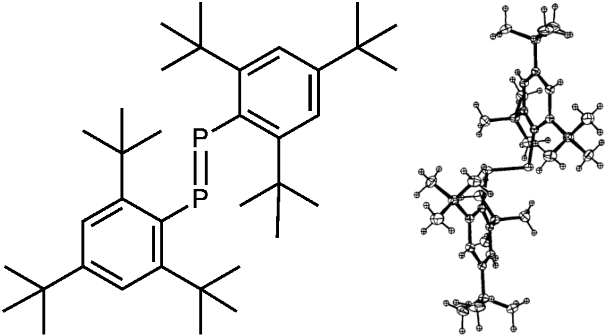

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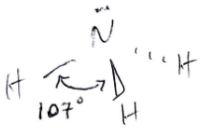

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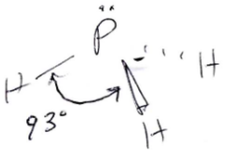
basic, a good electron pair donor



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bonds form with 3p orbitals

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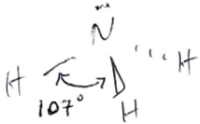

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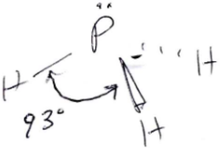

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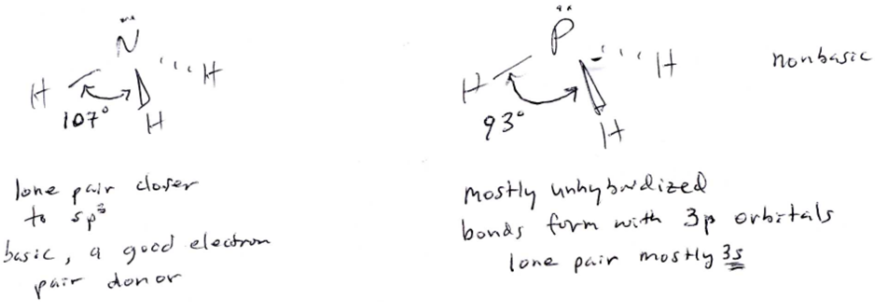

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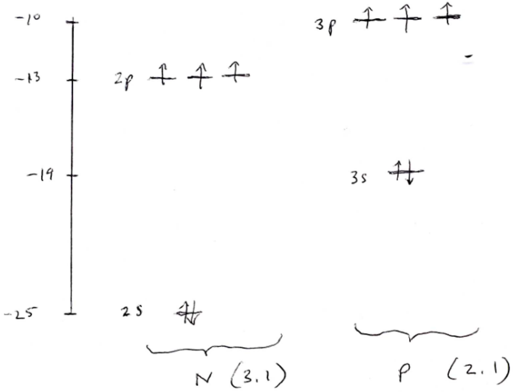

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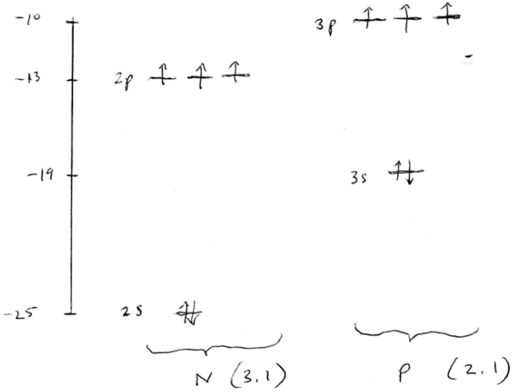

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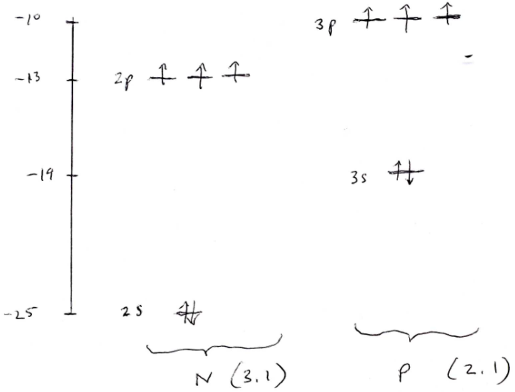

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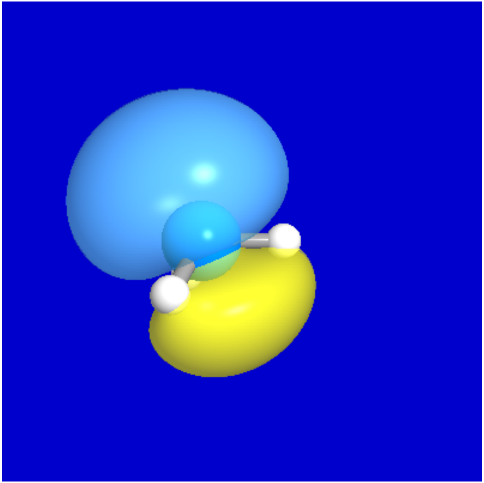

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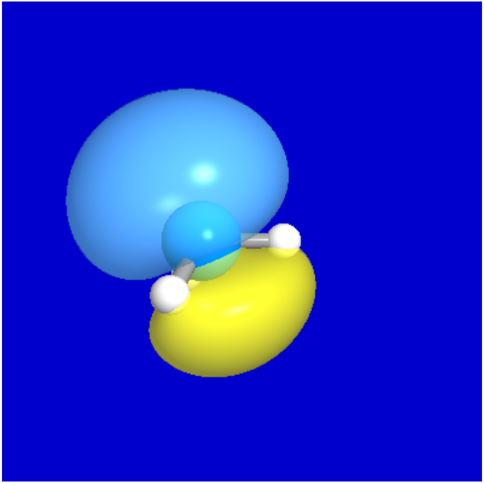

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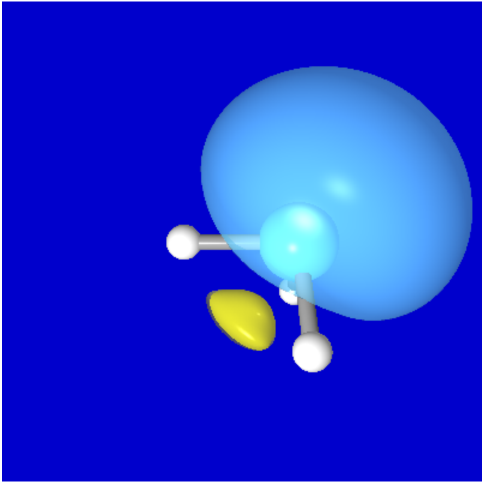

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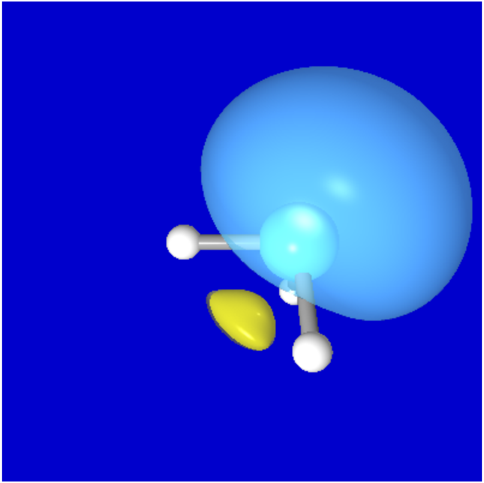

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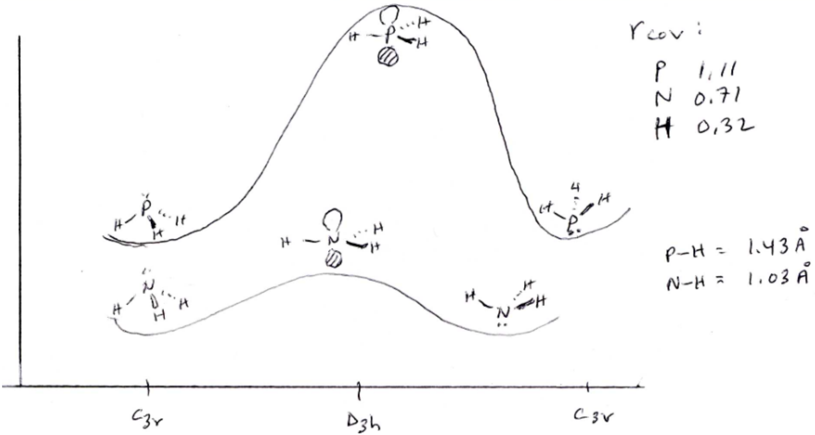
Inversion Frequency NH_3 vs. PH_3

Ammonia inversion involves an umbrella motion of the atoms



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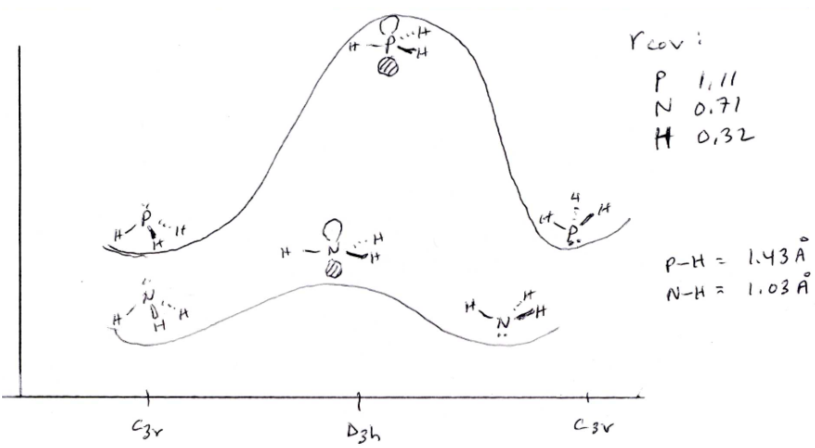

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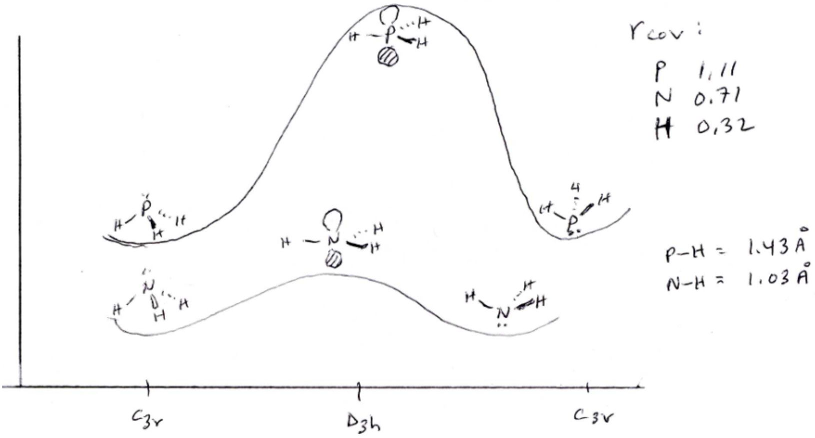

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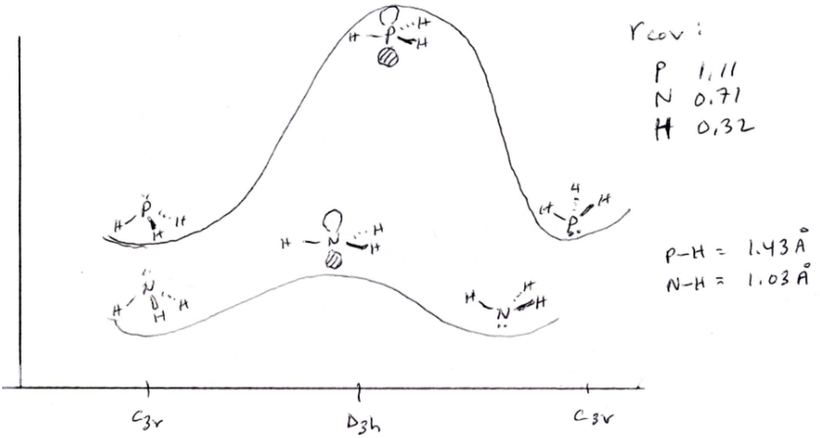

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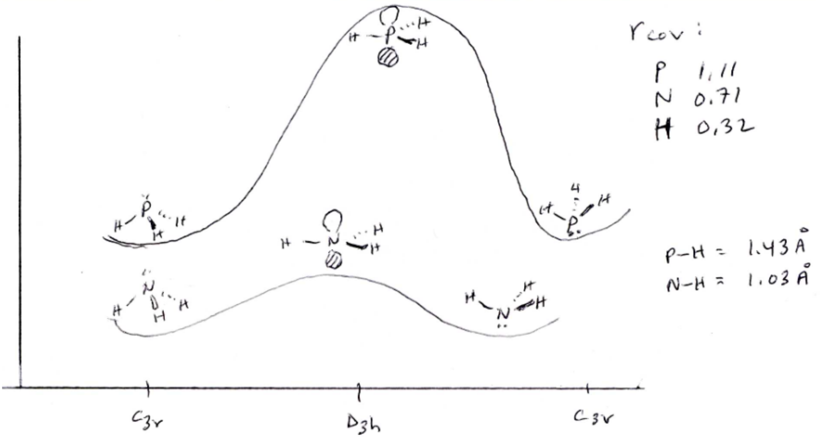

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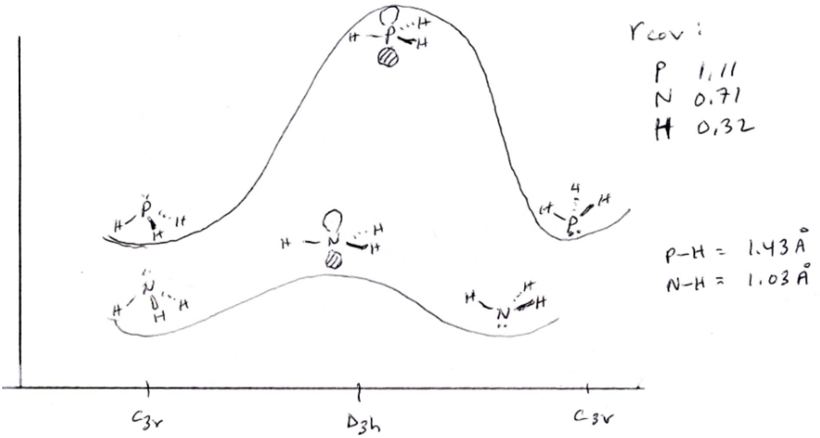

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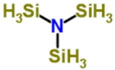
- A lone pair is like a bond to a group of infinite electropositivity
- Properties of inversion barrier: increases with increasing relative substituent EN
- Example: trisilylamine is planar at nitrogen



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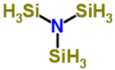

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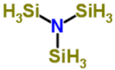

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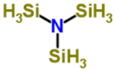

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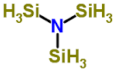

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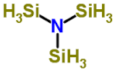

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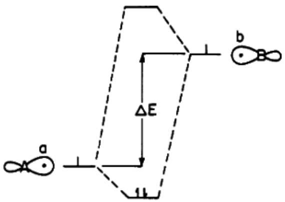
The Walsh–Bent rule can be understood qualitatively using simple perturbation theory arguments.[12] Consider two orbitals, of unequal energy, a and b, centered on atoms A and B, respectively. We now allow them to interact to form a bond:



Their interaction increases with (1) decreasing energy separation ΔE and (2) increasing overlap of the two orbitals. As A becomes more electronegative, a's energy drops, its spatial distribution contracts, and its overlap with b diminishes. Reduced interaction with b is the result. In reacting to the perturbation, b tries to improve its overlap with the now more contracted orbital a. It does so by increasing its directionality, i.e., p character. The rehybridization of B which this requires must, of course, reduce the p character, hence increase the s character, of the remaining less electronegative substituents.

- N_2 is less basic than pyridine
- Pyridine is less basic than ammonia
- The lone pair in these compounds: sp, sp^2, sp^3
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s Character and Base Strength

Distribution of atomic s character in molecules and its chemical implications

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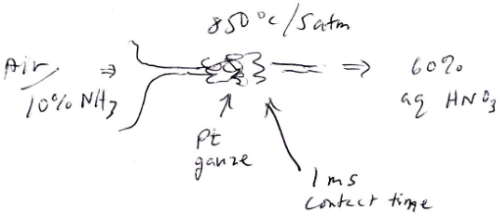
Nitric Acid Synthesis

Modern HNO_3 Synthesis: Catalytic oxidation of NH_3

W. Ostwald (NP 1909) over heated Pt, selective for NO

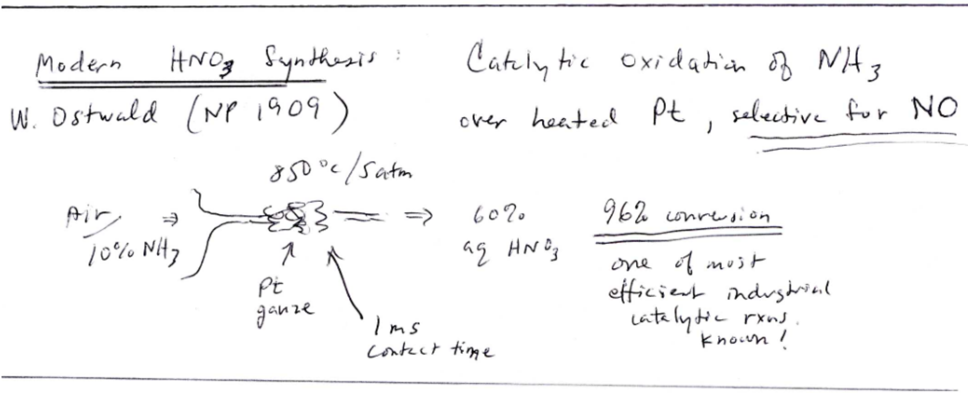


96% conversion

one of most efficient industrial catalytic rxns known!

- Commercialization relied upon large scale NH_3 availability via Haber-Bosch
- Largest use is for ammonium nitrate fertilizer production

Nitric Acid Synthesis



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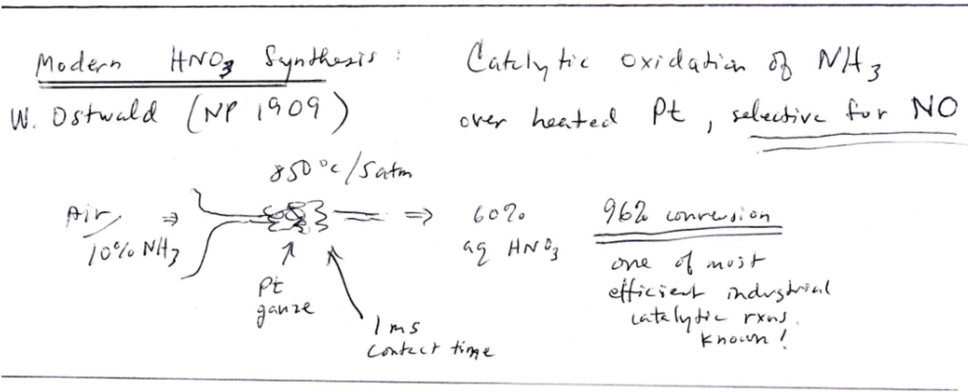

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Nitric Acid Synthesis

$$NH_3 + 1\tfrac{1}{4}\,O_2 \rightarrow NO + 1\tfrac{1}{2}\,H_2O$$

mult by 3/2:

$$NO + \tfrac{1}{2}\,O_2 \rightarrow NO_2$$

$$NO_2 + \tfrac{1}{3}\,H_2O \rightarrow \tfrac{2}{3}\,HNO_3 + \tfrac{1}{3}\,NO$$

$$NH_3 + 2\,O_2 \rightarrow HNO_3 + H_2O \qquad \Delta H \; -412.6 \text{ kJ/mol}$$

- Depends upon catalyst selectivity for NO over other thermodynamically favorable products

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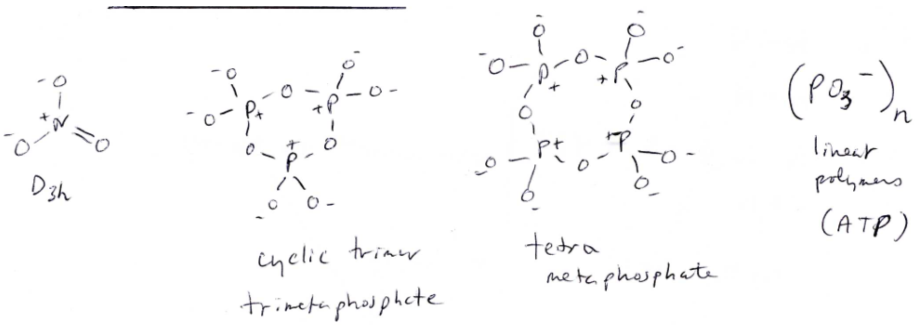
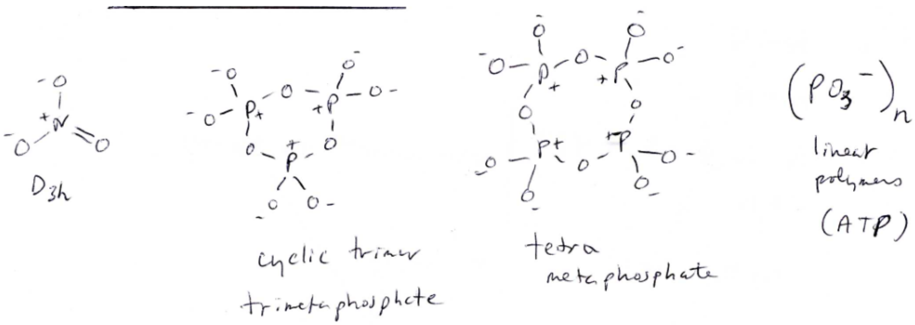


- Nitrate ion has D_{3h} symmetry (isoelectronic to BF_3)
- Nitrate enjoys delocalized π bonding
- Metaphosphate is not seen as a monomer, but rather forms rings
- Opening metaphosphate rings gives chains such as is found in ATP

Nitrate versus Metaphosphate



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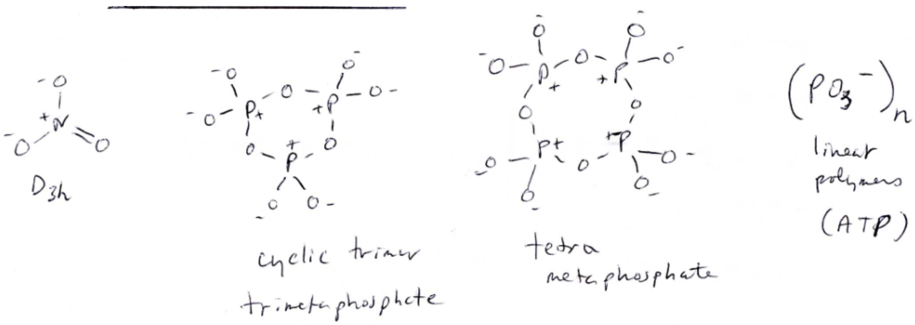
- Nitrate enjoys delocalized π bonding
- Metaphosphate is not seen as a monomer, but rather forms rings
- Opening metaphosphate rings gives chains such as is found in ATP

Nitrate versus Metaphosphate



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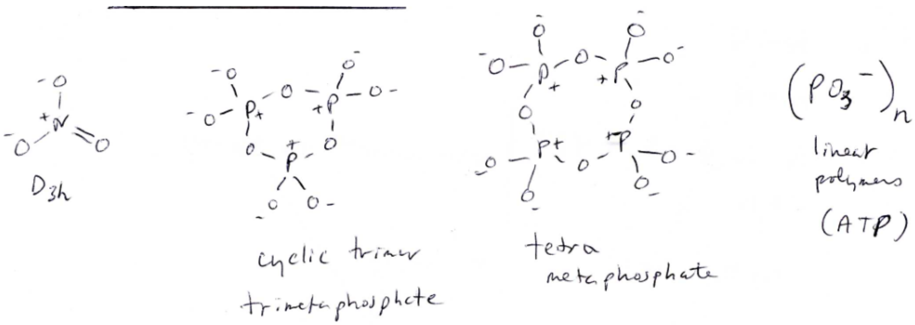

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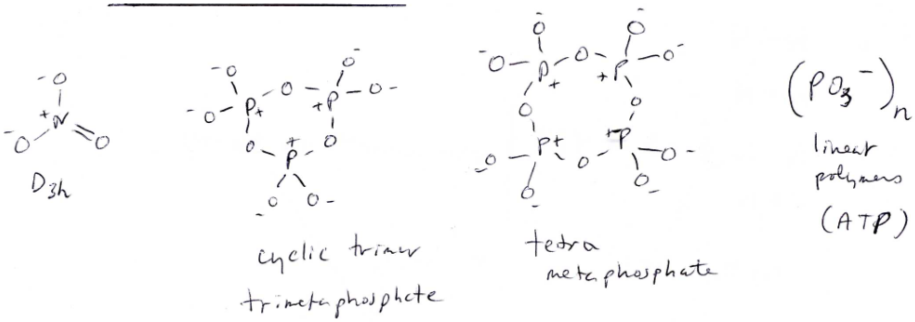

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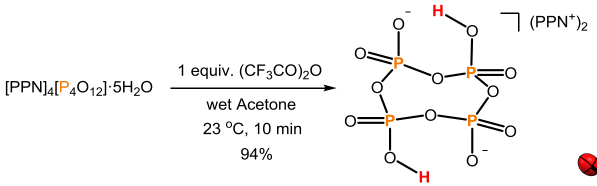
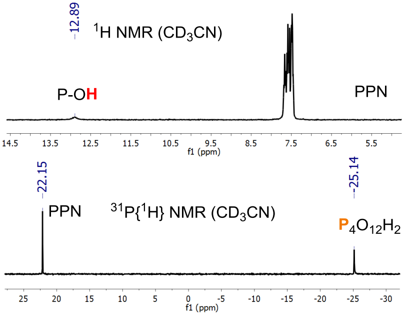
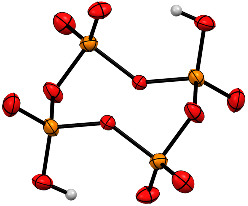
Dihydrogen Tetrametaphosphate

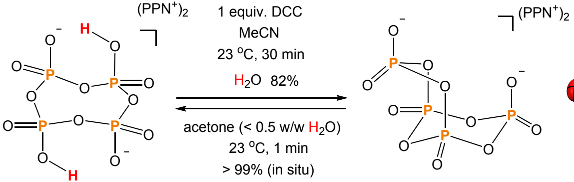


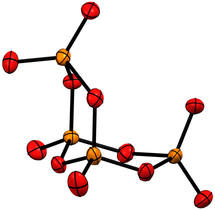




pK_a = 15.83 ± 0.11
(MeCN, 23 °C)

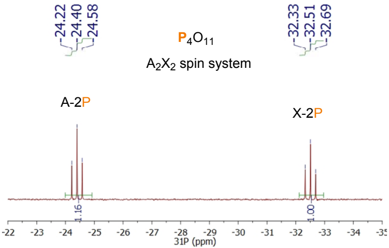
Tetrametaphosphate Anhydride

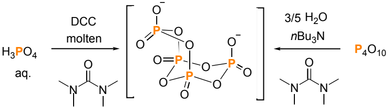




DCC = N,N'-dicyclohexylcarbodiimide

$^{31}P\{^1H\}$ NMR (CD_3CN)





Glonek, T.; Myers, T. C.; Han, J. R.
J. Am. Chem. Soc. **1970**, *92*, 7214-7216
Glonek, T.; Van Wazer, J. R.; Kleps, R. A.; Myers, T. C.
Inorg. Chem. 1974, *13*, 2337-2345

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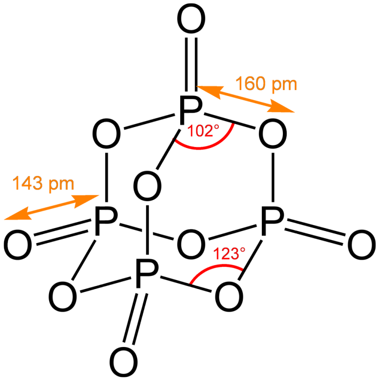
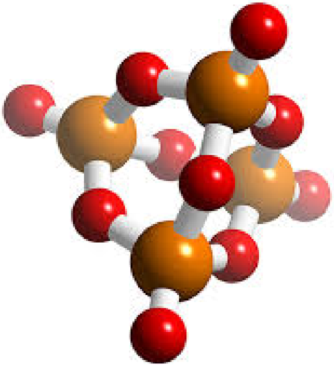
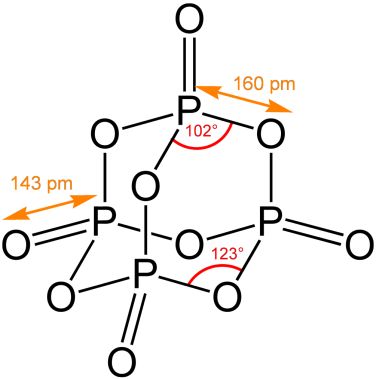
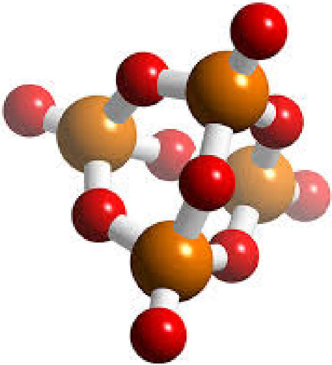




- A nice inorganic example of T_d symmetry!





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MOLECULE OF THE YEAR

NO News Is Good News

A startlingly simple molecule unites neuroscience, physiology, and immunology and revises scientists' understanding of how cells communicate and defend themselves

A decade ago, nitric oxide (NO) was just another toxic molecule, one of a lengthy list of environmental pollutants found in unsavory haunts such as cigarette smoke and smog. Destroyer of ozone, suspected carcinogen, and precursor of acid rain, this gas had a bad reputation.

But over the past 5 years, diverse lines of

lar physiology, and carcinogenesis—suddenly realized they were studying the same molecule. Like a squirt of some powerful perfume, a puff of nitric oxide spurs different cells into an array of different activities, from communication to defense to regulation.

A thousand times NO. In 1992, scientists probed the reasons behind these multiple personalities. One significant clue: the biochemistry of nitric oxide manufacture. Cells rely

ing out how the enzyme works.

NO cure for heartache. This year, clinical applications of NO knowledge bloomed in several directions at once, but much effort focused on nitric oxide's role as the body's own blood pressure police. In blood vessels, NO is released by endothelial cells on the inside of the vessel wall, migrates to nearby muscle cells, and relaxes them. This dilates the vessel and lowers blood pressure.

Other Oxides of Nitrogen

- Nitrous oxide, N_2O, is known as laughing gas
- N_4O isolated in 1993 as a pale yellow solid
- NO_2 is a brown paramagnetic gas that dimerizes reversibly
- Nitrite is the $[NO_2]^-$ anion
- Nitrate is the $[NO_3]^-$ anion

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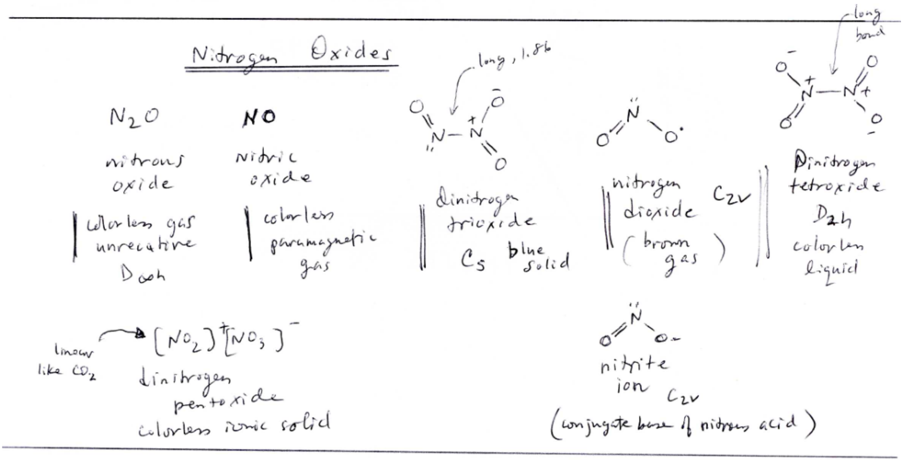
The Variety of Nitrogen Oxides



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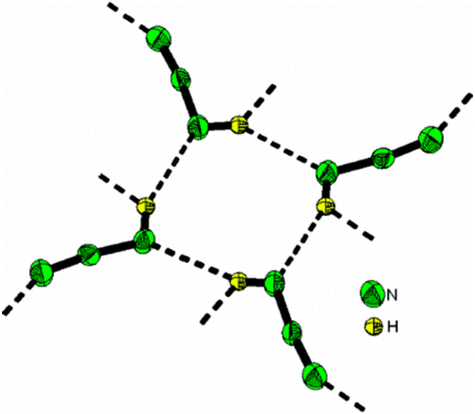
Molecular Structure of Hydrazoic Acid

Hydrogen-bonded tetramers in nearly planar layers DOI: 10.1021/ja2027053



- The crystalline acid is 97.7 wt % nitrogen!

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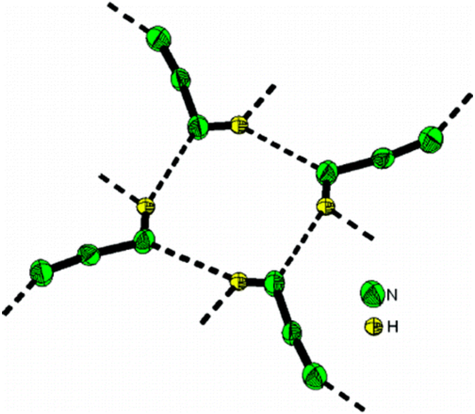

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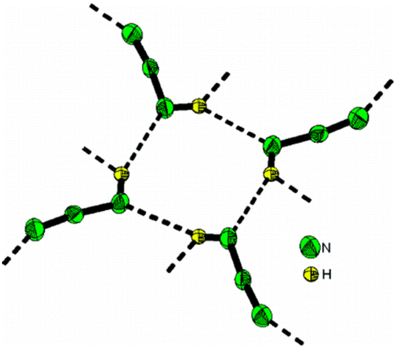

- For the structure determination, single crystals were grown in situ in the X-ray capillary … near the melting point of HN_3 at ca. 193 K in several melting and crystallizing cycles
- "The tip of a finger, carefully touching the capillary, was used as the heating source"

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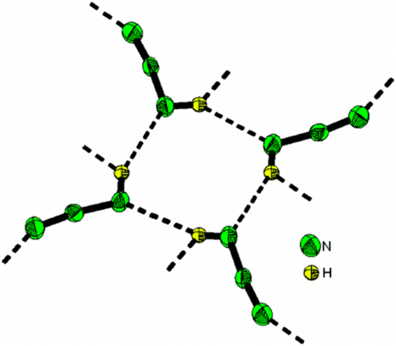

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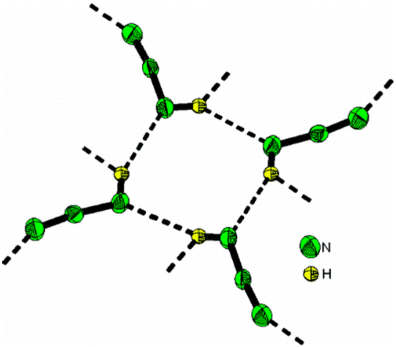

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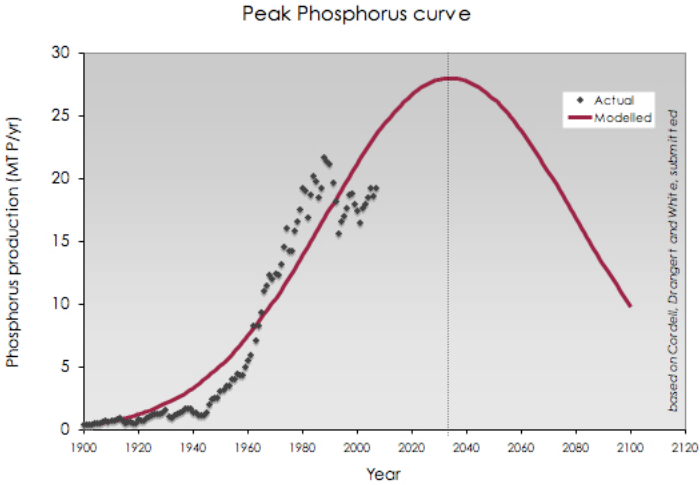
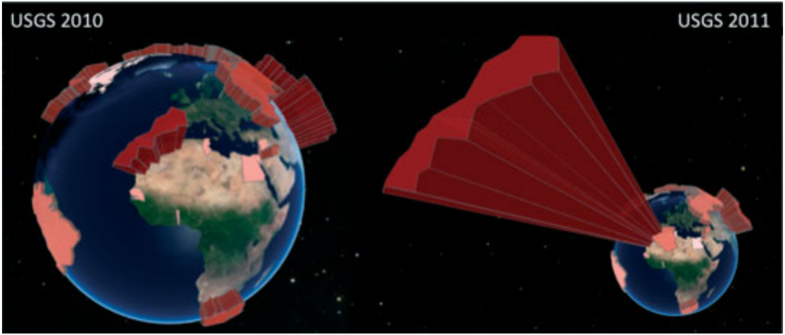
Phosphate Rock Mining: Peak Phosphorus

http://phosphorusfutures.net/peak-phosphorus



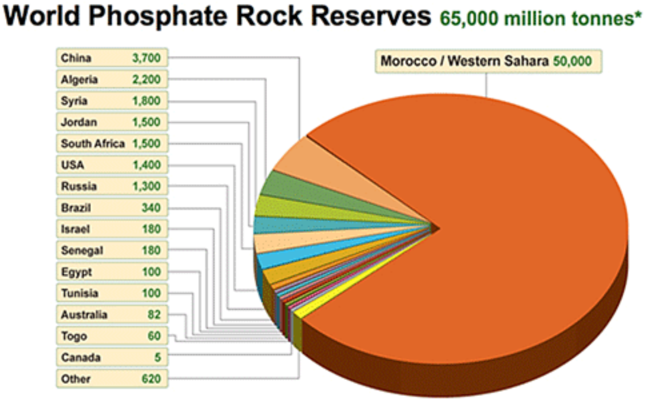
Phosphate Rock Reserves

Neset2012, http://dx.doi.org/10.1002/jsfa.4650



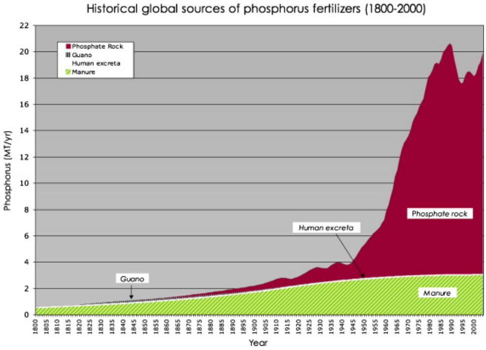
Phosphate Rock Reserves

http://www.worldresourcesforum.org/resource-snapshot-5-phosphorus



Global Sources of Phosphorus Fertilizers

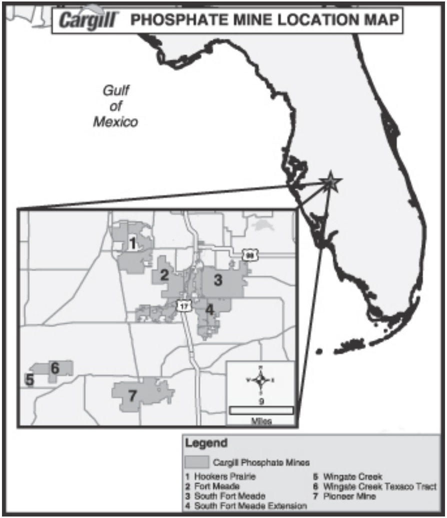
Cordell2009, http://dx.doi.org/10.1016/j.gloenvcha.2008.10.009



Phosphate Mining in Morocco

Phosphate rock loading. Khouribga, Morocco.

Cargill Phosphate Mines in Florida

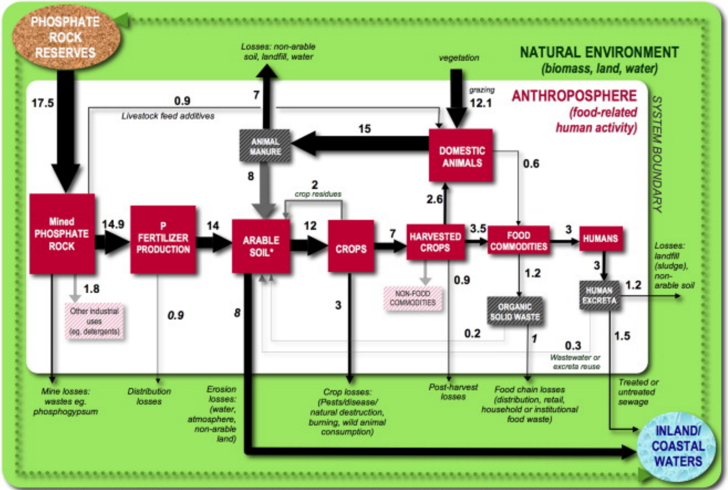


Central Florida Mined Out

http://www.manasota88.org/phosphate.html

Phosphorus Flow in Africa

Cordell2009, http://dx.doi.org/10.1016/j.gloenvcha.2008.10.009



= Industrial P flows occurring at rate of 'days to years' = Recirculated P flows from organic sources to arable land = Natural biogeochemical P flows occurring at rate of 'millions of years'

* only a fraction of applied mineral P is taken up by crops in a given year, the balance comes from the soil stocks, either from natural soil P, or build up from previous years and decades of fertilizer application.

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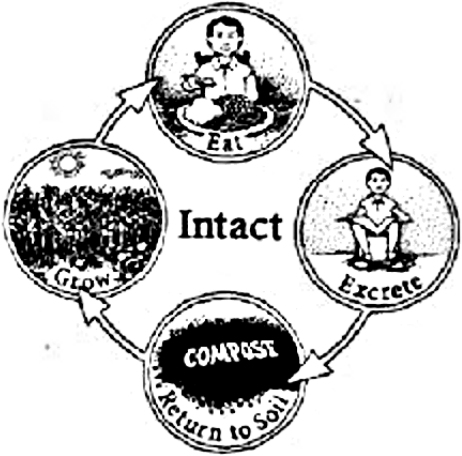
Reuse of Human Excreta

Cordell2009, http://dx.doi.org/10.1016/j.gloenvcha.2008.10.009

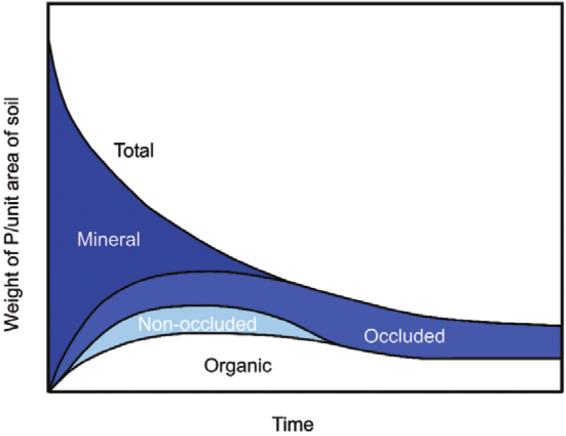
Composting to Recycle Human Excreta

Composting saves water and energy as well as nitrogen and phosphorus!



Changes in Soil Phosphorus Availability with Time

Note that phosphorus is continually lost from the system; from Filippelli2008 DOI: 10.2113/GSELEMENTS.4.2.89



Phosphorus Recycling

Steve Safferman of MSU pursuing iron-based precipitation scheme

Science News *... from universities, journals, and other research organizations*

New Method to Remove Phosphorus from Wastewater

Aug. 15, 2012 — A professor at Michigan State University is part of a team developing a new method of removing phosphorus from wastewater -- a problem seriously affecting lakes and streams across the United States.

Steve Safferman (r), associate professor of biosystems and agricultural engineering, and student Hayley Betker are working to develop a new method of removing phosphorus from wastewater. Phosphorus runoff into lakes and streams can seriously affect the health of the water. (Credit: Photo by Kurt Stepnitz)

In addition, Steven Safferman, an associate professor of biosystems and agricultural engineering, and colleagues at Columbus, Ohio, based-MetaMateria Technologies, are devising a cost-effective way of recovering the phosphorus, which then can be reused for fertilizer products.

Although its use is regulated in many states, including Michigan, in items such as detergents and fertilizer, phosphorus is part of all food and

Enviropig, U. of Guelph

Genetically engineered pig breaks down and absorbs more phosphorus, excretes less