The Periodic Table

"Biogenic Elements" needed in large quantities to make living things

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.96	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 **Uus** —	ununoctium 118 **Uuo** [294]

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Massachusetts Institute of Technology

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sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.96	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 **Uus** —	ununoctium 118 **Uuo** [294]

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Massachusetts Institute of Technology

The Periodic Table

"Biogenic Elements" needed in large quantities to make living things

Key: element name / atomic number / symbol / atomic weight (mean relative mass)

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hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [267]	dubnium 105 Db [268]	seaborgium 106 Sg [271]	bohrium 107 Bh [272]	hassium 108 Hs [270]	meitnerium 109 Mt [276]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [280]	ununbium 112 Uub [285]	ununtrium 113 Uut [284]	ununquadium 114 Uuq [289]	ununpentium 115 Uup [288]	ununhexium 116 Uuh [293]	ununseptium 117 Uus —	ununoctium 118 Uuo [294]

*lanthanoids	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.06
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

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sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.38	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
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caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [267]	dubnium 105 **Db** [268]	seaborgium 106 **Sg** [271]	bohrium 107 **Bh** [272]	hassium 108 **Hs** [270]	meitnerium 109 **Mt** [276]	darmstadtium 110 **Ds** [281]	roentgenium 111 **Rg** [280]	ununbium 112 **Uub** [285]	ununtrium 113 **Uut** [284]	ununquadium 114 **Uuq** [289]	ununpentium 115 **Uup** [288]	ununhexium 116 **Uuh** [293]	ununseptium 117 **Uus** —	ununoctium 118 **Uuo** [294]

*lanthanoids	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.06
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

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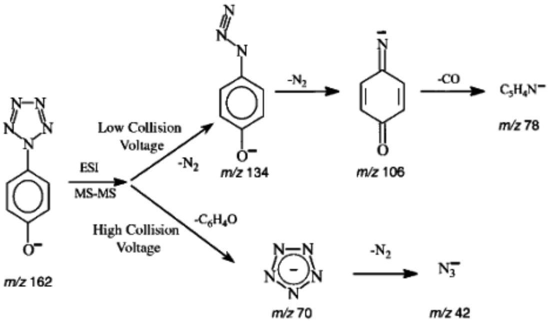
Forms of Nitrogen
Karl O. Christe et al., ACIE 1999, 38, 2004



Scheme 1. ESI-MS-MS fragmentation of the mass-selected unlabeled 4-pentazolylphenolate anion at low and high collision voltages.

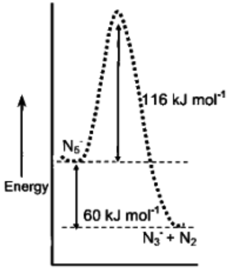


Figure 3. Activation energy barrier and decomposition enthalpy of the pentazolate anion calculated at the CCSD(T)/aug-cc-pVTZ level of theory.[8]

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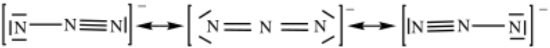
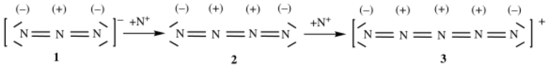
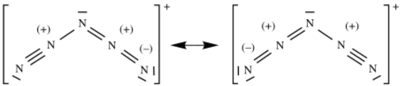


Scheme 1. Resonance structures of N_3^- (**1**).



Scheme 2. Addition of N^+ to N_3^- (**1**) to form N_4 (**2**) and N_5^+ (**3**) as well as the electronic charge distrubutions in **1**–**3**.



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Forms of Nitrogen

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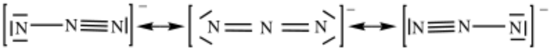

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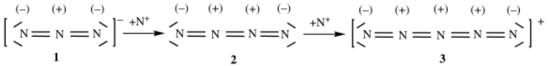

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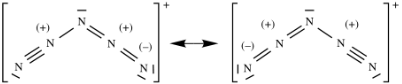

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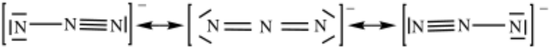

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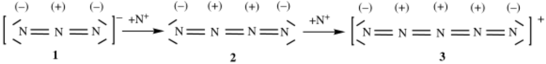
- 

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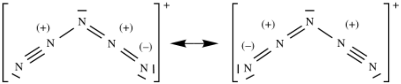
- 

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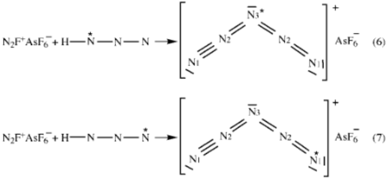
-

Forms of Nitrogen

Karl O. Christe et al., ACIE 1999, 38, 2004

The reaction of labeled HN_3 with $N_2F^+AsF_6^-$ produced a roughly equimolar mixture of N_5^+ with ^{15}N in either the 1- or 3-position [Eqs. (6), (7)].



The $N_5^+AsF_6^-$ salt is a white solid that is sparingly soluble in anhydrous HF. It is marginally stable at 22 °C and can be stored for weeks at −78 °C without noticeable decomposition. It can be handled both in HF solution or as a solid and, in our experience, has not exploded during careful normal handling or when squashed with a stainless steel spatula at −196 °C. It

- N_2 is 78.1% of Earth's atmosphere by volume
- The number of moles of industrially produced NH_3 exceeds that of any other commercial compound
- Proteins on average are about 15% nitrogen by weight
- In 1886 it was shown that N_2 can be "fixed" by certain organisms in root nodules
- Global N fixation, Haber:biological:atmospheric, 36:140:30 (in 10^6 tons). The mass of Earth's atmosphere is approximately 5×10^9 million tons.

Dinitrogen

One of Nature's most inert molecules

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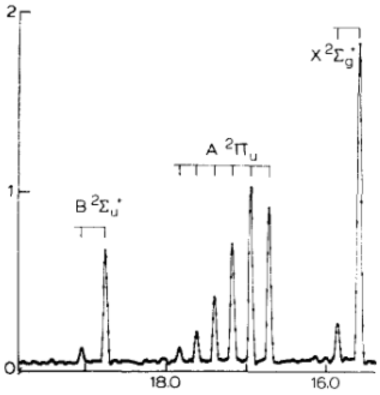
N_2 Photoelectron Spectrum (PES)

304 Å (40.8 eV) spectrum from J. Chem. Phys. 1975, vol. 62, 1447.



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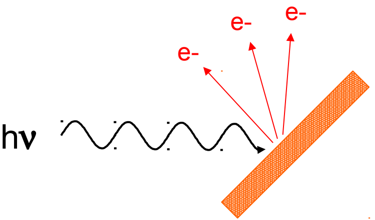
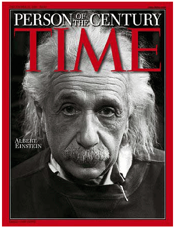
Photoelectric Effect

Ionization occurs when matter interacts with light of sufficient energy (Heinrich Hertz, 1886)
(Einstein, A. Ann. Phys. Leipzig 1905, 17, 132-148.)





E_{hn} = electron kinetic energy + electron binding energy

Photoelectron spectroscopy uses this phenomenon to learn about the electronic structure of matter

General Overview of Spectroscopy

- Spectroscopy uses interaction of electromagnetic radiation with matter to learn something about the matter.
- If electromagnetic radiation present is in resonance with the energy spacing between different states (electronic, vibrational, rotational, etc) of matter, radiation will be absorbed and transitions will occur.
- The radiation that is transmitted through the sample is measured, and spectrum can be reported as either transmittance or absorbance of radiation.
- Photoelectron spectroscopy is entirely different!

Photoelectron vs Other Spectroscopies

Others

- Photon must be in resonance with transition energy
- Measure absorbance or transmittance of photons
- Scan photon energies

Photoelectron

- Photon just needs enough energy to eject electron
- Measure kinetic energy of ejected electrons
- Monochromatic photon source

Why would a chemist care about ionizations anyway?

- Models for description of electronic structure are typically based on an orbital approximation.
- Tjalling C. Koopmans, "Ordering of Wave Functions and Eigenvalues to the Individual Electrons of an Atom." Physica 1933, 1, 104
- Koopmans' Theorem: "The negative of the energy of an occupied orbital from a theoretical calculation is equal to the vertical ionization energy due to the removal of an electron from that orbital."

$$\Psi = \prod_{i}^{N} \phi_i \qquad (I.E.)_i = -\varepsilon(\phi_i)$$

Ionization is still a transition between states

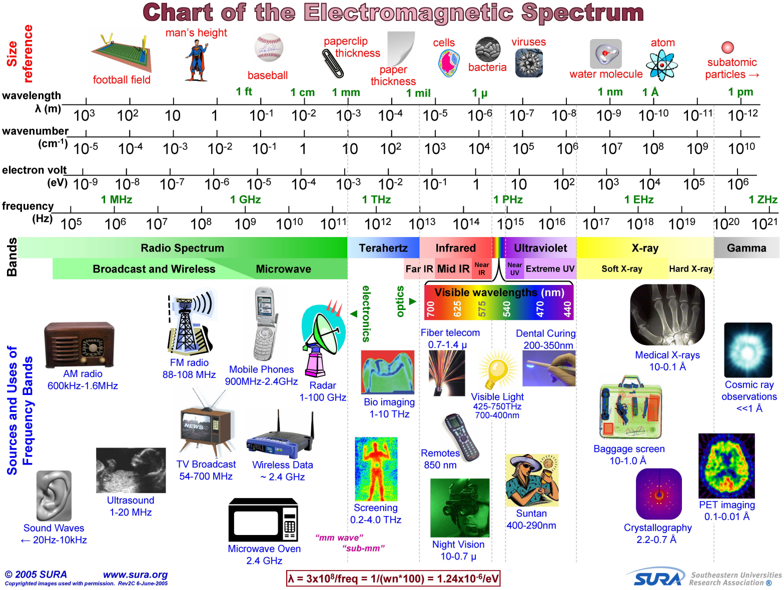
- Initial State: Neutral (or anion)
- Final State: Atom/Molecule/Anion after an electron is removed, plus the ejected electron
- $M \rightarrow M^{+} + e^{-}$
- More on this next time

Historical Timeline

- First spectrophotometer: 1850s
- First IR:1880s
- First crystallography: 1912
- First NMR: 1938
- First EPR: 1944
- First PES: 1957

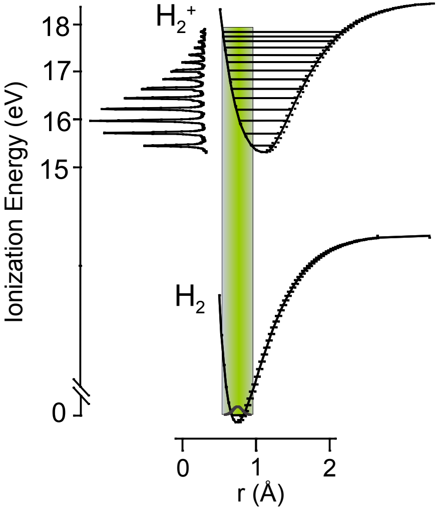
What took so long?

- Development of electron kinetic energy analyzers with sufficient resolution to be useful.
- Development of suitable sources of ionizing radiation – vacuum UV, soft X-ray
- Development of electron detectors
- Development of UHV technology

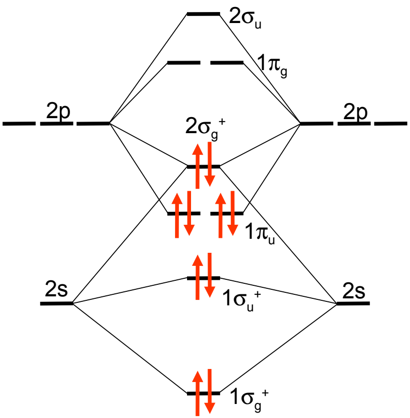


First Ionization Energies:	cesium	3.89 eV (319 nm)
	ferrocene	7.90 eV (157 nm)
	water	12.61 eV (98 nm)

Potential Energy Surface Description of the Ionization of Dihydrogen



Consider Dinitrogen



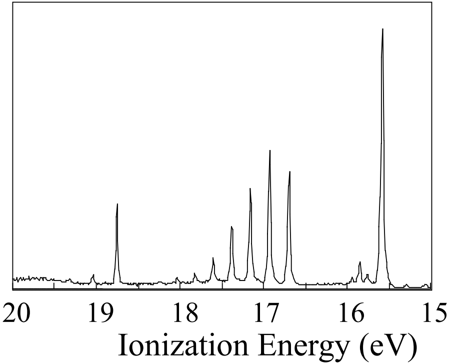
:N≡N:

Ground state (X) = $^1\Sigma_g^+$

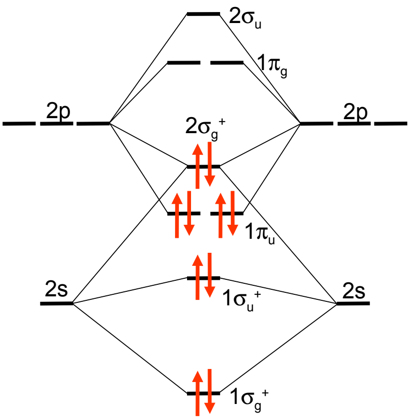
First ion state (X) = $^2\Sigma_g^+$

Second ion state (A) = $^2\Pi_u$

Third ion state (B) = $^2\Sigma_u^+$



Potential Well Description



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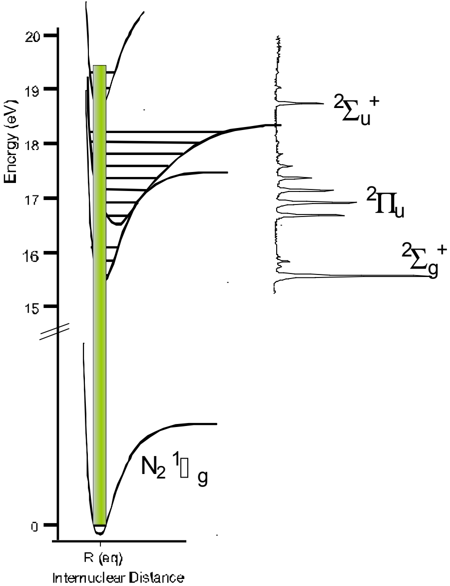
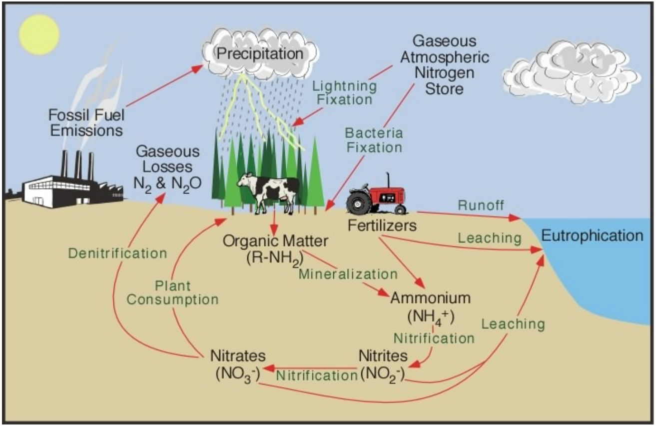
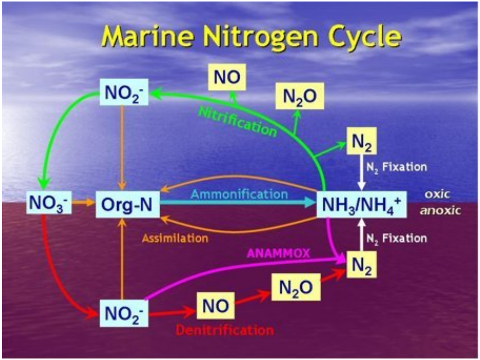


Nitrogen Cycle



Nitrogen Cycle in the Oceans



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- The N_2 triple bond energy of 226 kcal/mol is nearly the strongest bond in chemistry
- For comparison, a typical N-N single bond energy is only 38 kcal/mol.
- Thus, it is more favorable to have N_2 than three N-N single bonds by 226-(3×38) = 112 kcal/mol!
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- In 1909 Haber's catalytic synthesis of NH_3 was discovered and industrialized rapidly with Bosch

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Early Industrialized Nitrogen Fixation Processes

- 1903 electric arc furnace process
- $0.5\ N_2 + 1.25\ O_2 + 0.5\ H_2O \longrightarrow HNO_3$
- $\Delta H^\circ_{\rm rxn} = -30.3$ kJ/mol
- High kinetic barrier leads to requirement for immense energy input to effect this reaction
- Otherwise, our atmosphere would be devoid of oxygen and the world's oceans would consist of dilute aqueous nitric acid!

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- $N_2 + CaC_2 \longrightarrow CaCN_2 + C$
- First decades of the 20th century, calcium cyanamide dominated the market for synthetic fertilizer
- Odda, Norway had largest factory producing 12,000 ton/year

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Fritz Haber

Fritz Haber, sketched in 1911 by W. Luntz.

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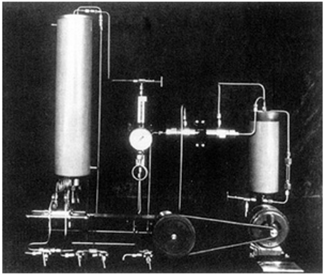
Careful Studies of the Ammonia Equilibrium

Graphic from the 1918 Nobel lecture

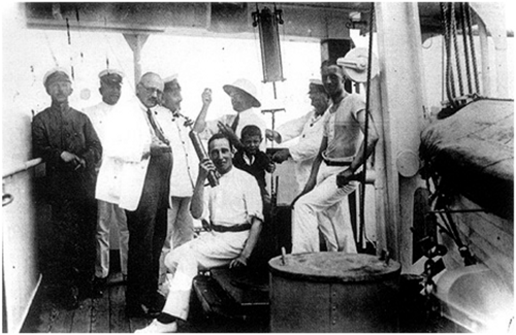
t (°C)	T (degr. abs.)	$\frac{P_{NH_3}}{P_{N_2}^{\frac{1}{2}} P_{H_2}^{\frac{3}{2}}}$	$-\log \frac{P_{NH_3}}{P_{N_2}^{\frac{1}{2}} P_{H_2}^{\frac{3}{2}}}$	Percentage of NH_3 at equilibrium at 1 atm	at 30 atm	at 100 atm	at 200 atm
200	473	0.1807	0.660	15.3	67.6	80.6	85.8
300	573	1.1543	0.070	2.18	31.8	52.1	62.8
400	673	1.8608	0.0138	0.44	10.7	25.1	36.3
500	773	2.3983	0.0040	0.129	3.62	10.4	17.6
600	873	2.8211	0.00151	0.049	1.43	4.47	8.25
700	973	3.1621	0.00069	0.0223	0.66	2.14	4.11
800	1,073	3.4417	0.00036	0.0117	0.35	1.15	2.24
900	1,173	3.6736	0.000212	0.0069	0.21	0.68	1.34
1,000	1,273	3.8679	0.000136	0.0044	0.13	0.44	0.87

Fritz Haber's Original Reactor



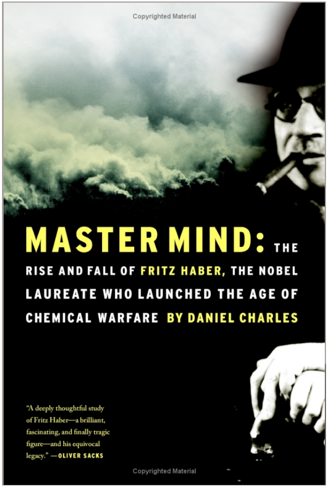
The laboratory apparatus designed by Fritz Haber and Robert Le Rossignol for producing ammonia from hydrogen and nitrogen, which was scaled up in the Haber-Bosch process. The catalytic process took place in the large cylinder on the left. Courtesy Archiv zur Geschichte der Max-Planck-Gesellschaft, Berlin-Dahlem.

Fritz Haber's Quest for Gold



Fritz Haber, third from the left, on board a ship to Buenos Aires. He hoped to mine the ocean's minuscule percentage of gold to pay Germany's reparations imposed by the Versailles treaty that signaled the end of World War I. Courtesy Archiv zur Geschichte der Max-Planck-Gesellschaft, Berlin-Dahlem.

Master Mind: A Fritz Haber Biography



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- The ability to fix nitrogen is found in certain bacteria and archaea
- Biological nitrogen fixation requires complex enzyme systems and large expenditures of ATP
- Early crystallographic structure determinations of the nitrogenase enzyme suggested the presence of 7 three-coordinate iron centers in the iron-molybdenum cofactor (FeMo-co), thought to be the active site for N_2 binding and reduction
- Recent high-resolution structures have invalidated the three-coordinate iron hypothesis
- Read about nitrogenase at the protein data bank molecule of the month archive

The Nitrogenase Enzyme
A large and complex metalloenzyme system

- The ability to fix nitrogen is found in certain bacteria and archaea
- Biological nitrogen fixation requires complex enzyme systems and large expenditures of ATP
- Early crystallographic structure determinations of the nitrogenase enzyme suggested the presence of 7 three-coordinate iron centers in the iron-molybdenum cofactor (FeMo-co), thought to be the active site for N_2 binding and reduction
- Recent high-resolution structures have invalidated the three-coordinate iron hypothesis
- Read about nitrogenase at the protein data bank molecule of the month archive

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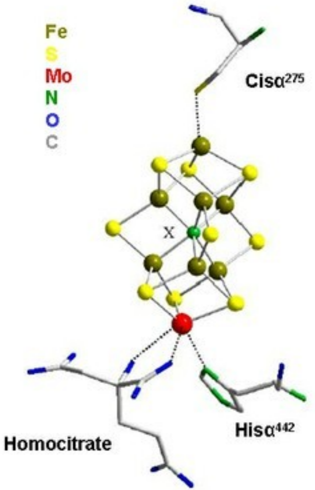
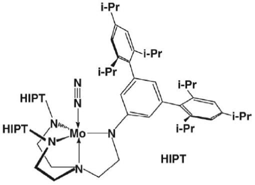
Current View of FeMo-co Structure



Schrock's Molybdenum Catalyst System

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*To whom correspondence should be addressed. E-mail: rrs@mit.edu



1

Scheme 1.

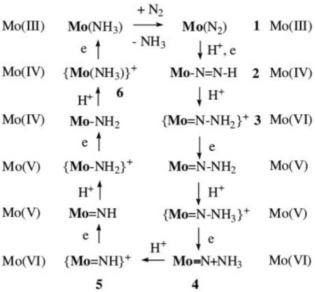


Fig. 1. Proposed intermediates in the reduction of dinitrogen at a [HIPTN_3N]Mo (**Mo**) center through the stepwise addition of protons and electrons.

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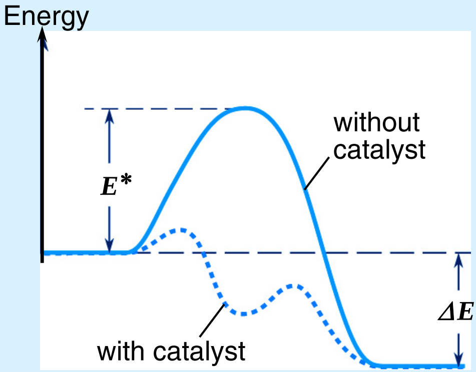
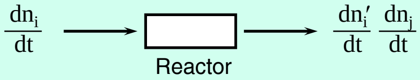
Progress of a chemical reaction



Heterogeneous catalysis

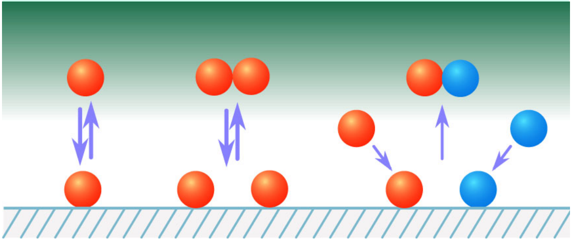


i: reactants

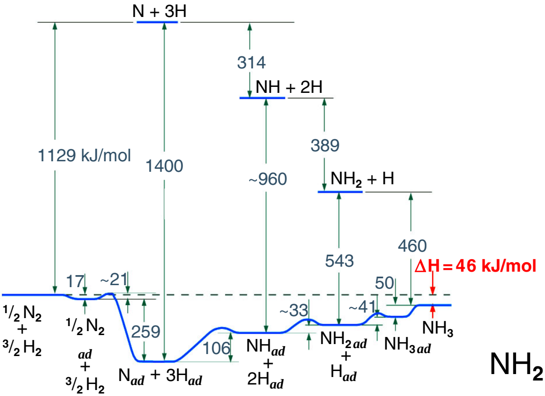
j: products

Steady-state reaction rate:

$$\frac{dn_j}{dt} = r = f\,(p_i, p_j, T, \text{catalyst})$$



Mechanism of catalytic ammonia synthesis



$$N_2 \rightleftarrows N_{2\,ad} \rightleftarrows 2N_{ad}$$

$$H_2 \rightleftarrows 2H_{ad}$$

$$N_{ad} + H_{ad} \rightleftarrows NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftarrows NH_{2\,ad}$$

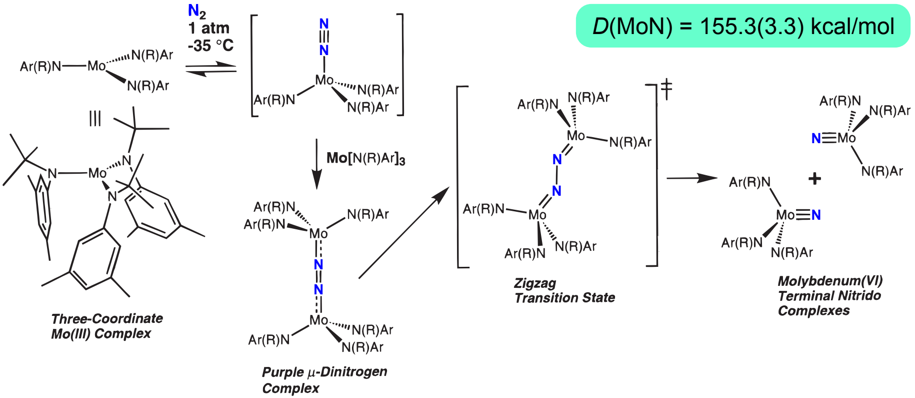
$$NH_{2\,ad} + H_{ad} \rightleftarrows NH_{3\,ad} \rightleftarrows NH_3$$

G. Ertl, Catal.Rev.Sci.Eng. **21** *(1980), 201*

Dinitrogen Cleavage by a Molybdenum Complex

Laplaza and Cummins, 1995

$D(\text{MoN}) = 155.3(3.3)$ kcal/mol



Dinitrogen Hydrogenation and Cleavage by a Zirconium Complex

Nature 427, 527-530 (05 Feb 2004), doi: 10.1038/nature02274

letters to nature

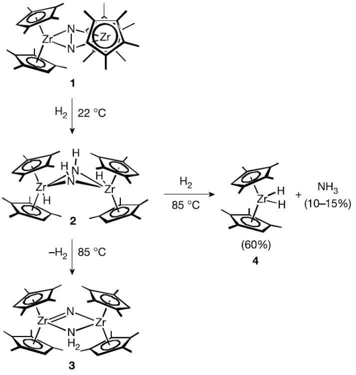


Figure 1 Hydrogenation and cleavage of N_2.

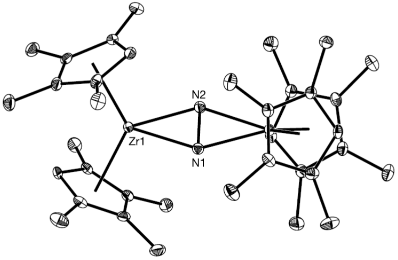


Figure 2 X-ray crystal structure of $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ (**1**). Molecular structure at 30% probability ellipsoids, with hydrogen atoms omitted for clarity. Selected bond lengths and angles: N(1)–N(2): 1.377(3) Å, Zr(1)–N(1): 2.118(1) Å, Zr(1)–N(2): 2.131(1) Å, Zr(1A)–N(1): 2.119(1) Å, Zr(1A)–N(2): 2.131(1) Å, N(1)–Zr(1)–N(2): 37.81(9)°, N(2)–N(1)–Zr(1A): 171.57(7)°, N(2)–N(1)–Zr(1): 71.56(7)°, Zr(1A)–N(1)–Zr(1): 143.13(14)°, N(1)–N(2)–Zr(1A): 70.62(7)°, N(1)–N(2)–Zr(1): 70.62(7)°, Zr(1A)–N(2)–Zr(1): 141.25(14)°.

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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