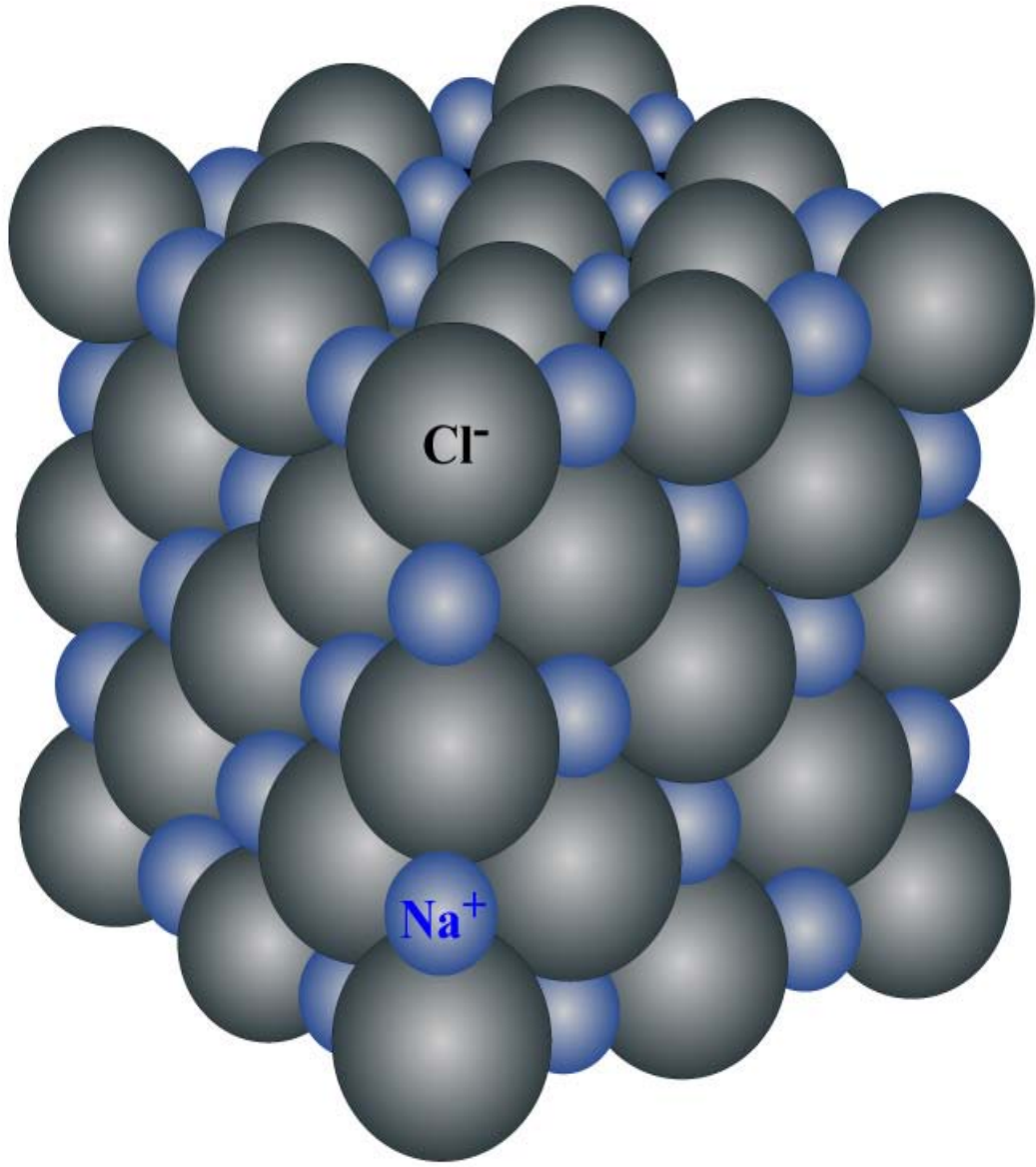


Welcome to 3.091

Lecture 8

September 25, 2009

Ionic Crystals; Born-Haber Cycle



Properties of Ionic Crystals

- ⇒ solid at room temperature
- ⇒ high melting points & boiling points
- ⇒ transparent to visible light
- ⇒ electrical insulators
- ⇒ hard & brittle
- ⇒ soluble in water & other polar solvents
- ⇒ melt to form ionic liquids (useful in electrolytic extraction of metals)

where to search for ionicity???

The usual suspects

																		18 VIII 0																																																
																		13 IIIB IIIA	14 IVB IVA	15 VB VA	16 VIB VIA	17 VIIB VIIA																																												
1.00794 -259.34 -252.87 0.0899 2.20 13.598 151 Hydrogen	3 1 1 Li		9.012182 24.3050 1287 2471 1.8477 1.57 9.322 [He]2s ¹ Lithium		4 2 2 Be																				4.002602 -272.226 am -268.93 0.1785 - 24.587 1s ² Helium																																									
22.989768 97.72 883 0.97 0.93 5.139 [Ne]3s ¹ Sodium	11 1 1 Na		24.3050 1090 1.74 1.31 7.646 [Ne]3s ² Magnesium		12 2 2 Mg																				20.1797 -248.59 246.08 9002 564 [He]2s ² p ⁶ Neon																																									
39.0983 63.38 759 0.86 0.82 4.341 [Ar]4s ¹ Potassium	19 3 1 K		44.955910 1541 2830 2.989 1.36 6.54 [Ar]3d ⁴ 4s ² Scandium		21 3 3 Sc		47.88 16.8 3287 4.5 5.96 6.82 [Ar]3d ⁴ 4s ² Titanium		22 3 3 Ti		50.9415 1910 3407 7.20 1.66 6.74 [Ar]3d ⁴ 4s ² Vanadium		23 3 3 V		51.9961 1907 2671 7.47 1.55 7.435 [Ar]3d ⁴ 4s ¹ Chromium		24 3 3 Cr		54.93805 1246 2061 7.47 1.55 7.435 [Ar]3d ⁵ 4s ¹ Manganese		25 3 3 Mn		55.847 1538 2861 7.86 1.83 7.870 [Ar]3d ⁵ 4s ² Iron		26 3 3 Fe		58.93320 1495 2927 8.92 1.88 7.635 [Ar]3d ⁶ 4s ² Cobalt		27 3 3 Co		58.6934 1455 2913 8.90 1.91 7.626 [Ar]3d ⁶ 4s ² Nickel		28 3 3 Ni		63.546 1084.62 2562 8.94 1.74 ^{255c} 6.995 9.394 [Ar]3d ⁹ 4s ¹ Copper		29 1,2 2 Cu		65.39 29.76 2204 6.599 5.271 9.394 [Ar]3d ¹⁰ 4s ¹ Zinc		30 2 2 Zn		69.723 29.76 2204 6.599 5.271 9.394 [Ar]3d ¹⁰ 4s ² Gallium		31 3 3 Ga		72.61 938.25 2833 5.35 5.782 ^{25c} 9.727 [Ar]3d ¹⁰ 4s ² Germanium		32 4 4 Ge		74.92159 8177P 2221 6149 6.85 9.752 [Ar]3d ¹⁰ 4s ² Arsenic		33 3,5 5 As		78.96 221 2833 6.85 5.98 9.752 [Ar]3d ¹⁰ 4s ² Selenium		34 -2,4,6 6 Se		79.904 -7.2 221 6149 6.85 9.752 [Ar]3d ¹⁰ 4s ² Bromine		35 ±1,5 5 Br		83.80 -157.3 157.2 3.119 2.96 11.814 [Ar]3d ¹⁰ 4s ² Krypton		36 -157.3 3.74 13.999 [Ar]3d ¹⁰ 4s ² Krypton	
85.4678 39.31 688 1.532 0.82 4.177 [Kr]5s ¹ Rubidium	37 1 1 Rb		88.90585 1526 3469 4.474 6.49 1.33 6.84 [Kr]4d ⁵ 5s ² Yttrium		39 3 3 Y		91.224 1855 3409 4.744 6.49 1.33 6.84 [Kr]4d ⁵ 5s ² Zirconium		40 4 4 Zr		92.90638 1910 3409 4.744 6.49 1.6 7.099 [Kr]4d ⁵ 5s ² Niobium		41 3,5 5 Nb		95.94 2477 4039 10.63 1.2 7.28 [Kr]4d ⁵ 5s ¹ Molybdenum		42 3,5 5 Mo		97.9072 2157 4150 11.5 7.37 7.46 [Kr]4d ⁵ 5s ¹ Technetium		43 3,5 5 Tc		101.07 2334 4150 12.4 2.2 7.37 [Kr]4d ⁵ 5s ¹ Ruthenium		44 2,3,4,6,8 6 Ru		102.90550 1964 3695 12.4 2.2 7.37 [Kr]4d ⁵ 5s ¹ Rhodium		45 2,3,4 4 Rh		106.42 1964 2963 10.5 2.2 7.37 [Kr]4d ¹⁰ Palladium		46 2,4 4 Pd		107.8582 961.78 2162 10.5 1.93 8.993 [Kr]4d ¹⁰ 5s ¹ Silver		47 2 2 Ag		114.818 156.60 2072 7.28 1.78 5.786 [Kr]4d ¹⁰ 5s ² Cadmium		48 2 2 Cd		118.710 231.93 2602 7.28 1.96 7.344 [Kr]4d ¹⁰ 5s ² Indium		49 2,4 4 In		121.757 630.63 1587 6.842 ^{25c} 2.05 9.001 [Kr]4d ¹⁰ 5s ² Tin		50 3,5 5 Sn		127.60 449.51 988 6.25 2.09 10.51 [Kr]4d ¹⁰ 5s ² Antimony		51 -2,4,6 6 Sb		126.90447 116.907 184.4 4.93 2.66 10.451 [Kr]4d ¹⁰ 5s ² Tellurium		52 ±1,5,7 7 Te		131.29 -117.7 -108.0 5.89 2.66 12.00 [Kr]4d ¹⁰ 5s ² Iodine		53 -108.0 5.89 2.66 10.451 [Kr]4d ¹⁰ 5s ² Iodine		54 -117.7 -108.0 5.89 2.66 12.00 [Kr]4d ¹⁰ 5s ² Iodine			
132.90543 28.44 671 1.879 0.79 3.894 [Xe]6s ¹ Cesium	55 1 1 Cs		138.9055 920 3463 6.46 1.31 5.422 [Xe]5d ¹ 6s ² Lanthanum		57 3 3 La		178.49 2233 3463 6.46 1.31 5.422 [Xe]5d ¹ 6s ² Cerium		72 4 4 Hf		183.84 3017 5458 7.0 7.89 [Xe]4f ¹⁴ 5d ² 6s ² Tantalum		73 3,5 5 Ta		186.207 3186 5525 8.16 7.89 [Xe]4f ¹⁴ 5d ² 6s ² Tungsten		74 3,5,6 6 W		190.23 3033 5012 10.2 22.61 2.2 9.1 [Xe]4f ¹⁴ 5d ⁴ 6s ² Osmium		75 2,3,4,6,8 8 Re		192.22 2446 4428 10.2 22.61 2.2 9.1 [Xe]4f ¹⁴ 5d ⁵ 6s ² Iridium		76 2,3,4,6,8 8 Os		196.96654 1064.18 2856 1.3 19.31 2.54 9.225 [Xe]4f ¹⁴ 5d ⁶ 6s ¹ Platinum		77 1,2 2 Ir		199.464 1678.4 2856 1.3 19.31 2.54 9.225 [Xe]4f ¹⁴ 5d ⁷ 6s ¹ Gold		78 1,3 3 Pt		196.96654 1064.18 2856 1.3 19.31 2.54 9.225 [Xe]4f ¹⁴ 5d ⁸ 6s ¹ Mercury		79 1,2 2 Au		207.2 304 1473 11.85 2.04 6.108 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Thallium		80 2 2 Hg		208.98037 271.40 1564 9.78 2.02 7.289 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Lead		81 3,5 5 Tl		208.98037 271.40 1564 9.78 2.02 7.289 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Bismuth		82 3,5 5 Pb		208.98037 271.40 1564 9.78 2.02 7.289 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Polonium		83 3,5 5 Bi		208.98037 271.40 1564 9.78 2.02 7.289 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Astatine		84 3,5 5 Po		208.98037 271.40 1564 9.78 2.02 7.289 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Radon		85 3,5 5 At		222.0176 302 337 71 -61.7 9.73 10.748 [Xe]4f ¹⁴ 5d ¹⁰ 6s ² Francium		86 3,5 5 Rn	
(223.0197) 27 677 -0.7 [Rn]7s ¹ Francium	87 3 3 Fr		(227.0287) 105 107 107 [Rn]6d ¹ 7s ² Actinium		89 3 3 Ac		(261) 105 107 107 [Rn]5f ¹⁴ 6d ¹ 7s ² Rutherfordium**		104 4 4 Rf		(262) 105 107 107 [Rn]5f ¹⁴ 6d ² 7s ² Dubnium**		105 4 4 Db		(262) 106 107 107 [Rn]5f ¹⁴ 6d ³ 7s ² Seaborgium**		106 4 4 Sg		(262) 107 107 107 [Rn]5f ¹⁴ 6d ⁴ 7s ² Bohrium**		107 4 4 Bh		(265) 108 109 109 [Rn]5f ¹⁴ 6d ⁵ 7s ² Hassium**		108 4 4 Hs		(266) 109 109 109 [Rn]5f ¹⁴ 6d ⁶ 7s ² Meitnerium**		109 4 4 Mt		(269) 110 109 109 [Rn]5f ¹⁴ 6d ⁷ 7s ² Ununnilium**		110 4 4 Uun		(272) 111 109 109 [Rn]5f ¹⁴ 6d ⁸ 7s ² Ununnilium**		111 4 4 Uuu		(277) 112 109 109 [Rn]5f ¹⁴ 6d ⁹ 7s ² Ununquadium		112 4 4 Uub		(283) 113 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununquadium		113 4 4 Uut		(289) 114 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununhexium		114 4 4 Uuq		(289) 115 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununhexium		115 4 4 Uup		(293) 116 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununseptium		116 4 4 Uuh		(293) 117 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununseptium		117 4 4 Uus		(293) 118 109 109 [Rn]5f ¹⁴ 6d ¹⁰ 7s ² Ununseptium		118 4 4 Uuo	

* 140.115 799 3424 6.770 1.12 5.466 [Xe]4f ¹⁴ 5d ¹ 6s ² Cerium	58 3,4 4 Ce		140.90765 931 3510 6.773 1.13 5.489 [Xe]4f ¹⁴ 6s ² Praseodymium		59 3,4 4 Pr		144.24 1016 3066 7.00 1.14 5.489 [Xe]4f ¹⁴ 6s ² Neodymium		60 3 3 Nd		(144.9127) 1042 3000 7.254 1.13 5.666 [Xe]4f ¹⁴ 6s ² Promethium		61 3 3 Pm		150.36 1072 1790 7.536 1.17 5.631 [Xe]4f ¹⁴ 6s ² Samarium		62 2,3 3 Sm		151.965 822 1596 5.244 1.2 5.666 [Xe]4f ¹⁴ 6s ² Europium		63 3 3 Eu		157.25 1314 3263 7.901 1.2 6.141 [Xe]4f ¹⁴ 5d ¹ 6s ² Gadolinium		64 3 3 Gd		158.92534 1359 3221 8.230 1.2 5.842 [Xe]4f ¹⁴ 6s ² Terbium		65 3,4 4 Tb		162.50 1411 2561 8.80 1.22 6.018 [Xe]4f ¹⁴ 6s ² Dysprosium		66 3 3 Dy		164.93032 2694 8.551 1.24 6.184 [Xe]4f ¹⁴ 6s ² Holmium		67 3 3 Ho		167.26 1529 2862 9.066 1.21 6.121 [Xe]4f ¹⁴ 6s ² Erbium		68 3 3 Er		168.93421 1946 9.321 1.24 6.18436 [Xe]4f ¹⁴ 6s ² Thulium		69 2,3 3 Tm		173.04 1194 6.966 1.1 5.42589 [Xe]4f ¹⁴ 6s ² Ytterbium		70 2,3 3 Yb		174.967 3393 9.84 1.27 5.42589 [Xe]4f ¹⁴ 6s ² Lutetium		71 3 3 Lu	
** 232.0381 1750 4788 11.72 1.3 6.08 [Rn]6d ² 7s ² Thorium	90 4 4 Th		231.03588 1572 4131 15.37 1.38 5.89 [Rn]5f ¹⁴ 6d ¹ 7s ² Protactinium		91 4,5 5 Pa		238.0289 138 195+0.02 1.38 6.05 [Rn]5f ¹⁴ 6d ¹ 7s ² Uranium		92 3,4,5,6 6 U		(237.0482) 644 20.45 1.28 6.19 [Rn]5f ¹⁴ 6d ² 7s ² Neptunium		93 3,4,5,6 6 Np		(244.0642) 640 3228 19.816 1.3 5.8 [Rn]5f ¹⁴ 6d ² 7s ² Plutonium		94 3,4,5,6 6 Pu		(243.0614) 1176 2507 13.67 1.3 5.993 [Rn]5f ¹⁴ 6d ³ 7s ² Americium		95 3,4,5,6 6 Am		(247.0703) 1345 2507 13.51 1.3 6.02 [Rn]5f ¹⁴ 6d ⁴ 7s ² Curium		96 3 3 Cm		(247.0703) 1050 14.78 6.23 [Rn]5f ¹⁴ 6d ⁵ 7s ² Berkelium		97 3,4 4 Bk		(251.0796) 900 13 6.30 [Rn]5f ¹⁴ 6d ⁶ 7s ² Californium		98 3 3 Cf		(252.083) 860 1.3 6.42 [Rn]5f ¹⁴ 7s ² Einsteinium		99 3 3 Es		(257.0951) 827 1.3 6.50 [Rn]5f ¹⁴ 7s ² Fermium		100 3 3 Fm		(258.10) 827 1.3 6.58 [Rn]5f ¹⁴ 7s ² Mendelevium		101 2,3 3 Md		(259.1009) 827 1.3 6.65 [Rn]5f ¹⁴ 7s ² Nobelium		102 2,3 3 No		(252.11) 1627 - - [Rn]5f ¹⁴ 6d ¹ 7s ² Lawrencium		103 3 3 Lr	

1 1A							18 8A
H ⁺ H ⁻ Hydride	2 2A		13 3A	14 4A	15 5A	16 6A	17 7A
Li ⁺	Be ²⁺				N ³⁻ Nitride	O ²⁻ Oxide	F ⁻ Fluoride
Na ⁺	Mg ²⁺		Al ³⁺			S ²⁻ Sulfide	Cl ⁻ Chloride
K ⁺	Ca ²⁺		Ga ³⁺			Se ²⁻ Selenide	Br ⁻ Bromide
Rb ⁺	Sr ²⁺		In ³⁺	Sn ²⁺ Sn ⁴⁺		Te ²⁻ Telluride	I ⁻ Iodide
Cs ⁺	Ba ²⁺		Tl ⁺ Tl ³⁺	Pb ²⁺ Pb ⁴⁺			

Max Born - Biography

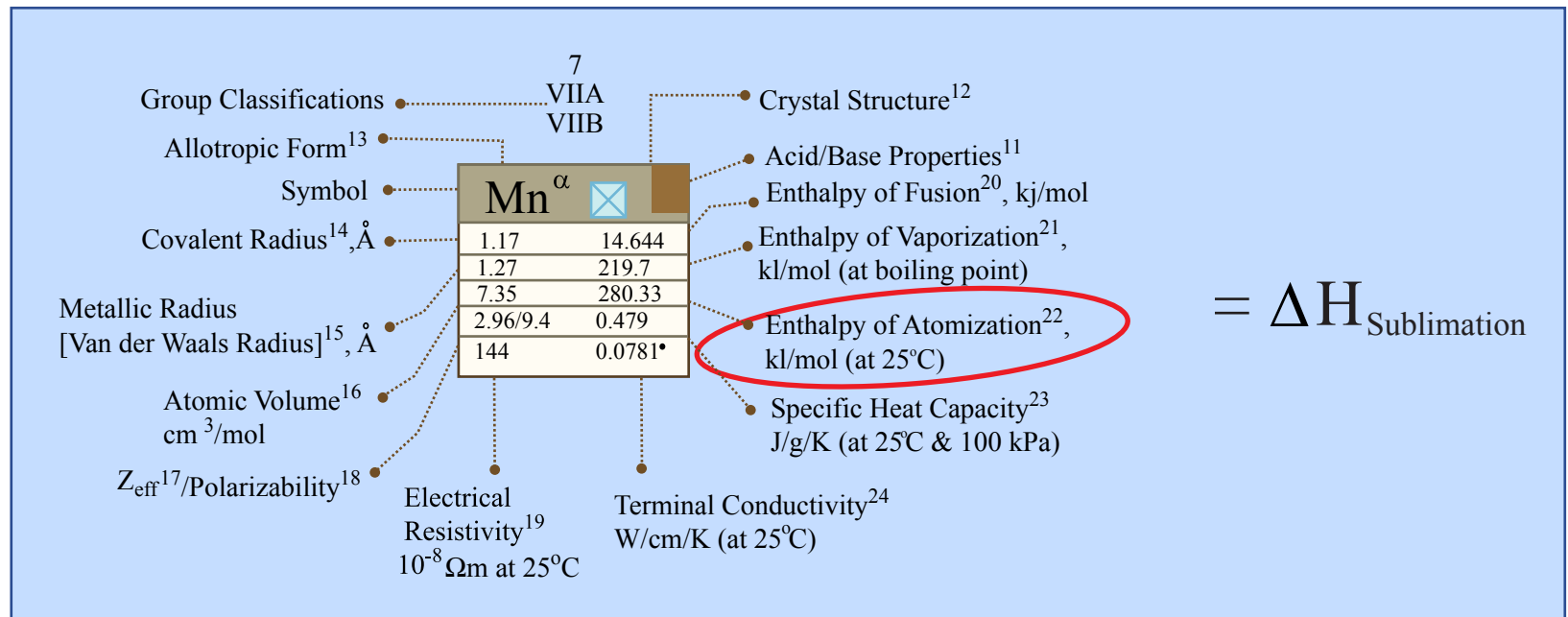
Max Born was born in Breslau on the 11th December, 1882, to Professor Gustav Born, anatomist and embryologist, and his wife Margarete, née Kauffmann, who was a member of a Silesian family of industrialists.

Max attended the König Wilhelm's Gymnasium in Breslau and continued his studies at the Universities of Breslau (where the well-known mathematician Rosanes introduced him to matrix calculus), Heidelberg, Zurich (here he was deeply impressed by Hurwitz's lectures on higher analysis), and Göttingen. In the latter seat of learning he read mathematics chiefly, sitting under Klein, Hilbert, Minkowski, and Runge, but also studied astronomy under Schwarzschild, and physics under Voigt. He was awarded the Prize of the Philosophical Faculty of the University of Göttingen for his work on the stability of elastic wires and tapes in 1906, and graduated at this university

Fritz Haber - Biography

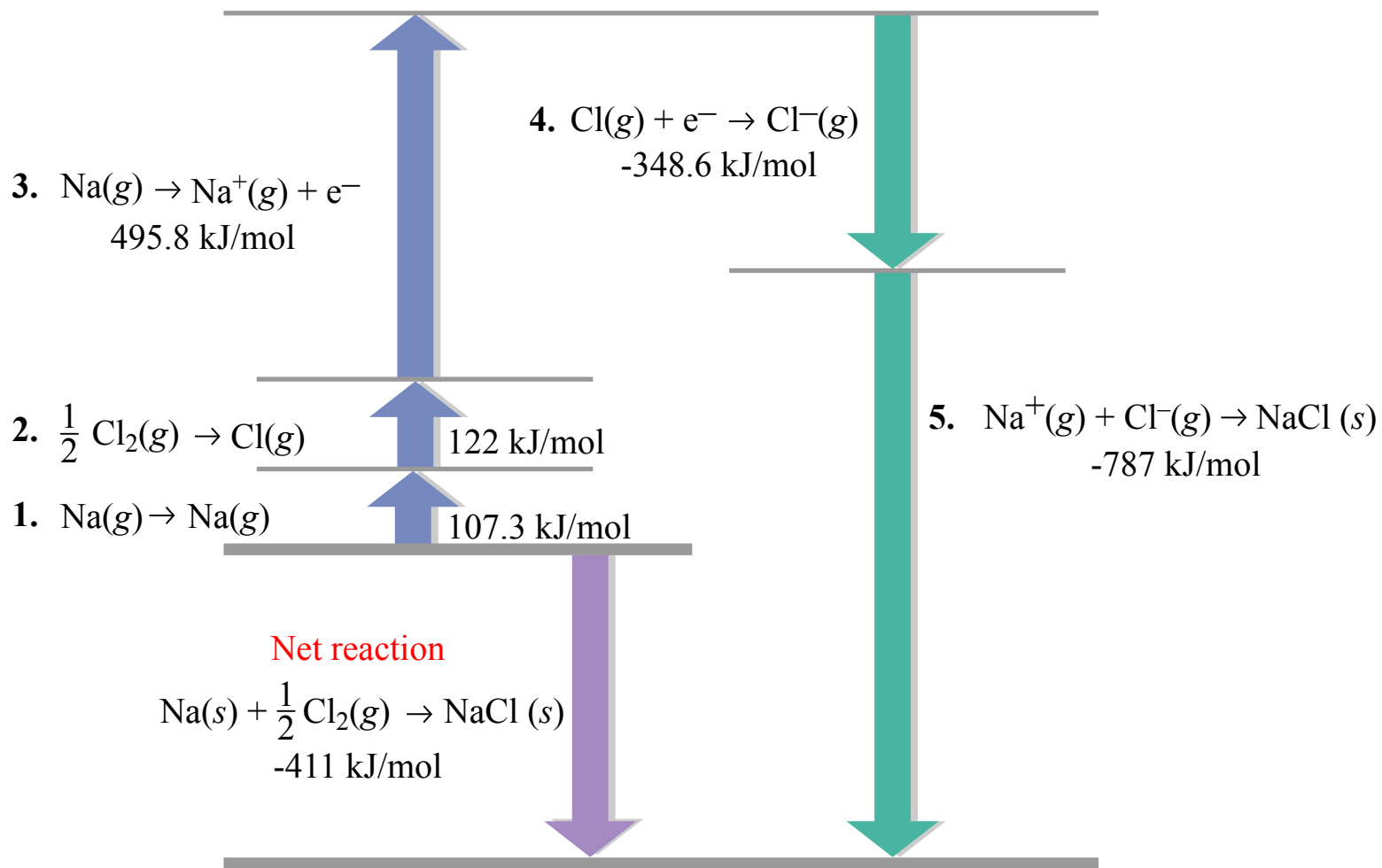
Fritz Haber was born on December 9, 1868 in Breslau, Germany, in one of the oldest families of the town, as the son of Siegfried Haber, a merchant. He went to school at the St. Elizabeth classical school at Breslau and he did, even while he was at school, many chemical experiments.

From 1886 until 1891 he studied chemistry at the *University of Heidelberg* under Bunsen, at the University of Berlin under A.W. Hoffmann, and at the Technical School at Charlottenberg under Liebermann. After completing his University studies he voluntarily worked for a time in his father's chemical business and, being interested in chemical technology, he also worked for a while under Professor Georg Lunge at the *Institute of Technology at Zurich*. He then finally



Na	
1.54	2.594
1.90	80.04
23.70	108.37
1.84/23.6	1.228
4.88	1.42

= $\Delta H_{\text{sublimation}}$



A Born – Haber Cycle for NaCl

Cation	Anion				
	F ⁻	Cl ⁻	Br ⁻	I ⁻	O ²⁻
Li ⁺	1036	853	807	757	2925
Na ⁺	923	787	747	704	2695
K ⁺	821	715	682	649	2360
Be ²⁺	3505	3020	2914	2800	4443
Mg ²⁺	2957	2524	2440	2327	3791
Ca ²⁺	2630	2258	2176	2074	3401
Al ³⁺	5215	5492	5361	5218	15916

Lattice energies of some Ionic solids (kJ/mol)



Ionic Radii (Å) for Ions with Noble-gas Electron Configurations

Na⁺ 0.98 Mg²⁺ 0.65 Al³⁺ 0.45

Rb⁺ 1.48 Sr²⁺ 1.10 Y³⁺ 0.90

[Ne]

[Kr]

O²⁻ 1.45 F⁻ 1.33

Se²⁻ 2.02 Br⁻ 1.96

[He]

Li⁺ 0.68 Be²⁺ 0.30

K⁺ 1.33 Ca²⁺ 0.94 Sc³⁺ 0.68

Cs⁺ 1.67 Ba²⁺ 1.31 La³⁺ 1.22

[Ar]

[Xe]

S²⁻ 1.90 Cl⁻ 1.81

Te²⁻ 2.22 I⁻ 2.19

Voltage Component	Volts	% of Total
External	.16	3.4
Anode	.32	6.9
Polarizations	.60	12.9
Bath	1.76	38.0
Decomposition	1.20	25.9
Cathode	.47	10.1
Other	.13	2.8
Total	4.64	100.0

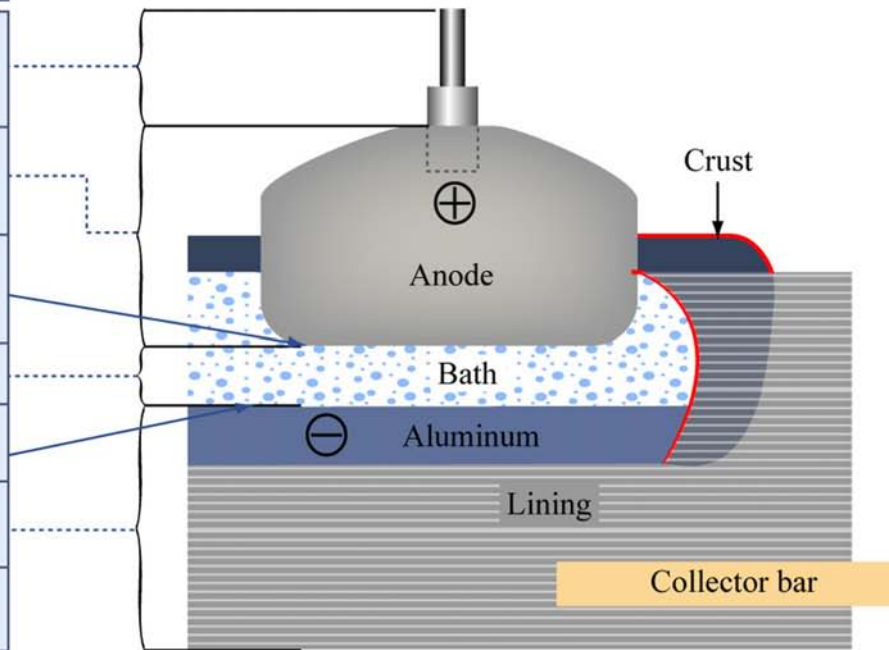
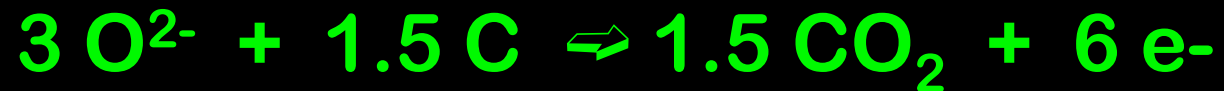


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consumable carbon anode

0.45 kg C / kg Al

aluminum produced by electrolytic reduction of Al_2O_3
world capacity: ~40 million tonnes/year

1886

Charles Martin Hall, USA
Paul L.T. Héroult, France



decompose Al_2O_3 dissolved in Na_3AlF_6 ($T = 960^\circ\text{C}$)

👉 liquid Al (-) and CO_2 (+)

👉 find an inert anode

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inert anode

no CO_2 ; no CF_4



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3.091SC Introduction to Solid State Chemistry
Fall 2009

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