Universi St Andre	ity ws				1	Frans [S <mark>itio</mark> Dr. Eli Rm	n Mo Zysn	etal nan-(in Pi	<mark>Che</mark> i Colma	mist an	ry					1
CH250)1									nuic							
H	I .				eli.z	zysma	an-co	lmar	n@st-	andr	ews.a	ac.uk					He
Physical Street		http	o://w	ww.z	ysma	n-co	man	.com	/cour	rses/o	ch250)1_2()16ai	ut_er	n.php		Patan 44886
Li	Be											B	C	N	0	F	Ne
Litrum	Berylans Adda											Banan ta att	Carton	Mitosper 16.885	Orygan 12.001	Puesta ILAN	Name 34.019
11	12	1	AI SI P S CI A														18
Na	Mg											AI	Si	P	S	CI	Ar
Sodkers 22.880	Magrossium 24.285											A0.41931611 26.081	Silluon 26.000	Phosphorus 38,873	5.0%s 12.065	Chiutes 35,455	Argon 18.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	SC	TI	V	Cr	Mn	Fe	CO	Ni	Cu	Zn	Ga	Ge	AS	Se	Br	Kr
Polassium 36.8.80	Catsian 44.879	Scorelists 64,805	18.00%Lafe 47.867	Victoria State	St.886	Mangariane S4,538	55.945	Colorit SA.820	146.946 08.945	Copper 63.946	2.es. 68.56	Gallun 64.725	Gertraskan 72.64	Arbeith: 24,821	Taterion 78,86	Doursing TRADE	Rayslave 83.8
37	38	39	40	41	42	43	44	45	46	47	48	49 T	50	S1	52	53	54
RD	Sr	Y	Zr	IND	MO	IC	Ru	Rn	Pa	Ag	Ca	In	Sn	SD	Ie	1	xe
81.427	BTAD	10.005	11.214	82.005	85.04	54.828	404.87	10.8	185.42	407.06	HEAI	194.81	118.71	121.76	121.4	126.00	131.20
Ce	Ra		LIF	Ta	IN	Do	Oc.	Tr	D+	A	Ha	TI	Dh	Di	Do	A+	Dn
Custom	Batura		Fatheren	Tantan	Tungatan	Rhankarn	Ounium	11 House	Pateren	au	Ing	Thatium	Last	DI	Putter	AL	Rater
152.96	197.32		104	105	106	107	1108	109	110	1111	200.00	194.38	201.8	391.85	399	218	718
Fr	Ra	A.	Rf	Dh	Sa	Bh	Hs	Mt	Ds	Ra	Llub						
Frankin	Radum		Actualization	Dutwister	Laborer	Butterete	Hashim	Hubselum	Dormaladhum	Resetpendent	Unurbaute						
	28	51	-	1 100	744	1 104	arr	1	1 201		1 200						
			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
		K.	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Im	Yb	Lu
		11	13LBD	HEH	14LIE	tel34	Patrinita,m 141	Servers III	tit.H	Godorskute 187.36	Tathian Riskiki	NES	164.65	5754,00 168.26	168.63	Tradition 172.04	Elitedium Elitedium
		1	A.0	Th	Da	92	Nin	Du	A	Cm	DL	1ª CE	50	Em	Md	No	103
		1	AC	Treton	Pd	U	IND	Pu	Am	CIII	DK	Catherine	ES	rmn.	Mana	NO	LI
			447	110.43	201.85	220.42	117	344	245	347	247	267	242	167	204	258	262



Transition Metal Chemistry

Dr. Eli Zysman-Colman

Rm 244 in Purdie

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http://www.zysman-colman.com/courses/ch2501_2016aut_en.php



Home

Important Announcements

Welcome to CH2501: Transition Metal Chemistry AND Molecules in the Atmosphere course modules page Class hours: Please see calendar on main teaching page

Course Notes

- Transition Metal Chemistry Course Notes Notes to be uploaded shortly
- Molecules in the Atmosphere Course Notes Notes to be uploaded shortly

Suggested Reading & Resources

Please go to here for recommended texts. A useful site for understanding the overlap of atomic orbitals towards the formation of molecular orbitals may be found here. Another useful site for understanding the overlap of atomic orbitals towards the formation of molecular orbitals may be found here. A useful site for understanding Jahn Teller distortion may be found here. A useful site for understanding basic spectroscopy (IR, NMR, UV) may be found here. Another good resource for understanding IR spectrscopy is IR Tutor.



Transition Metal Chemistry

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- Introduction to transition metal chemistry
- Trends in the d-block
- Coordination chemistry
- Basic notions in organometallic chemistry
- Crystal Field Theory/Ligand Field Theory
- Some chemistry of transition metal complexes





Inorganic Chemistry, Sixth Edition Mark Weller, Tina Overton, Jonathan Rourke, and Fraser Armstrong



Organotransition Metal Chemistry From Bonding to Catalysis John Hartwig



The Periodic Table of Elements

P-BLOCK – MAIN GROUP ELEMENTS

1																	18
1																	2
н																	He
hydrogen																	heium
[1.007; 1.009]	2		Key:									13	14	15	16	17	4.003
3	4		atomic num	ber								5	6	7	8	9	10
Li	Be		Symbo									B	С	N	0	F	Ne
lithium	berylium		name			_						boron	carbon	nitrogen	axygen	fluorine	neon
[6.938; 6.997]	9.012		standard atomic v	voight D-	-BLOCK	(-IRA	ANSITI	on Me	ETALS			[10.80; 10.83]	[12.00; 12.02]	[14.00; 14.01]	[15.99; 16.00]	19.00	20.18
11	12											13	14	15	16	17	18
Na	Ma											AI	Si	P	S	CL	Ar
sodium	magnesium											aluminium	silicon	phosphorus	sulfur	chlorine	argon
22.99	24.31	3	4	5	6	7	8	9	10	11	12	26.98	[28.08; 28.09]	30.97	[32.05; 32.08]	[35.44; 35.48]	39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
potassium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38(2)	69.72	72.63	74.92	78.96(3)	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Aq	Cd	In	Sn	Sb	Те		Xe
rubidium	strontium	yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	siver	cadmium	indium	tin	antimony	tellurium	iodine	xenon
85.47	87.62	88.91	91.22	92.91	95.96(2)		101.1	102.9	108.4	107.9	112.4	114.8	118.7	121.8	127.6	126.9	131.3
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	lanthanoids	Hf	Та	W	Re	Os	lr	Pt	Au	Ha	TI	Pb	Bi	Po	At	Rn
caesium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polorium	astatine	radon
132.9	137.3		178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6	[204.3; 204.4]	207.2	209.0			
87	88	89-103	104	105	106	107	108	109	110	111	112		114		116		
Fr	Ra	actinoids	Rf	Db	Sq	Bh	Hs	Mt	Ds	Rg	Cn		FI		Lv		
francium	radium		rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		ivermorium		
									0			l ₂ 2	2			1	
			1														
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
			Co	Dr	Nd	Dm	Cm	Eu	Cd	Th	Du	Ца	Er	Tm	Vh	1	
		La	Ce	Pr	Na	Pm	SIII	Eu	Ga	d	Dy	по	El	Im	TD	Lu	

La Ianthanum 138.9	Ce cerium 140.1	Pr praseodymium 140.9	Nd neodymium 144.2	Pm	Sm samarium 150.4	Eu europium 1520	Gd gadolinium 157.3	Tb terbium 158.9	Dy dysprosium 162.5	Ho holmium 164.9	Er erbium 167.3	Tm Pulium 168.9	Yb ytterbium 173.1	Lu lutetium 175.0
89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr Iawrencium



A Tour Through the Periodic Table of Elements

CH25BLOCK

89

Ac

actinium

90

Th

thorium

232.0

92

U

uranium

238.0

91

Pa

protactinium

231.0

93

Np

neptunium

94

Pu

plutonium

95

Am

americium

	" S-B EC	DCK	Δικ		TAIC								P-BLO	ск — Л	AAIN C	GROUP	Elem	ENTS
	1 H		ALK/	ALINE	EARTH	METAL	S						13	14	15	16	17	18 ² He
	hydrogen [1.007; 1.009]	2		Key:									13	14	15	16	17	4.003
	3	4		atomic num	iber								5	6	7	8	9	10
	Li	Be		Symbo	ol								В	С	N	0	F	Ne
	lithium [6.938; 6.997]	berylium 9.012		name standard atomic v	weight D-	BLOCK	— TRA	ANSITIC	ON ME	TALS			boron [10.80; 10.83]	carbon [12.00; 12.02]	nitrogen [14.00; 14.01]	cxygen [15.99; 16.00]	fluorine 19.00	neon 20.18
	11	12	3	Δ	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Na	Mg	5	-	5	U	,	0	5	10		12	AI	Si	Р	S	CI	Ar
	22.99	24.31	3	4	5	6	7	8	9	10	11	12	26.98	[28.08; 28.09]	30.97	[32.05; 32.08]	[35.44;35.48]	39.95
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	39.10	40.08	scandium 44.96	47.87	50.94	sp.00	manganese 54.94	1000 55.85	cobat 58.93	58.69	copper 63.55	Zinc 65.38(2)	gallum 60.72	germanium 72.63	arsenic 74.92	58kenium 78.96(3)	79.90	83.80
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	1	Xe
	rubidium 85.47	strontium 87.62	yttrium 88.01	zirconium 91.22	niobium 92.91	molybdenum 95.9920	technetium	ruthenium	rhodium	palladium 106.4	siver	cadmium	indium	6n 118.7	antimony 121.8	tellurium	iodine 126.9	xenon
ľ	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	lanthanoids	Hf	Та	W	Re	Os	Ir	Pt	Au	Ha	TI	Pb	Bi	Po	At	Rn
	caesium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon
ŀ	87	88	89-103	1/8.5	10.5	106	186.2	190.2	192.2	195.1	111	112	[204.3; 204.4]	114	209.0	116		
	Fr	Ra	actionide	Rf	Db	Sa	Bh	Hs	Mt	Ds	Ra	Cn		FI		Lv		
	francium	radium	acanoida	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		Ivernorium		
															1 0		1	
		į																
			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
L	ANTHA	ANIDES	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			138.9	140.1	140.9	144.2	promeetium	150.4	152.0	157.3	158.9	162.5	164_9	167.3	168.9	173.1	175.0	

98

Cf

californium

100

Fm

fermium

99

Es

einsteinium

101

Md

mandelevium

102

No

nobelium

103

Lr

lawrencium

97

Bk

berkelium

96

Cm

curium

ACTINIDES



CH35BLOCK

Everyone Can Learn the Periodic Table of Elements!

P-BLOCK – MAIN GROUP ELEMENTS





CH2581	ЭСК		P-BLO	ск — Л	AAIN C	GROUP	Elem	ENTS
1 1 H]		13	14	15	16	17	18 18 ² He
hydrogen [1.007; 1.009]	2	Kay:	13	14	15	16	17	helium 4.003
3	4	atom	5	6	7	8	9	10
Li	Be	States of the state of the stat	В	C	N	0	F	Ne
lithium 16.938: 6.9971	berylium 9012		boron [10.80: 10.83]	carbon [12.00: 12.02]	nitrogen [14.00; 14.01]	cxygen (15.99: 16.00)	fluorine 19.00	neon 2018
11	12		13	14	15	16	17	18
Na	Mg		AI	Si	Р	S	CI	Ar
sodium	magnesium		aluminium	silicon	phosphorus	sulfur	chlorine	argon
19	20	the second s	31	32	33	34	35	36
K	Ca		Ga	Ge	As	Se	Br	Kr
potassium	calcium		gallium	germanium	arsenic	selenium	bromine	krypton
39.10	38		49	50	51	78.96(3) 52	53	54
Rb	Sr		In	Sn	Sb	Te	Ĩ	Xe
rubidium	strontium		indium	tin	antimony	tellurium	iodine	xenon
85.47	87.62		114.8	118.7	121.8	127.6	126.9	131.3
Ce	Ba		TI	Dh	Di Di	Po	ο5 Λ+	Dn
caesium	barium		thallium	lead	bismuth	polonium	astatine	radon
132.9	137.3		[204.3; 204.4]	207.2	209.0			
87	88	60-103 112 112		114		116		
francium	radium	actinoids Cn		fierovium		LV		
			1				ļ	

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy dvsprosium	Ho	Er	Tm	Yb	Lu
138.9	140.1	140.9	144.2		150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.1	175.0
						2								
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th thorium	Pa protactinium	U uranium 2380	Np	Pu	Am	Cm	Bk	Cf	Es einsteinium	Fm	Md mendelevium	No	Lr lawrencium



CH35BLC	ОСК											P-BLO	ск — Л	AAIN G	ROUP	Elem	ENTS	
1 H hydrogen [1007; 1009]	2		Kev:									13	14	15 15	<i>16</i>	17	18 182 He heium 4.003	
3 Li Rhium [6.938; 6.997]	4 Be berylium 9.012		atomic num Symbo name standard atomic v	ber ol wight D-	BLOCK	r — Tra	ANSITIC	on Me	TALS			5 B	6 C	7 N	8 0	9 F	10 Ne	
¹¹ Na	¹² Mg	3	4	5	6	7	8	9	10	11	12			~				
sodium 22.99	24.31	3	4	5	6	7	8	9	10	11	12		1	0.5	-			
19 K	²⁰ Ca	21 Sc	22 Ti	23 V	24 Cr	²⁵ Mn	²⁶ Fe	27 Co	28 Ni	29 Cu	30 Zn			-		-		
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38(2)				100			
37	38	39	40	41	42	43	44	45	46	47	48		- and	STON T	ALC: N	and a		l
Rb rubidium 85.47	Sr strontium 87.62	Y yttrium 88.91	Zr zirconium 91.22	Nb niobium 92.91	Mo molybdenum 95.98(2)	Tc technetium	Ru ruthenium 101.1	Rh rhodium 102.9	Pd palladium 106.4	Ag siver 107.9	Cd cadmium 112.4	-		1				
55	56	57-71	72	73	74	75	76	77	78	79	80							
Cs caesium 132.9	Ba barium 137.3	lanthanoids	Hf hafnium 178.5	Ta tantalum 180.9	tungsten 183.8	Re rhenium 186.2	OS osmium 190.2	iridium 192.2	Pt platinum 195.1	Au gold 197.0	Hg mercury 200.6	and a						
87	88	89-103	104	105	106	107	108	109	110	111	112	Real Property						
Fr	Ra	actinoids	Rf	Db dubnium	Sg seaborgium	Bh	Hs	Mt	Ds darmstadtium	Rg	Cn		FI	_	Lv	_		
			1											± 1		4		
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	T	
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu		
		lanthanum 138.9	ceifium 140.1	praseodymium 140.9	neodymium 144.2	promethium	samarium 150.4	europium 152.0	gadolinium 157.3	terbium 158.9	dysprosium 162.5	holmium 164.9	erbium 167.3	thulium 168.9	ytterbium 173.1	lutetium 175.0	1	
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	I	
		Ac	Th thorium 232.0	Pa protactinium 231.0	U uranium 238.0	Np	Pu	Am	Cm	Bk	Cf	Es einsteinium	Fm	Md mendelevium	No	Lr lawrencium		







Similarities and differences between transition metal and p-block chemistry



Chem. Commun., 2013, 49, 5106









Similarities and differences between transition metal and p-block chemistry

					Physical	Propertie	s				
	ΛΛσταιμο	• LAF	RGE NUMB	ER OF OXID	ATION STAT	ES AVAILABL	E	13		22	
	Tend to lo	Se e	ORDINATIO	N COMPOU	NDS ARE Q	UITE STABLE		Sec.			1
	3	4	5	6	7	8			-		
T	21	22	23	24	25	26	27	28	29	30	T
l	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	l
	Ser.	TO STREET	- 🛞 -					- 🐼 -	- 🌌 -		
	Oxida	tion State		Examp	les	łu	1.12	- 1	Ag	Cd	
		-2	Na ₂ [Cr(0	CO)₅]		nium *			silver 107.9	cadmium 112.4	
İ		-1	Na ₂ [Cr ₂	(CO) ₁₀]		6			79	80	Ī
	h	0	Cr(CO) ₆)S	1		Au	Hg	
	_	+1				82 -			,197.0	200.6	ļ
		+2	CrO, CrO	Cl _{2,} CrS		'iquid					
		+3	Cr ₂ O ₃ , C	crCl ₃ , [Cr(H ₂	₂ 0) ₆] ³⁺						
		+4	CrO ₂ , Cr	·F ₄							
		+5	CrF_5				×		/		
		+6	CrO ₃ , Na	a ₂ CrO ₄ , Na	$_2Cr_2O_7$		6		/		

C. at







Similarities and differences between transition metal and p-block chemistry

						10
	Physical I	PROPERTIES				2
						He
						heium
ЛАGI	NETIC ¹³	14	15	16	17	4.003
	5	6	7	8	9	10
	B	C	N	0	F	Ne
	boron	carbon	nitrogen	axvaen	fluorine	neon
	[10.80; 10.83]	[12.00; 12.02]	[14.00; 14.01]	[15.99; 16.00]	19.00	20.18
	13	14	15	16	17	18
	A 1	Si	P	S	CL	Ar
	aluminium	eilean	nhoenhonie	en thur	chiorina	-
	26.98	[28.08; 28.09]	30.97	[32.05; 32.08]	[35.44; 35.46]	39.95
	31	32	33	34	35	36
	Ga	Ge	As	Se	Br	Kr
	gallium	oemanium	arsenic	selenium	bromine	krypton
	60.72	72.63	74.92	78.96(3)	79.90	83.80
	49	50	51	52	53	54
	In	Sn	Sb	Те		Xe
	indium	fin	antimony	tellurium	iodine	xenon
	114.8	118.7	121.8	127.6	126.9	131.3
	81	82	83	84	85	86
	TI	Pb	Bi	Po	At	Rn
	thallium	lead	bismuth	polonium	astatine	radon
	[204.3; 204.4]	207.2	209.0			
ac						

• COMPOUNDS USUALLY COLOURLESS

- ALMOST ALL COMPOUNDS ARE DIAGMAGNETIC
- MOST COMPOUNDS HAVE ONLY ONE OR TWO OXIDATION STATES
- OXIDATION STATES ARE SEPARATED BY TWO UNITS

E.G., I: -1, 1, 3, 5, 7

At 322 K (24 °C) – blue = liquid, red = gas



Similarities and differences between transition metal and p-block chemistry

	PHYSICAL P	PROPERTIES				2
Noble Gases Halogens Tend to gain e ⁻	13	14	15	16	17	He heium 4.003
Metalloids Post-transition metals Other nonmetals ALLOTROPES Tend to lose e ⁻ Tend to gain e ⁻	5 B boron (10.80; 10.83)	6 C carbon [12.00; 12.02]	7 N nitrogen [14.00; 14.01]	8 O axygen [15.99; 16.00]	9 F fluorine 19.00	10 Ne neon 20.18
	13 Al aluminium 26.98	14 Si silicon [28.08; 28.09]	15 P phosphorus 30.97	16 S sulfur [32.05; 32.08]	17 Cl chlorine [3544;35.46]	18 Ar argon 39.95
	31 Ga gallium 60.72	32 Ge germanium 72.63	33 As arsenic 74.92	34 Se selenium 78.96(3)	35 Br bromine 79.90	36 Kr krypton 83,80
	49 In indium 114.8	50 Sn 50 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 iodine 126.9	54 Xe xenon 131.3
	81 TI thallium (204.3; 204.4)	82 Pb lead 207.2	83 Bi bismuth 200.0	84 Po polorium	85 At astatine	86 Rn radon



Penetration and shielding

- REMEMBER: PAULI EXCLUSION PRINCIPLE STATES THAT A MAXIMUM OF 2 ELECTRONS CAN OCCUPY
- A SINGLE ORBITAL. THE AUFBAU PRINCIPLE STATES THAT ORBITAL OF LOWER ENERGY ARE FILLED IN FIRST WITH THE ELECTRONS
- THE NUCLEAR CHARGE EXPERIENCED BY AN ELECTRON IS REDUCED BY THE SHIELDING OF THE OTHER ELECTRONS THAT ARE CLOSER TO THE NUCLEUS
- The electrons that are closer are called <u>core</u> electrons. The electrons that are furthest are called <u>valence</u> electrons
- THE CLOSER AN ELECTRON CAN GET TO THE NUCLEUS, THE TIGHTER IT WILL BE BOUND AND THE LOWER IN ENERGY IT WILL BE. THIS IS CALLED **PENETRATION**.
- RADIAL PROBABILITY DISTRIBUTION = $4\pi r^2 X R^2(r)$





Penetration and shielding

- REMEMBER: PAULI EXCLUSION PRINCIPLE STATES THAT A MAXIMUM OF 2 ELECTRONS CAN OCCUPY
- A SINGLE ORBITAL. THE AUFBAU PRINCIPLE STATES THAT ORBITAL OF LOWER ENERGY ARE FILLED IN FIRST WITH THE ELECTRONS
- THE NUCLEAR CHARGE EXPERIENCED BY AN ELECTRON IS REDUCED BY THE SHIELDING OF THE OTHER ELECTRONS THAT ARE CLOSER TO THE NUCLEUS
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Penetration and shielding

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- THE CLOSER AN ELECTRON CAN GET TO THE NUCLEUS, THE TIGHTER IT WILL BE BOUND AND THE LOWER IN ENERGY IT WILL BE. THIS IS CALLED **PENETRATION**.
- RADIAL PROBABILITY DISTRIBUTION = $4\pi r^2 X R^2(r)$



Radial Probability



Penetration and shielding

CH2501

Radial Probability

REMEMBER: PAULI EXCLUSION PRINCIPLE STATES THAT A MAXIMUM OF 2 ELECTRONS CAN OCCUPY A SINGLE ORBITAL. THE AUFBAU PRINCIPLE STATES THAT ORBITAL OF LOWER ENERGY ARE FILLED IN

FIRST WITH THE ELECTRONS

- THE NUCLEAR CHARGE EXPERIENCED BY AN ELECTRON IS REDUCED BY THE SHIELDING OF THE OTHER ELECTRONS THAT ARE CLOSER TO THE NUCLEUS
- The electrons that are closer are called <u>core</u> electrons. The electrons that are furthest are called <u>valence</u> electrons
- THE CLOSER AN ELECTRON CAN GET TO THE NUCLEUS, THE TIGHTER IT WILL BE BOUND AND THE LOWER IN ENERGY IT WILL BE. THIS IS CALLED PENETRATION.
- RADIAL PROBABILITY DISTRIBUTION = 4ΠR² X R²(R)





Effective nuclear charge (Z_{eff})

- Z_{EFF} IS THE POSITIVE CHARGE EXPERIENCED BY AN ELECTRON
- CH2501 THE MORE ELECTRONS SHIELDING AN ELECTRON, THE LOWER IS Z_{EFF} AND THE MORE WEAKLY BOUND THAT ELECTRON IS TO THE NUCLEUS
 - ROUGHLY Z_{EFF} = Z-S (Z is the ATOMIC NUMBER AND S is the NUMBER OF CORE ELECTRONS)
 E.G., Z_{EFF} FOR Li = 3 2 = 1
 - More precisely $Z_{EFF} = Z \sigma(\sigma \text{ is the shielding constant, empirically derived})$

Question: What is Z_{eff} for O and for Ca? \checkmark O = 8-2 = 6 \checkmark Ca = 20-18 = 2

Н							He
1			7				2
1.00				EFF			1.69
Li	Be	В	С	Ν	0	F	Ne
3	4	5	6	7	8	9	10
2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
		2.42	3.14	3.83	4.45	5.10	5.76
Na	Mg	AI	Si	Р	S	CI	Ar
11	12	13	14	15	16	17	18
10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
		4.07	4.29	4.89	5.48	6.12	6.76
	H 1 1.00 Li 3 2.69 1.28 Na 11 10.63 6.57 6.80 2.51	H 1 1.00 Li Be 3 4 2.69 3.68 1.28 1.91 Na Mg 11 12 10.63 11.61 6.57 7.39 6.80 7.83 2.51 3.31	H 1 1.00 Li Be B 3 4 5 2.69 3.68 4.68 1.28 1.91 2.58 2.42 2.42 Na Mg AI 11 12 13 10.63 11.61 12.59 6.57 7.39 8.21 6.80 7.83 8.96 2.51 3.31 4.12 4.07 1.01 1.01	HIZ1.00IIIIIILiBeBC34562.693.684.685.671.281.912.583.222.423.142.423.14NaMgAlSi1112131410.6311.6112.5913.576.577.398.219.026.807.838.969.942.513.314.124.904.074.2910.53	H Image: second	H J J 100 J J 100 J J Li Be B C N O 3 4 5 6 7 8 2.69 3.68 4.68 5.67 6.66 7.66 1.28 1.91 2.58 3.22 3.85 4.49 2.42 3.14 3.83 4.45 Ma Mg AI Si P S 11 12 13 14 15 16 10.63 11.61 12.59 13.57 14.56 15.54 6.57 7.39 8.21 9.02 9.82 10.63 6.80 7.83 8.96 9.94 10.96 11.98 2.51 3.31 4.12 4.90 5.64 6.37	HIImage: Constraint of the sector of t





1 1

Okay. So how does this help me here?

- 4S PENETRATES THE CORE MORE THAN 3D AND SO IS LOWER IN ENERGY
- This is why K and CA precede Sc, Ti etc. in the periodic table CH2501
 - HOWEVER, FROM SC TO ZN, THEIR 3D ORBITALS ARE LOWER IN ENERGY THAN THEIR 4S ORBITALS,

WHICH WILL DEFINE THE REACTIVITY AND CHEMISTRY OF THE D-BLOCK





Trends

ATOMIC RADIUS

		1																	18	
Г		1																[2	1
		-																	He	
	hy	ogen	2		Marca 1									13	14	15	16	17	heium	l
+	(10	3	4	r	stomic num	hor								5	6	7	8	9	4.003	ł
			Be		Symbo									B	Ċ	N	Ő	F	Ne	l
		ium	berylium		name									boron	carbon	nitrogen	axygen	fluorine	neon	l
┢	[6.9	(6.997]	9.012		standard atomic v	weight								[10.80; 10.83]	[12.00; 12.02]	[14.00; 14.01]	[15.99; 16.00]	19.00	20.18	$\left \right $
		11	12											13	14	15	16	17	18	l
		a	IVIG											Al	SI	P	S	chlorine	Ar	l
		99	24.31	3	4	5	6	7	8	9	10	11	12	26.98	[28.08; 28.09]	30.97	[32.05; 32.08]	[35.44;35.46]	39.95	
		9	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	I
		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	l
	pa	uto	40.08	44.96	47.87	50.94	52.00	manganese 54.94	55.85	58.93	58.69	63.55	2inc 65.38(2)	galium 69.72	germanium 72.63	arsenic 74.92	78.96(3)	79.90	83.80	l
Γ		37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	1
		b	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	1	Xe	l
	ru	dium	strontium 87.62	yttrium 88.91	zirconium 91.22	niobium	molybdenum 95.9920	technetium	ruthenium	rhodium	palladium 106.4	siver	cadmium	indium 114.8	6n 118.7	antimony 121.8	tellurium	iodine 126.9	xenon	l
F		5	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	1
		s	Ba	lanthanoids	Hf	Та	W	Re	Os	Ir	Pt	Au	Ha	TI	Pb	Bi	Po	At	Rn	l
	a	sium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon	l
+	-	29	137.3 88	89-10.3	178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6	[204.3; 204.4]	207.2	209.0	116		_	1
		r	Ra	antinaida	Rf	Dh	Sa	Bh	Hs	Mt	Ds	Ra	Cn		FI		Lv			
	fri	cium	radium	domoids	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		ivermorium			
L	-											- 44 		32 12		ା				
			1		1															
				57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
	•			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		7		lanthanum 138.9	0erfum 140.1	praseodymium 140.9	neodymium 144.2	promethium	samarium 150.4	europium 152.0	gadolinium 157.3	terbium 158.9	dysprosium 162.5	holmium 164.9	erbium 167.3	thulium 168.9	ytterbium 173.1	lutetium 175.0		
				00	00	04	00	02	04	OF	00	07	0.0	00	100	404	40.2	400		
				Ac	Th	Pa	92	Np	Du	Am	Cm	BL	Cf	Ec	Em	Md	No	105		
				actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium	lawrencium		
					232.0	231.0	238.0			ų.										





Trends

ATOMIC RADIUS

Trends in Atomic Radius



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IONIC RADIUS – FAJANS' RULES



The contraction is due to poorer shielding of the valence electrons resulting in stronger interaction with the nucleus and tighter binding



IONIC RADIUS - FAJANS' RULES





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1.009

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l ium

[6.9 (6.997]

11

[1.0

2

4

Be

bervlium

9.012

12

Trends

IONIZATION POTENTIALS (IPS)

The IP measures the amount of energy required to remove an electron from an atom or ion and so measures how strongly the atom or ion holds onto its electronics. Vare 17

wy.
atomic number
Symbol
name
standard atomic weight

 $A(g) \rightarrow A^+(g) + e^-(g)$ $I = E(A^+,g) - E(A,g)$

 $IP \propto Z^2_{eff}/n^2 \propto$ nuclear radii n is the principal quantum number

	Id	ivig				is the	princi	pai qu	antui	nnum	DEI		AI	31	F	3	CI	AI
	10m 299	24.31	3	4	5	6	7	8	9	10	11	12	aluminium 26.98	[28.08; 28.09]	30.97	[32.05; 32.08]	[35.44;35.48]	argon 39.95
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
po	ssium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton
	0.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38(2)	69.72	72.63	74.92	78.96(3)	79.90	83.80
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	lb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1	Xe
n	idium	strontium	yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	siver	cadmium	indium	tin	antimony	tellurium	iodine	xenon
	5.47	87.62	88.91	91.22	92.91	95.96(2)		101.1	102.9	106.4	107_9	112.4	114.8	118.7	121.8	127.6	126.9	131.3
	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	s	Ba	lanthanoids	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
ľ	32.9	137.3		178.5	180.9	183.8	186.2	190.2	192.2	195.1	197.0	200.6	[204.3; 204.4]	207.2	209.0	poonum	dsidunio	rauon
	37	88	89-103	104	105	106	107	108	109	110	111	112		114		116		
	۶r	Ra	actinoids	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		FI		Lv		
fr	kium	radium		rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		ivermorium		
_															1		4	

57 La Ianthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 1442	61 Pm promethium	62 Sm samarium 150.4	63 Eu europium 1520	64 Gd gadoinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 1625	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm #ulium 168.9	70 Yb ytterbium 173.1	71 Lu Iutetium 1750
89 Ac actinium	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr Iawrencium

18 2

He heium

4.003

10

Ne

neon

20.18

18

9

F

fluorine

19.00

17

0

15

N

nitrogen

[14.00; 14.01]

15

6

С

carbon

[12.00; 12.02]

14

в

boron

[10.80; 10.83]

13

16

8

0

axygen

[15.99; 16.00]



1

Trends

IONIZATION POTENTIALS (IPS)

1	H 1312.0	2			375.7 kJ/	mol			237	72.3 kJ/mol			13	14	15	16	17	He 2372.3
2	Li 520.2	Be 899.5											B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
3	Na 495.8	Mg 737.7	3	4	5	6	7	8	9	10	11	12	Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe 762.5	Co 760.4	Ni 737.1	Cu 745.5	Zn 906.4	Ga 578.8	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
5	Rb 403.0	Sr 549.5	Y 599.9	Zr 640.1	Nb 652.1	Mo 684.3	Tc 702	Ru 710.2	Rh 719.7	Pd 804.4	Ag 731.0	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	 1008.4	Xe 1170.3
6	Cs 375.7	Ba 502.9	La 538.1	Hf 658.5	Ta 728.4	W 758.8	Re 755.8	Os 814.2	Ir 865.2	Pt 864.4	Au 890.1	Hg 1007.1	TI 589.4	Pb 715.6	Bi 703.0	Po 812.1	At	Rn 1037.1
7	Fr 393.0	Ra Ac 509.3 498.8		Rf 580	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
	Lanthanides 6		Ce 534.4	Pr 528.1	Nd 533.1	Pm 538.6	Sm 544.5	Eu 547.1	Gd 593.4	Tb 565.8	Dy 573.0	Ho 581.0	Er 589.3	Tm 596.7	Yb 603.4	Lu 523.5		
			Actinides 7	Th 608.5	Pa 568	U 597.6	Np 604.5	Pu 581.4	Am 576.4	Cm 578.1	Bk 598.0	Cf 606.1	Es 619	Fm 627	Md 635	No 642	Lr 472.8	



IONIZATION POTENTIALS (IPS)

_	1		The	IP inc	rease	es with	n eacł	n succ	essiv	e rem	oval c	of an	electr	on as	Z _{eff} ir	ncreas	ses	18
1	H 1312.0	2	and	elect	ron-е 375.7 kJ/r		n rep	ulsior	237.	eases 2.3 kJ/mol			13	14	15	16	17	He 2372.3
2	Li 520.2	Be 899.5											B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
3	Na 495.8	Mg 737.7	3	4	5	6	7	8	9	10	11	12	Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe 762.5	Co 760.4	Ni 737.1	Cu 745.5	Zn 906.4	Ga 578.8	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
5	Rb 403.0	Sr 549.5	2 nd	1309	1414	1592	1509	1561	1644	1752	1958	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	 1008.4	Xe 1170.3
6	Cs 375.7	Ba 502.9	3 rd	2650 4173	2828 4600	3056 4900	3251 5020	2956 5510	3231 5114	3489 5404	3954 5683	Hg 1007.1	TI 589.4	Pb 715.6	Bi 703.0	Po 812.1	At	Rn 1037.1
7	Fr 393.0	Ra 509.3	Ac 498.8	Rf 580	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
L																		
		Laı	nthanides 6	Ce 534.4	Pr 528.1	Nd 533.1	Pm 538.6	Sm 544.5	Eu 547.1	Gd 593.4	Tb 565.8	Dy 573.0	Ho 581.0	Er 589.3	Tm 596.7	Yb 603.4	Lu 523.5	
			Actinides 7	Th 608.5	Pa 568	U 597.6	Np 604.5	Pu 581.4	Am 576.4	Cm 578.1	Bk 598.0	Cf 606.1	Es 619	Fm 627	Md 635	No 642	Lr 472.8	



IONIZATION POTENTIALS (IPS)

	1		The	IP ind	crease	s witl	n eacł	n succ	essiv	e rem	oval c	of an	electi	ron as	Z _{eff} ir	ncreas	ses	18
1	H		and	elect	ron-e	lectro	n rep	ulsior	n decr	eases								He
	1312.0	2			375.7 kJ/r	nol			237.	2.3 kJ/mol			13	14	15	16	17	
2	Li 520.2	Be 899.5	The	se IPs	are a	ll low	<mark>er</mark> tha	n exp	ected	d due	to inc	rease	₿ 20 ^{60.6}	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
	Na	Ma	stak	oility f	rom h	alf-fil	led sh	nell (3	d ⁶ to	3d ⁵)			AI	Si	Р	S	CI	Ar
3	495.8	737.7	3	4	5	6	7	8	9	10	11	12	577.5	786.5	1011.8	999.6	1251.2	1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ac. Ti V Mn Fe Co Ni Cu Zn Ga Ge As Se Br Ma 3.1 658.8 650.9 Mn 717.3 762.5 760.4 737.1 745.5 906.4 578.8 Ge As 941.0 1139.9 135 3.1 0.0														Kr 1350.8
5	Rb 403.0	Sr 549.5	2 nd	1309	1414	1592		1561	1644	1752	1958	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	 1008.4	Xe 1170.3
6	Cs	Ba	3 rd	2650	2828	3056	3251		3231	3489	3954	Hg	ТΙ	Pb	Bi	Ро	At	Rn
-	375.7	502.9	4 th	4173	4600	4900	5020	5510		5404	5683	1007.1	589.4	715.6	703.0	812.1		1037.1
7	Fr 393.0	Ra	Ac 498.8	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
L																		
		Laı	nthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			6	534.4	528.1	533.1	538.6	544.5	547.1	593.4	565.8	573.0	581.0	589.3	596./	603.4	523.5	
			Actinides	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
			7	608.5	568	597.6	604.5	581.4	576.4	578.1	598.0	606.1	619	627	635	642	472.8	



IONIZATION POTENTIALS (IPS)

	1		The	IP inc	crease	es witl	h each	n succ	essiv	e rem	oval d	of an	elect	ron as	Z _{eff} ir	ncreas	ses	18
1	H		and	elect	ron-e	lectro	on rep	ulsior	n decr	eases			12		45	1.5	17	He
	1312.0	2			375.7 kJ/r	nol			237	2.3 kJ/mol			13	14	15	16	17	
2	Li	Be											В	C	Ν	0	F	Ne
	520.2	899.5	The	se IPs	are a	ll higł	her th	an ex	pecte	d due	e to		800.6	1086.5	1402.3	1313.9	1681.0	2080.7
	Na	Mg	disr	uptio	n of tł	ne hal	lf-fille	d she	ll (3d ^e	[;] to 3c	⁵)		AI	Si	Ρ	S	CI	Ar
3	495.8	737.7	3	4	5	6	7	8	9	10	11	12	577.5	786.5	1011.8	999.6	1251.2	1520.6
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4	418.8	589.8	633.1	658.8	650.9	652.9	717.3	762.5	760.4	737.1	745.5	906.4	578.8	762.2	944.5	941.0	1139.9	1350.8
	Rh	Sr	7 nd	1200	1/1/		1500	1561	1644	1752	1059	Cd	In	Sn	Sh	Τo	1	Xe
5	403.0	549.5	2	1309	1414		1309	1301	1044		1930	867.8	558.3	708.6	830.6	869.3	1008.4	1170.3
-			3 rd	2650	2828	3056		2956	3231	3489	3954						_	
6	Cs	Ba										Hg	TI	Pb	Bi	Ро	At	Rn
	375.7	502.9	4 th	4173	4600	4900	5020		5114	5404	5683	1007.1	589.4	715.6	703.0	812.1		1037.1
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
<i>`</i>	393.0	509.3	498.8	580														
		Lai	nthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
			6	534.4	528.1	533.1	538.6	544.5	547.1	593.4	565.8	573.0	581.0	589.3	596.7	603.4	523.5	
			Actinides	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
			7	608.5	568	597.6	604.5	581.4	576.4	578.1	598.0	606.1	619	627	635	642	472.8	



IONIZATION POTENTIALS (IPS)

	1		The	IP in	crease	es wit	h eacl	n succ	cessiv	e rem	oval d	of an	electi	ron as	Z _{eff} ir	ncreas	ses	18
1	H		and	elect	ron-e	electro	on rep	ulsior	n decr	eases								He
	1312.0	2			375.7 kJ/	/mol			237	2.3 kJ/mol			13	14	15	16	17	
2	Li 520.2	Be 899.5	The	4 th IF	o for S	is ve	ery hig	gh as (electr	on is I	now		B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
	Na	Mg	rem	noved	from	2p or	bital						AI	Si	Ρ	S	CI	Ar
3	495.8	737.7	3	4	5	6	7	8	9	10	11	12	577.5	786.5	1011.8	999.6	1251.2	1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe	Ga 578.8	Ge	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8				
														6	CI.	-		N
5	KD 403.0	2 ⁿ d	1235	1309	1414	1592	1509	1561	1644	1752	1958	Cd 867.8	In 558.3	Sn 708.6	SD 830.6	Iе 869.3	1008.4	Xe 1170.3
6	Cs	3 rd	2389	2650	2828	3056	3251	2956	3231	3489	3954	Hg	ті	Pb	Bi	Ро	At	Rn
-	375.7	4 th		4173	4600	4900	5020	5510	5114	5404	5683	1007.1	589.4	715.6	703.0	812.1		1037.1
7	Fr	па	AL		DD	Sy	DII	пз	1410	US	ny	Jub	Uut	Uuq	Uup			
	393.0	509.3	498.8	580														
		I	Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
	U		6	534.4	528.1	533.1	538.6	544.5	547.1	593.4	565.8	573.0	581.0	589.3	596.7	603.4	523.5	
			Actinides	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
			7	608.5	568	597.6	604.5	581.4	576.4	578.1	598.0	606.1	619	627	635	642	472.8	



ELECTRON AFFINITY (EA)

CH250	1			The	e EA	mea	sure	s the	e am	ount	t of e	ener	gy ga	ined	whe	en a	gase	eous	atom	l	40
1 H hydrogen				gair	ns ar	i ele	ctroi	า.													2 He
1.007; 1.004 3 Li Ithium 6.938; 6.947	7]	2 4 Be beryllium 9012	r	Key: atomic Syn standard a	number nbol ame tomic weight	A E	A(g)	+e	-(g)) → - F	A- C(A-	-(g) . g)			13 5 B boro (10.80; 1	n (0.83] [12	14 6 C arbon 00; 12.02]	15 7 N nitrogen [14.00; 14.01]	16 8 0 axygen [15.99; 16.00]	17 9 F fluorine 1900	4.003 10 Ne neon 20.18
11 Na sodium 2299	e	¹² eme H	nts w	/ith h	nigh E	EA ca	a n acc	omn	nodat	te an	extra	•6/ a e ⁻ v	vhere	ein e⁻	¹³ expe	rien	¹⁴ ces a	15 stro	16 Ng18Z _{eff} He _	17 Cl (3544;35.46) 35	18 Ar argon 3995
K		-72.8	2 Bo			≥0 kJ	/mol			-3	48.6 kJ/mol			13 R	14	15 N	16	17 E	≥0	Br	Kr krypton
39.10 37	2	- 59.6	De ≥0											-27.0	-121.8	≥0	-141.0	-328.2	≥0	79.90 53	54
rubidium 85.47 55	3	Na -52.9	Mg ≥0	3	4	5	6	7	8	9	10	11	12	Al -41.8	Si -134.1	P -72.0	S -200.4	Cl -348.6	Ar ≥0	iodine 126.9 85	xenon 131.3 86
Cs caesium 132.9	4	K −48.4	Ca -2.4	Sc −18	Ti −8	V -51	Cr -65.2	Mn ≥0	Fe -15	Co -64.0	Ni -111.7	Cu -119.2	Zn ≥0	Ga -40	Ge -118.9	As -78	Se -195.0	Br -324.5	Kr ≥0	At	Rn
87 Fr francium	5	Rb -46.9	Sr -5.0	Y −30	Zr -41	Nb -86	Mo -72.1	Tc −60	Ru -101.0	Rh -110.3	Pd -54.2	Ag -125.9	Cd ≥0	In -39	Sn -107.3	Sb -101.1	Te -190.2	-295.2	Xe ≥0		
	6	Cs -45.5	Ba - 14.0	La -45	Hf ≥0	Ta −31	W 79	Re -20	Os -104.0	Ir -150.9	Pt - 205.0	Au -222.7	Hg ≥0	TI -37	Pb -35	Bi -90.9	Po -180	At -270	Rn ≥0	71	
	7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup				Lu Iutelium 1750	
														1			103 Lr				
	Lanthanid					Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu		lawrencium	
				Actinides 7	Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			




Trends

ELECTRON AFFINITY & IONIZATION ENERGY

METALLIC CHARACTER

		IVIE IALLIC CHARACTER																
			Me	tallic	chara	cter r	elates	s to h	ow ea	asily a	n ato	m or	ion ca	an los	e		ſ	18
	H		an e	electr	on													He
(1.0	ogen ; 1.009	2	an .	Key:	011								13	14	15	16	17	4.003
	3	4		atomic num	ber								5	6	7	8	9	10
	.i	Be		Symbo	l								В	С	N	0	F	Ne
16.9	ium 16.9971	berylium 9012		name standard atomic v	veight								boron (10.80: 10.83)	carbon [12.00: 12.02]	nitrogen	axygen (15.99; 16.00)	fluorine 19.00	neon 20.18
	11	12											13	14	15	16	17	18
	la	Mg											AI	-1	Р	S	CI	Ar
5	tium 199	magnesium 24.31	3	4	5	6	7	8	9	10	11	12	aluminium	silicon [28.08; 28.09]	phosphorus 30.97	sulfur (32.05; 32.08)	chlorine [35.44;35.46]	argon 39.95
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	<u>_n</u>	Ga	Ge	As	Se	Br	Kr
pa	ssium	40.08	scandium 44.96	titanium 47.87	50.94	sp.00	manganese 54.94	iron 55.85	cobalt 58.93	nickel 58.69	00000	zinc 65.38(2)	gallium 69.72	germanium 72.63	arsenic 74.92	5elenium 78.96(3)	79.90	krypton 83,80
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	lb	Sr	Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1	Xe
ru	dium	strontium 87.62	yttrium 88.91	zirconium 91.22	niobium 92.91	molybdenum 95.99(2)	technetium	ruthenium	rhow a	palladium 105.4	siver 107.9	cadmium 112.4	indium 114.8	tin 1187	antimony 121.8	tellurium 127.6	iodine 126.9	xenon 1313
	5	56	57-71	72	73	74	75	70	77	78	79	80	81	82	83	84	85	86
	s	Ba	lanthanoids	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
G	sium	barium		hafnium	tantalum	tungsten	the arth	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth 200 0	polonium	astatine	radon
	37	88	89-103	104	105		107	108	109	110	111	112	[2010, 2017]	114	2.00.0	116		
	ir 🗌	Ra	actinoids	Rf	Db	Sq	Bh	Hs	Mt	Ds	Ra	Cn		FI		Lv		
fra	cium	radium		rutherfordium	unum	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		ivernorium		
															1)		l	
			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dv	Но	Er	Tm	Yb	Lu	
			lanthanum	cerium	praseodymium	neodymium	promethium	samarium	europium	gadolinium	terbium	dysprosium	holmium	erbium	thulium	ytterbium	lutetium	
			138.9	142.1	140.9	144.2		150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	1/3.1	1750	
			89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
			acarriant	232.0	231.0	238.0	naparian	paranam	anonciam	Curicin	Jakaiun	canornam	Gristanum	Jorringun	indification alm	hoonum	awaroun	



Trends

POLARIZABILITY (α)

"A polarizable atom or ion is one with orbitals that lie close in energy." Large, heavy atoms and ions tend to be highly polarizable

hy	1 - rogen			Laige	, nea	vyatu			is ter			giny p	Ulariz	able	15	46	17	2 He heium	
.0	1.009	2		Key:	A r	polari:	zable	atom	or io	n can	be	33	13	14	15	10	1/	4.003	-
	:	Po		Sumb					01.10				D	ĉ	N	ô	F	No	
	ium	berylium		Symbo	" leas	silv di	storte	ed by	an EN	∕l field			boron	carbon	nitrogen	axvaen	fuorine	ne	
	(6.997)	9.012		standard atomic v	wight	··· / ···		/					[10.80; 10.83]	[12.00; 12.02]	[14.00, 14.01]	[15.99; 18.00]	19.00	20.18	
	11	12											13	14	15	16	17	18	
	la	Mg											AI	Si	P	S	CI	Ar	
8	tium 199	magnesium 24.31	3	4	5	6	7	8	9	10	11	12	aluminium 26.98	silicon [28.08; 28.09]	phosphorus 30.97	sulfur [32.05; 32.08]	chlorine [35.44;35.46]	argon 39.95	
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	Ī
L	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
o	ssium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	coball	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton	
+	7	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38(2)	60.72	72.63	74.92	78.96(3)	79.90	83.80	-
	h	Cr.	V	7.	Nb	Mo	To	Du	Dh	Dd	Ac	Cd	In	Sn	Sh	To	35	Ya	
~	idium	strontium	vttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	siver	cadmium	indium	511 fin	antimony	tellurium	ipdine	xenon	
	5.47	87.62	88.91	91.22	92.91	95.96(2)		101.1	102.9	106.4	107.9	112.4	114.8	118.7	121.8	127.6	128.9	131.3	
	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	s	Ba	lanthanoids	Hf	Ta	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn	
G	sium	barium		hafnium	tantalum 180.9	tungsten 193.8	rhenium	osmium	iridium	platinum 195.1	gold	mercury 200.6	thallium (2043: 204.4)	lead	bismuth 209.0	polonium	astatine	radon	
	37	88	89-103	104	105	106	107	108	109	110	111	112	1000, 2000	114	2.00.0	116			ī
	Fr	Ra	actionide	Rf	Db	Sa	Bh	Hs	Mt	Ds	Ra	Cn		FI		Lv			
÷.	cium	radium	acanoida	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium		flerovium		ivermorium			
-									2				3 E				1		
I.		i		1															
I			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			lanthanum	cerium	praseodymium	neodymium	promethium	samarium	europium	gadoinium	terbium	dysprosium	holmium	erbium	thulium	ytterbium	lutetium		
		L	138.9	140.1	140.9	144.2		150.4	152.0	157.3	158.9	162.5	164.9	187.3	162.9	1/3.1	1/50		
			89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		

Np

Pu

plutonium

Am

americium

Cm

curium

Bk

berkelium

Cf

californium

Es

einsteinium

Fm

fermium

Md

mandelevium

No

nobelium

Lr

lawrencium

Ac

actinium

Th

thorium

232.0

Pa

protactinium

231.0

U

uranium

238.0

18



Calculated atomic radius (pm)



Magnitude of electron affinity (kJ/mol)







The Elements Possess Diverse Properties

CH2501





Coordination Chemistry





Coordination Chemistry

Metal complexes are, to a first approximation, held together by electrostatic forces

2+



A coordination complex is composed of 1) a metal – the Lewis Acid;

2) organic atoms or molecules attached to the metal that are called **ligands** - Lewis Bases

Fe



Switching Gears Lewis Structures – A Review



CH2501

Each atom shares electrons to achieve but not exceed 8 electrons in outer shell



Method:

- 1. Count up total number of valence electrons plus/minus overall molecular charge for NF₃ it is 5+3x7=26
- 2. Arrange atoms in desired order and place lone pairs and bonds (shared electron pairs) around atoms to achieve octet for each atom with lowest formal charge on as many atoms as possible
- Lewis structures give number of bonds and bond orders



Bonding of Small Molecules

VSEPR = Valence Shell Electron Pair Repulsion Theory

Basically says that substituent atoms around a central atom will be positioned as to maximize their distance and minimize Coulombic repulsion. Non-bonded lone pairs must also be taken into consideration and these have an even larger effect in terms of electronic repulsion.

The relative disposition of substituents defines the geometry of the molecule.

This theory works quite well for p-block molecules but not so well for transition metal compounds (for those Crystal Field Theory does a better job). There are also some other exceptions



Bonding of Small Molecules

University St Andrews VSEPR = Valence Shell Electron Pair Repulsion Theory CH2501 A = Central atom, X = atomic substituent, E = lone pair



45



Bonding of Small Molecules

University st Andrews VSEPR = Valence Shell Electron Pair Repulsion Theory CH2501 A = Central atom, X = atomic substituent, E = lone pair





Bonding of Small Molecules

University st Andrews VSEPR = Valence Shell Electron Pair Repulsion Theory CH2501 A = Central atom, X = atomic substituent, E = lone pair

CN: 8 AX_8 square antiprismatic (73, 78°) **CN**: 9 AX₉

tricapped trigonal prismatic



- Charge
 - Anionic:
 - Cl⁻ Donor Atom: Cl
 - CN⁻ Donor Atom: C
 - OH⁻ Donor Atom: O



Ligand Classification

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral:
 - $H_2O Donor Atom: O$
 - NH₃ Donor Atom: N
 - CO Donor Atom: C
 - 2,2'-bipyridine Donor Atom: N 2 donor atoms present





Ligand Classification

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral: e.g., H_2O , NH_3 , CO, 2,2'-bipyridine
 - Cationic: e.g., NO⁺



Ligand Classification

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral: e.g., H_2O , NH_3 , CO, 2,2'-bipyridine $\langle \rangle \rightarrow \langle \rangle$
 - Cationic: e.g., NO⁺
- Binding mode
 - Attached to one metal atom terminal





Ligand Classification

Ligands are classified based on their:

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral: e.g., H_2O , NH_3 , CO, 2,2'-bipyridine $\langle \rangle \rightarrow \langle \rangle$
 - Cationic: e.g., NO⁺
- Binding mode
 - Attached to one metal atom terminal
 - Ambidentate can attach at metal at different atoms e.g., NCS⁻, CN⁻, NO₂



5 Nitrito-ĸO ligand

NOMENCLATURE

The κ (kappa) is used to denote the atom to which the metal is ligated



Ligand Classification

Ligands are classified based on their:

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral: e.g., H_2O , NH_3 , CO, 2,2'-bipyridine $\langle \rangle \rightarrow \langle \rangle$
 - Cationic: e.g., NO⁺
- Binding mode
 - Attached to one metal atom terminal
 - Ambidentate can attach at metal at different atoms e.g., NCS⁻, CN⁻, NO₂
 - Attached to two or more metal atoms bridging



12 $[(H_3N)_5CoOCo(NH_3)_5]^{4+}$

NOMENCLATURE

The μ (mu) is used to denote the atom to which two or more metals are bridged.

If the number of centers bridged > 2 then a subscript is added.

e.g., μ₃-Η



Ligand Classification

- Charge
 - Anionic: e.g., Cl⁻, CN⁻, OH⁻
 - Neutral: e.g., H₂O, NH₃, CO, 2,2'-bipyridine
 - Cationic: e.g., NO⁺
- Binding mode
 - Attached to one metal atom terminal
 - Ambidentate can attach at metal at different atoms e.g., NCS⁻, CN⁻, NO₂
 - Attached to two or more metal atoms bridging
- Chelate number (Greek for 'Claw')
 - Monodentate, bidentate ..., polydentate



Prefix	Meaning
mono-	1
di-, bis-	2
tri-,tris-	3
tetra-, tetrakis-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12



Isomerism in Transition Metal Complexes





Isomerism in Transition Metal Complexes

LINKAGE ISOMERISM ambidentate ligands





Isomers that differ in the way the ligand is bound to the metal.

56







GEOMETRIC ISOMERISM (STEREOISOMERISM) square planar complexes Isomers that differ in the way the ligand is bound to the metal.





MA₄B₂ octahedral complex, cis isomer

MA4B2 octahedral complex, trans isomer



(a) Red form



(b) Green form





mer-[CoCl₃(NH₃)₃]



Isomerism in Transition Metal Complexes

GEOMETRIC ISOMERISM (STEREOISOMERISM) octahedral complexes Isomers that differ in the way the ligand is bound to the metal.

fac and mer isomers





Isomerism in Transition Metal Complexes

GEOMETRIC ISOMERISM (STEREOISOMERISM) octahedral complexes Isomers that differ in the way the ligand is bound to the metal.

Summary



Phys. Chem. Chem. Phys., 2010, 12, 2126



Isomerism in Transition Metal Complexes

IONIZATION ISOMERISM

CH2501

 $[CoBr(H_2O)_5]$ Cl

 $[CoCl(H_2O)_5]Br$

Isomers that are identical except that an inner sphere ligand(s) has exchanged with an outer sphere counterion(s)

SOLVATE ISOMERISM (A SPECIAL TYPE OF IONIZATION ISOMERISM)

 $[CrCl(H_2O)_5]Cl_2H_2O$

 $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$



grey-green

COORDINATION ISOMERISM

 $[Co(bpy)_2(CN)_2]^+[Fe(bpy)(CN)_4]^ [Fe(bpy)_2(CN)_2]^+[Co(bpy)(CN)_4]^ [Fe(bpy)_3]^{3+}[Co(CN)_6]^{3-}$

These are ionization isomers where a ligand exchanges with a solvent molecule

$[Cr(H_2O)_6]Cl_3$



Isomers that are contain both complex cations and anions wherein the ligands are exchanged between the two ions



Isomerism in Transition Metal Complexes

OPTICAL ISOMERISM (STEREOISOMERISM) *tetrahedral complexes* Isomers that are non-superimposable mirror images of each other



48 [MABCD] enantiomers





Isomerism in Transition Metal Complexes

OPTICAL ISOMERISM (STEREOISOMERISM) *octahedral complexes* Isomers that are non-superimposable mirror images of each other





Isomerism in Transition Metal Complexes





Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration that determines the geometry

2 - COORDINATION

Often found for Group 11 ions such as Cu⁺, Ag⁺ and Au⁺ and other d₁₀ metals such as Pt⁰; frequently with bulky ligands. **Geometry:** linear. **Symmetry:** $D_{\infty h}$





Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration which determines the geometry

3 - COORDINATION

Rarely found amongst metal complexes and requires bulky ligands. **Geometry:** trigonal planar. **Symmetry**: D_{3h} with three identical ligands.



13 [Pt(PCy₃)₃], Cy= cyclo-C₆H₁₁





Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration which determines the geometry

4 – COORDINATION – TWO POSSIBILITIES EXIST

Geometry: tetrahedral. **Symmetry**: T_d . This geometry is favoured over higher coordinate complexes when the metal is small or the ligands are large. Very common geometry and especially common with d⁵ and d metal complexes





Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration which determines the geometry

4 – COORDINATION – TWO POSSIBILITIES EXIST

Geometry: tetrahedral. **Symmetry**: T_d . This geometry is favoured over higher coordinate complexes when the metal is small or the ligands are large. Very common geometry and especially common with d⁵ and d metal complexes

Geometry: square planar. **Symmetry**: D_{4h} . This geometry is typically observed for d⁸ Group 10 metal complexes such as Pd⁰ or Pt⁰ or d⁹ Group 11 metal complexes, especially so for 2nd and 3rd row elements.





Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration which determines the geometry

5 – COORDINATION – TWO POSSIBILITIES EXIST

Geometry: trigonal bipyramidal. **Symmetry**: D_{3h} if all the ligands the same. This geometry is less common than 4- or 6-coordinate complexes. Distortions from this geometry are common. This geometry minimizes ligand-ligand repulsion



Berry Twist (Pseudorotation)

In the ¹³CNMR spectrum of Fe(CO)₅, only one signal is seen (204 ppm) despite the fact that there are two different environments for the carbonyls. The compound is **fluxional** because there is a low energy pathway which interconverts rapidly the two environments via a square pyramidal intermediate.



Coordination Geometry

For the main group, the Valence Shell Electron Pair Repulsion Theory works well and explains most geometries. For transition metals this is not the case and some geometries do not fit VSEPR theory. Often it is the d electron configuration which determines the geometry

5 – COORDINATION – TWO POSSIBILITIES EXIST

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Geometry: square pyramidal. **Symmetry**: C_{4v} if all the ligands the same. This geometry occurs when conformational constraints exist with multidentate ligands




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6 – COORDINATION – FIVE POSSIBILITIES EXIST

Geometry: Octahedral. **Symmetry**: *O*_h if all the ligands the same. This geometry is by far the most common for 6-coordination complexes. Octahedral complexes are highly symmetric.





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Distortions from this geometry lead to complexes of lower symmetry. These include tetragonal (D_{4h}) , rhombic (D_{2h}) , trigonal (D_{3d}) , trigonal prismatic (D_{3h})





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 $[Cu(OH_2)_6]^{2+} - d^9$

due to Jahn-Teller distortion

 Λ -Mn(acac)₃ – d⁴ HS

 d^4 high spin, d^7 low spin, d^9



tetragonal



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7 – COORDINATION – THREE POSSIBILITIES EXIST

Geometries: Pentagonal Bipyramidal, Capped Octahedron and Capped Trigonal Prism. These geometries are encountered mainly with larger cations – 4d and 5d complexes.





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Coordination Geometry



CH2501

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Coordination Number



Coordination Geometry

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HIGHER COORDINATION MODES EXIST



but we'll stop here



Hey How Do You Name These Compounds? Nomenclature of Coordination Compounds

CH2501 Step-by-step instructions – Just follow them in the right order

1. ORDER OF LISTING IONS – CATION FIRST THEN ANION

- [Cr(NH₃)₆][NO₃]₃ hexaamminechromium (III) nitrate
- K₂[PtCl₆] potassium hexachloroplatinate (IV)
- 2. NONIONIC COMPLEXES ARE GIVEN A ONE-WORD NAME
 - $[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)

3. NAMES OF LIGANDS – NEUTRAL LIGANDS ARE NAMED AS THE MOLECULE; NEGATIVE LIGANDS END

- IN O AND POSITIVE LIGANDS END IN IUM
 - $C_{5}H_{5}N$ pyridine
- Cl⁻ chloro
 NH₂NH₃⁺ hydrazinium

7. OXIDATION STATES – DESIGNATED

BY A ROMAN NUMERAL IN () AT THE

END OF THE NAME OF THE COMPLEX

- $(C_6H_5)_3P$ triphenylphosphine $CH_3CO_2^-$ acetato exceptions – H_2O = aqua; NH_3 = ammine
- 4. ORDER OF LIGANDS ALPHABETICAL
 - [Pt(NH₃)₄(NO₂)Cl]SO₄ tetraamminechloronitroplatinum (IV) sulfate
- 5. NUMERICAL PREFIXES GO BEFORE LIGAND TO INDICATE NUMBER (DI, TRI, TETRA ETC. BUT BIS, TRIS, TETRAKIS USED BEFORE COMPLEX NAMES
 - [Co(en)₂Cl₂]₂SO₄ dichlorobis(1,2-diaminoethane) cobalt (III) sulfate •
- 6. TERMINATION OF NAMES ANIONIC COMPLEXES END IN –ATE; OTHERWISE NOTHING SPECIAL
 - $Ca_{2}[Fe(CN)_{6}]$ calcium hexacyanoferrate (II) •
 - $[Fe(H_2O)_6]SO_4$ hexaaquoiron (II) sulfate •



Hey How Do You Name These Compounds? Nomenclature of Coordination Compounds

CH2501

Sample Problems

1. What is the formula of tetraamminebromochloroplatinum(IV) Chloride?

The central metal ion is written first, followed by the neutral ligands and then (in alphabetical order) by the negative ligands

Charge of the complex ion = charge of metal + total charge of ligands = $(4+) + [(4 \times 0) + (1 \times 1-) + (1 \times 1-) = 2+$

Therefore, we will need to Cl⁻ ions to balance the charge

[Pt(NH₃)₄BrCl]Cl₂

2. WHAT IS THE FORMULA OF HEXAAMMINECOBALT(III) TETRACHLOROFERRATE(III)?

This compound consists of two different complex ions.

The cation contains Co^{3+} and is $[Co(NH_3)_6]^{3+}$ and the anion contains Fe^{3+} and is is $[FeCl_4]^{-}$

Charge of the cation must balance the charge of the anion

[Co(NH₃)₆][FeCl₄]₃



Electronic Structure and Properties of Complexes: Crystal Field Theory

^{CH2501} Two theories are commonly used to rationalize electronic structure

- Crystal Field Theory (emerged from an analysis of the spectra of d-metal ions in the solid)
- Ligand Field Theory (emerged from an application of MO theory to d-metal complexes)

CFT Assumptions

- Complexes held together via electrostatic forces between the positively charged metal and the negatively charged or polarized ligands
- Models interactions based on electrostatics with the valence electrons of the metal in the d-orbitals and the ligands as negative charges (ion-ion interactions) or dipoles (ion-dipole) interactions (IONIC bonding model)
- Stronger interactions between electrons of the metal and the ligands result in greater destabilization
- The energy difference of d-orbitals correlates with the optical, magnetic and thermodynamic properties of the complex



Electronic Structure and Properties of Complexes: Crystal Field Theory









Electronic Structure and Properties of Complexes: Crystal Field Theory





Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex



- The energy difference between the two sets of orbitals is the crystal field splitting energy denoted Δ_0 (or $10D_q$)
- The e_g orbitals are raised in energy
- The t_{2g} orbitals are lowered in energy



Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties – A Refresher







Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties - $[Ti(H_2O)_6]^{3+}$





Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties - [Ti(H₂O)₆]³⁺



very very weak

Broad. $E_{abs} = \Delta_o$. Δ_o depends on the strength of the interaction between the d orbitals and the ligands. As the ligands vibrate, their distance from the metal center varies so that Δ_o will also vary. This means the energy of light absorbed will vary hence the broadness of the absorption.

Weak. As the absorptions are forbidden. The selection rule for electronic transitions is that $\bigotimes \Delta I = \pm 1$ (Laporte). So allowed transitions are: $I = 1: s \rightarrow p. p \rightarrow d \text{ or } I = -1: p \rightarrow s. d \rightarrow p$

Selection rules for Electronic Spectra of Complexes

1. $\Delta S = 0$ – The spin rule 2. $\Delta I = \pm 1$ – The orbital (Laporte Rule) Strictly true if molecule has a centre of symmetry

For a typical spin-allowed but Laporte forbidden transition in an octahedral complex, expect $\varepsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$.



Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties - [M(H₂O)₆]ⁿ⁺



If there is > 1 d electron, the spectra are complicated because of interactions between the electrons



Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties

 $[Mn(OH_2)_6]^{2+}$ is a d^5 high-spin octahedral complex with a **very** pale pink colour, owing to a series of weak spin-forbidden transitions (in addition to Laporte forbidden) – *notice magnitude of* ε !





Electronic Structure and Properties of Complexes: Crystal Field Theory – Octahedral Complex Optical Properties

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Electronic Structure and Properties of Complexes: Rules for Filling d orbitals

Rule 1: The Aufbau Principle: Electrons populate the lowest energy orbitals first

Rule 2: Hund's rule: Electrons occupy degenerate orbitals as to maximize the number of parallel spins

Rule 3: The Pauli exclusion principle: No two electrons can have all four quantum numbers the same. i.e. two electrons in the same orbital MUST have opposite spin





Electronic Structure and Properties of Complexes: Rules for Filling d orbitals

Electron configurations of high and low spin complexes

d electrons	High spin	Unpaired electrons	Low spin	Unpaired electrons
1	$t_{2g}^{1}e_{g}^{0}$	1	$t_{2g}^{1}e_{g}^{0}$	1
2	$t_{2g}^{2}e_{g}^{0}$	2	$t_{2g}^{2}e_{g}^{0}$	2
3	$t_{2g}^{3}e_{g}^{0}$	3	$t_{2g}^{3}e_{g}^{0}$	3
4	$t_{2g}^{3}e_{g}^{1}$	4	$t_{2g}^{4}e_{g}^{0}$	2
5	$t_{2g}^{3}e_{g}^{2}$	5	$t_{2g}^{5}e_{g}^{0}$	1
6	$t_{2g}^{4}e_{g}^{2}$	4	$t_{2g}^{6}e_{g}^{0}$	0
7	$t_{2g}^{5}e_{g}^{2}$	3	t2g ⁶ eg ¹	1
8	$t_{2g}^{6}e_{g}^{2}$	2	$t_{2g}^{6}e_{g}^{2}$	2
9	$t_{2g}^{6}e_{g}^{3}$	1	$t_{2g}^{6}e_{g}^{3}$	1
10	$t_{2g}^{6}e_{g}^{4}$	0	$t_{2g}^{6}e_{g}^{4}$	0

Note: There are two possibilities for d⁴⁻⁷, but only one for d^{1-3,8-10}.



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It all comes down to a balance between $\Delta_{\rm o}$ and the pairing energy, P (the energy required to pair two electrons in an orbital)

 $\Delta_{o} < P - high spin$ $\Delta_{o} > P - low spin$

For 1st row transition elements, P does not vary very much so it all comes down to Δ_o





Electronic Structure and Properties of Complexes: Rules for Filling d orbitals CFSE/LFSE

The CFSE of a complex provides an indication of the stability of a particular electron configuration

The CFSE is simply the sum of the energies of each electron plus any energy required to pair electrons

		d″	Example	N (high spin)	$LFSE/\Delta_0$	N (low spin)	LFSE/ Δ_0
Spherical Oc environment cr	Octahedral	d ^o		0	0		
	crystal field	d1	Ti ³⁺	1	0.4		
	e,	d²	V ³⁺	2	0.8		
d $\frac{\frac{3}{5}\Delta_0}{\frac{2}{5}\Delta_0}$		d³	Cr ³⁺ , V ²⁺	3	1.2		
		d4	Cr ²⁺ ,Mn ³⁺	4	0.6	2	1.6 <i>– P</i>
		d⁵	Mn ²⁺ , Fe ³⁺	5	0	1	2.0 - 2 <i>P</i>
	Δ_0	de	Fe ²⁺ ,Co ³⁺	4	0.4	0	2.4 – 2 <i>P</i>
	···¥·····	d7	Co ²⁺	3	0.8	1	1.8 <i>– P</i>
		d ⁸	Ni ²⁺	2	1.2		
		d ⁹	Cu ²⁺	1	0.6		
	* * t _{2g}	d ¹⁰	Cu ⁺ , Zn ²⁺	0	0		

* N is the number of unpaired electrons.



Electronic Structure and Properties of Complexes: Rules for Filling d orbitals CFSE/LFSE

It all comes down to a balance between Δ_0 and the pairing energy, P (the energy required to pair two electrons in an orbital)

 Δ_{o} < P – high spin Δ_{o} > P – low spin

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Electronic Structure and Properties of Complexes: Rules for Filling d orbitals LFSE – Real Life Consequences

Heat of hydration of metal ions $M^{2+}(s) + 6H_2O \rightarrow [M(OH_2)_6]^{2+} \Delta H_{hvdr}^{o}$ As ionic radius $I_{\Delta H_{hvdr}} \circ \uparrow$ As LFSE[↑]∆H_{hvdr}^o↑ 110 -Ca²⁺ 100 onic radius (pm) 90 Mn²⁺ Ti²⁺ 80 Cr²⁺ 1/2+ $7n^{2+}$ Fe²⁺ Cu²⁺ Co²⁻ 70 -Ni²⁺ 60 Increasing atomic number \rightarrow





Factors that determine magnitude of Δ_o :

1. The oxidation state of the metal

As the oxidation state increases, the attractive force between the ligands and the metal increases, which leads to a larger $\Delta_{\rm o}$

 $\Delta_{\rm o}$ for M²⁺: 7000-13 000 cm⁻¹ $\Delta_{\rm o}$ for M³⁺: 14 000-25 000 cm⁻¹

 $[V(H_2O)_6]^{3+}$ V(III) = d² ion $[V(H_2O)_6]^{2+}$ V(II) = d³ ion

violet light absorbed complex appears yellow yellow light absorbed complex appears violet





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 $\Delta_{\rm o} = 10\ 200\ {\rm cm}^{-1}$ for $[{\rm Co}^{\rm II}({\rm NH}_3)_6]^{2+}$ and 22 870 cm⁻¹ for $[{\rm Co}^{\rm III}({\rm NH}_3)_6]^{3+}$ $\Delta_{\rm o} = 32\ 200\ {\rm cm}^{-1}$ for $[{\rm Fe}^{\rm II}({\rm CN})_6]^{4-}$ and 35 000 cm⁻¹ for $[{\rm Fe}^{\rm III}({\rm CN})_6]^{3-}$



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2. The row of the metal

As you go down the periodic table the orbitals become more diffuse, which results in greater interactions with the ligands and larger Δ_0 AND the electrons are further away from each other leading to smaller P

For all 2nd and 3rd row complexes $\Delta_o > P$ and are low spin





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In groups, heavier analogues have larger Δ . For hexaammine complexes $[M^{III}(NH_3)_6]^{3+}$:

 $\Delta_{\rm o}$ = 22 870 cm⁻¹ (Co) $\Delta_{\rm o}$ = 34 100 cm⁻¹ (Rh) $\Delta_{\rm o}$ = 41 200 cm⁻¹ (Ir)



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For all 2nd and 3rd row complexes $\Delta_0 > P$ and are low spin 3. The nature of the ligand – the spectrochemical series



- ✓ All CN⁻ complexes are low spin
- ✓ All F⁻ complexes for 1^{st} row metals are high spin
- \checkmark Water complexes for 1st row are usually high spin

$$\begin{split} &\Delta_{\rm o} = 13\ 640\ {\rm cm^{-1}}\ [{\rm CrCl}_6]^{3-} \\ &\Delta_{\rm o} = 15\ 060\ {\rm cm^{-1}}\ [{\rm CrF}_6]^{3-} \\ &\Delta_{\rm o} = 17\ 830\ {\rm cm^{-1}}\ [{\rm Cr}({\rm OH}_2)_6]^{3+} \\ &\Delta_{\rm o} = 21\ 680\ {\rm cm^{-1}}\ [{\rm Cr}({\rm NH}_3)_6]^{3+} \\ &\Delta_{\rm o} = 26\ 280\ {\rm cm^{-1}}\ [{\rm Cr}({\rm CN})_6]^{3-} \end{split}$$

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Strong ∆_{oct} High energy, violet light absorbed Complex: yellow



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For all 2nd and 3rd row complexes $\Delta_o > P$ and are low spin

3. The nature of the ligand – the spectrochemical series




Electronic Structure and Properties of Complexes: Rules for Filling d orbitals Low Spin or High Spin ?

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Electronic Structure and Properties of Complexes: Rules for Filling d orbitals

Low Spin or High Spin ? – Magnetic Moment

Why is it called low spin and high spin?

It comes from the spin only magnetic moment (μ) differences between the two electronic configurations.

 μ is a measure of the number of unpaired electrons (gives rise to paramagnetism).

Diamagnetism occurs for all compounds. It is associated with <u>pairs of electrons</u> and is a weak effect in which the compound is repelled by a magnetic field.

Paramagnetism occurs only when there are <u>unpaired</u> <u>electrons</u>. It is a larger effect than diamagnetism and electrons are attracted into a magnetic field.



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Electronic Structure and Properties of Complexes: Rules for Filling d orbitals Low Spin or High Spin ? – Magnetic Moment

It is possible to measure μ by comparing the mass difference of a sample weighed outside and within a magnetic field.

Normally what is measured is the molar magnetic susceptibility, X_m by comparison with a standard sample, which is usually Hg[Co(SCN)₄]₂

 μ = 2.83(X_mT)^{1/2}

 μ is based on the overall spin quantum number, **S** (S = n/2, where n = number of unpaired e⁻) and the overall angular momentum quantum number, **L**

 μ_{S+L} = [4S(S+1) + L(L+1)] ^{1/2}

For 1st row transition metal complexes L is very small and so the second term can be ignored

 $\mu = [4S(S+1)]^{\frac{1}{2}} = [n(n+2)]^{\frac{1}{2}}$ with units of Bohr Magnetons (BM)

Gouy Balance





Electronic Structure and Properties of Complexes: Rules for Filling d orbitals

Low Spin or High Spin ? – Magnetic Moment

 $\mu = [4S(S+1)]^{\frac{1}{2}} = [n(n+2)]^{\frac{1}{2}}$ with units of Bohr Magnetons (BM)

This calculation applies to all geometries for all complexes

Comparison of calculated spin-only magnetic moments with experimental data for some octahedral complexes

Ion	Config	μ _{so} / B.M.	μ _{obs} / B.M.
Ti(III)	$d^1 (t_{2g}^{1})$	√3 = 1.73	1.6-1.7
V(III)	$d^{2}(t_{2g}^{2})$	$\sqrt{8} = 2.83$	2.7-2.9
Cr(III)	$d^3 (t_{2g}^{3})$	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin $(t_{2g}^3 e_g^1)$	$\sqrt{24} = 4.90$	4.7-4.9
Cr(II)	$d^4 \log spin(t_{2g}^4)$	$\sqrt{8} = 2.83$	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin $(t_{2g}^3 e_g^2)$	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	$d^5 \log spin(t_{2g}^5)$	$\sqrt{3} = 1.73$	1.8-2.1
Fe(II)	d^6 high spin $(t_{2g}^4 e_g^2)$	$\sqrt{24} = 4.90$	5.1-5.7
Co(III)	$d^6 \log spin(t_{2g}^6)$	0	0
Co(II)	d^7 high spin $(t_{2g}^5 e_g^2)$	$\sqrt{15} = 3.88$	4.3-5.2
Co(II)	$d^7 \log spin(t_{2g}^6 e_g^{-1})$	√3 = 1.73	1.8
Ni(II)	$d^{8}(t_{2g}^{6}e_{g}^{2})$	$\sqrt{8} = 2.83$	2.9-3.3
Cu(II)	$d^9 (t_{2g}^6 e_g^3)$	√3 = 1.73	1.7-2.2

For octahedral complexes fit is good except for high spin d⁶ and d⁷ and low spin d⁴ and d⁵ For tetrahedral complexes fit is good except for d³, d⁴, d⁸ and d⁹



Electronic Structure and Properties of Complexes: Octahedral Example Bringing it all together

Question: For the complex ion $[Fe(CI)_6]^{3-}$ determine the number of d electrons for Fe, sketch the d-orbital energy levels and the distribution of d electrons among them, list the number of lone electrons, and label whether the complex is paramagnetic or diamagnetic

Step 1: Determine the oxidation state of Fe.

Here it is Fe^{3+} (each Cl^{-1} counts for -1). \therefore Fe^{3+} has **5 d-electrons**.

Step 2: Determine the geometry of the ion.

Here it is an octahedral which means the energy splitting should look like:

Step 3: Determine whether the ligand induces is a strong or weak field spin by looking at the spectrochemical series. Cl^{-} is a weak field ligand $d_{x^{2}-y^{2}} = \frac{d_{z^{2}}}{d_{z^{2}}}$

Step 4: Count the number of lone electrons. Here, there are 5 electrons

Step 5: The five unpaired electrons means this complex ion is paramagnetic $\mu = [n(n+2)]^{\frac{1}{2}} = [5(5+2)]^{\frac{1}{2}} = 35^{\frac{1}{2}}$





Electronic Structure and Properties of Complexes: Octahedral Complexes The Irving-Williams Series

The Irving-Williams Series (IWS) describes an empirical increase in stability of HS M²⁺ octahedral complexes as a function of atomic radius, regardless of the nature of L for the following reaction:

 $[M(H_2O)_n]^{2+} + L \iff [M(H_2O)_{n-1}L]^{2+} + H_2O$

 K_{f} varies along: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$



Trends in Atomic Radius



Electronic Structure and Properties of Complexes: Octahedral Complexes The Irving-Williams Series

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reflects electrostatic effects smaller metal with same charge = greater charge density

Based purely on electrostatics we would expect stabilities to vary as $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} > Cu^{2+} > Zn^{2+}$

Exception: Cu²⁺ is actually more stable than Ni²⁺ and this is due to the <u>Jahn Teller Distortion</u>





Electronic Structure and Properties of Complexes: Crystal Field Theory – Tetrahedral Complex





The dz² and dx²-y² point towards the centres of the faces of the cube The dxy, dxz, and dyz all point towards the centres of the edges of the cube. **No** orbitals point directly at ligands, however d_{xy} , d_{xz} and d_{yz} interact more strongly.

Why is Δ_t less than Δ_o ?

- \checkmark There are four ligands rather than six smaller electrostatic effect
- \checkmark The ligands do not point at any of the orbitals smaller electrostatic effect



The dz² and dx²-y² point towards the centres of the faces of the cube The dxy, dxz, and dyz all point towards the centres of the edges of the cube. **No** orbitals point directly at ligands, however d_{xy} , d_{xz} and d_{yz} interact more strongly.

When to expect tetrahedral geometry?

- ✓ Ligands are large and so less ligand-ligand repulsion $[MX_4]^{n-}$ (X = I, Br) and so smaller Δ_t
- ✓ metal ions with zero CFSE (d⁰, d⁵, d¹⁰) or small CFSE (d¹, d², d⁶ and d⁷)
 e.g., [MnO₄]⁻ (d⁰), [FeCl₄]⁻ (d⁵, h.s.), [CoCl₄]²⁻ (d⁷, h.s.), [ZnCl₄]²⁻ (d¹⁰)





*N is the number of unpaired electrons





Ε

Occurs when you can asymmetrically fill orbitals that are degenerate in a non-linear complex. The geometry of the complex then distorts to reach a more stable electronic configuration



High spin d⁴ $t_{2g}^{3}e_{g}^{1}$ Low spin d⁷ $t_{2g}^{6}e_{g}^{1}$ or d⁹ $t_{2g}^{6}e_{g}^{3}$

Let's look at the case for LS $d^9 t_{2g}^{6} e_{g}^{3}$

If there are 2e in d_{z2} and 1e in d_{x2-y2} then greater repulsion along the z-axis \therefore elongation of these M-L bonds along the z-axis to compensate, leading to stabilization of the d_{z2} orbital – most common distortion







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If there are 2e in d_{x2-y2} and 1e in d_{z2} then greater repulsion along the xy-plane

: effective compression of the M-L bonds along the z-axis to compensate, leading to stabilization of the d_{x2-y2} orbital



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Occurs when you can asymmetrically fill orbitals that are degenerate in a non-linear complex. The geometry of the complex then distorts to reach a more stable electronic configuration

Jahn-Teller Theorem

"Any non-linear molecular system in a degenerate electronic state will be unstable and will distort to form a system of lower symmetry and lower energy, thereby removing the degeneracy"



High spin d⁴ $t_{2g}^{3}e_{g}^{1}$ Low spin d⁷ $t_{2g}^{6}e_{g}^{1}$ or d⁹ $t_{2g}^{6}e_{g}^{3}$

Let's look at the case for LS $d^9 t_{2g}^{6} e_{g}^{3}$





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Let's look at the case for LS $d^9\,t_{2g}{}^6e_g{}^3$

Important Facts about JT Distortions

- The JT theorem does not predict the type of distortion
- The JT theorem applies to all non-linear complexes where there is degeneracy of the electronic configurations
- There are ONLY 5 non-degenerate octahedral configurations
- For JT distortion in octahedral complexes the distortions are normally more pronounced if the degeneracy occurs in the e_g orbitals
- The driving force for the distortion is to stabilize the system



Electronic Structure and Properties of Complexes: Crystal Field Theory – Square Planar Complex

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Electronic Structure and Properties of Complexes: Crystal Field Theory – Square Planar Complex

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Square planar geometry: the limiting case of tetragonal elongation





Electronic Structure and Properties of Complexes: Crystal Field Theory – Square Planar Complex

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Square planar geometry: the limiting case of tetragonal elongation



d⁸ complexes are frequently square planar as extra stabilization of $\Delta_{\rm o}$

d⁸ complexes are frequently 16 electron complexes



here a 2nd row element already generates a strong field and so the complex is square planar



Electronic Structure and Properties of Complexes: Crystal Field Theory – Overview

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Figure 2 Crystal field splittings of d orbitals



Electronic Structure and Properties of Complexes: Crystal Field Theory Limitations & MO (LFT) Theory



Questions for which Crystal Field Theory has no answers:

- Why is KMnO₄ with Mn⁷⁺ and no d-electrons coloured?
- Why is OH⁻ a weaker field ligand that H₂O?
- Why are neutral ligands like CO, which are otherwise very poor Lewis bases such strong field ligands?
- Why in EPR spectra of high spin complexes is there hyperfine splitting, indicating that the spin is delocalized onto the ligands?





First Let's Start with MO Theory





Molecular Orbital Theory (MO Theory)

^{thews} MO theory considers the **entire molecule** and not in terms of isolated electron pairs.

CH2501 MO theory answers why specific molecules adopt specific shape and have specific reactivity

Consequence: An electron pair can be bonding/non-bonding/anti-bonding over more than 2 nuclei.

- Electrons are considered as a standing matter wave in the potential field set up by all the nuclei that make up the molecule.
- There are finite mathematical solutions to these standing matter waves (known as wavefunctions). What this means is that they can only assume certain shapes, that we know as <u>molecular orbitals</u>.

A molecular orbital (MO) is composed of a linear combination of atomic orbitals (LCAO)





Out of phase









MO Theory: Things You Need To Know

The total number of MOs = total number of contributing AOs



The shape and phasing of the orbitals (symmetry considerations)
 i.e., only AOs with the correct symmetry can combine to form MOs,. The greater the overlap in shape, the stronger will be the interaction.





MO Theory: Things You Need To Know

- The total number of MOs = total number of contributing AOs
- 1**+1**=2
- The shape and phasing of the orbitals (symmetry considerations)
 i.e., only AOs with the correct symmetry can combine to form MOs,. The greater the overlap in shape, the stronger will be the interaction.
- ✓ The relative energies of the orbitals (obtained from quantum mechanical calculations)
 i.e., the closer two sets of orbitals are in energy, the stronger will be the interaction





MO Theory: Things You Need To Know

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MO Theory: Things You Need To Know

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The shape and phasing of the orbitals (symmetry considerations) i.e., only AOs with the correct symmetry can combine to form MOs,. The greater the overlap in shape, the stronger will be the interaction.



Bond Order (BO) provides an indication between the strength and length of a bond and serves as a connection between formal Lewis structures, where the number of shared electron pairs is used to indicate single, double or triple bond.

BO = (number of bonding electrons – number of antibonding electrons)/2

For H₂ the BO = 1, [(2-0)/2], (and so there is a single σ bond between H-H) For He₂ the BO = 0, [(2-2)/2] (and so there is no bond between He-He)

1 + 1 = 2



MO Theory: Things You Need To Know

The total number of MOs = total number of contributing AOs



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 i.e., only AOs with the correct symmetry can combine to form MOs,. The greater the overlap in shape, the stronger will be the interaction.
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The MO Diagram for a Generic Diatomic Molecule (A₂) from the 2nd Period

^{CH2501} This diagram is really only useful for O₂ and F₂, where s and p orbitals are more than 12 eV apart and do not interact with each other



e.g., O₂



Here the 2s and $2p_z$ orbitals are closer in energy (though not evident in the figure) and "mix", resulting in a much destabilized $3\sigma_g$ MO.

You have already heard of this concept in CH1601 – it is called hybridization! 140



The MO Diagram for a Generic Diatomic Molecule (A₂) from the 2nd Period When s and p Orbitals Mix

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Lewis Structure of O₂ vs MO Picture of O₂



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o=o or o-o A B

Based on the preceding rules, we would conclude that structure **A** is correct BUT

The Lewis structure neglects the spin of the electrons and structure B is more accurate

A Molecular Orbital (MO) picture would better describe the true nature of bonding in O_2

- 12 valence e⁻s
- This picture obeys Hund's rule
- The result is that O₂ has 2 unpaired e⁻s
- O₂ is in the Triplet state & is paramagnetic (i.e. attracted to magnetic field)
- As a diradical, O₂ is very reactive (combustion!)
- The O-O bonding O₂ is 1.208 Å, much shorter than is typical (in H₂O₂ it is around 1.48 Å)
- The BDE of O₂ is 494 kJ/mol





Ε

The MO Diagram for a Generic Diatomic Molecule (A₂) Global Trends

Mixing results in a change-over of the energetic ordering of the HOMO/LUMO between N_2 and O_2 .





The MO Diagram for a Generic Diatomic Molecule (A₂) Global Trends



Ε

Are O_2^+ or N_2^+ diamagnetic or paramagnetic, and what is the bond order? **Recall: BO** = (number of bonding electrons-number of antibonding electrons)/2




The MO Diagram for a Generic Diatomic Molecule (A₂) Global Trends

Mixing results in a change-over of the energetic ordering of the HOMO/LUMO between N_2 and O_2 .





The Mixing of MOs is Quite General

We have so far looked at σ and π bonds. MO's can of also be formed by using d orbitals giving rise to σ , π and δ (delta) bonds





Let Us Now Look at a Heteronuclear Case: H-F

- F is so much more electronegative that its AOs are much lower in energy
- The 1s orbital of H can only mix with the 2p orbitals of F
- Only one combination: H(1s) with F(2p_z) is symmetry allowed
- As well, as it is F there is no mixing between its s and p orbitals ($\Delta E(2s-2p) > 12 \text{ eV}$)



















Beyond Diatomic Systems

- The LCAO concept can be applied to polyatomic molecules
- Symmetry analysis by group theory required to figure out which MO combinations are bonding, non-bonding and anti-bonding
- The energy of the MOs is measured by **P**hoto**E**lectron **S**pectroscopy, which measures ionization energy (i.e. energy it takes to eject an electron) or is estimated by computations (more on this later on in the atmospheric chemistry section of the course)





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Beyond Diatomic Systems: BeH₂

- This is a linear molecule where bonding will only occur along z-axis
- So Be2p_x and Be2p_y will only yield non-bonding interactions
- We can elongate our MO picture for H_2 and "insert" our Be







Beyond Diatomic Systems: H₂O



non-bonding interactions

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Beyond Diatomic Systems: H₂O

This is a bent molecule

So only O2p_y will yield non-bonding interactions

• We can elongate our MO picture for H₂ and "insert" our O





 $\Psi_{\rm A}$ interacts with O2s and O2p_z resulting in one bonding, one anti-bonding and one non-bonding interactions

Beyond Diatomic Systems: H₂O



 $\Psi_{\rm A}$ interacts with O2s and O2p_z resulting in one bonding, one anti-bonding and one non-bonding interactions



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Beyond Diatomic Systems: O₃

 O_3 has a bent geometry like H_2O and so MOs describing σ framework should be very similar





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Beyond Diatomic Systems: O₃

 O_3 has a bent geometry like H_2O and so MOs describing σ framework should be very similar





Back to Ligand Field Theory

Electronic Structure and Properties of Complexes: LFT Theory

What is Ligand Field Theory?

It is:

- A semi-empirical theory that applies to a <u>class of substances</u> (transition metal complexes)
- A language in which a vast number of experimental observations can be rationalized and discussed
- A model that applies only to a restricted part of reality

It is not:

- An *ab initio* theory that lets one predict the properties of a compound
- A physically rigorous treatment of the electronic structure of transition metal complexes



Electronic Structure and Properties of Complexes: LFT Theory

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Sigma (σ) bonding

- Neutral ligands (e.g., NH₃) or anionic ligands (e.g., F⁻) possess lone pairs that can bond to metal-based orbitals (s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{x2-y2}, d_{z2}) with σ-symmetry
- In an O_h complex, 6 symmetry-adapted linear combinations (SALCs) of the 6 ligand σ -symmetry orbitals can be formed
- MOs for the resulting complex are formed by combining the ligand SALCs and the metalbased d-orbitals of the same symmetry type
- With 6 SALCs combined with the metal MOs, we will get 6 bonding and 6 antibonding MOs – now called ligand group orbitals (LGOs)
- The resulting MO diagram now gets populated with the electrons according to the Aufbau process, Pauli exclusion principle and Hund's rule



Sigma (σ) bonding: Simple example showing interaction of ligand s-orbitals with metalbased orbitals





Sigma (σ) bonding: Simple example showing interaction of ligand s-orbitals with metalbased orbitals





not proper symmetry so <u>no</u> interaction



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Sigma (σ) bonding:

- For most ligands, their SALCs are lower in energy than the metal-based d-orbitals
- Therefore the 6 bonding MOs of the complex will be mostly ligand-based in character
- The d-electrons of the metal will occupy the *same* orbitals as in CFT
- Unlike CFT, the t_{2g} orbitals are non-bonding and the e_g orbitals are anti-bonding





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Example

Take $[Co(NH_3)_6]^{3+}$ NH₃ can σ -bond through its lone pair

To summarize:

- Of 9 valence orbitals (5x d, 3x p, 1x s) only 6 are suitable for σ-bonding
- The Δ_0 here is the same as in CFT
- Co³⁺ is d⁶ and there are 12e⁻ from the 6 NH₃ ligands
- As this is a diamagnetic LS complex, the
 6-d electrons occupy only the t_{2g} set





Pi (π) bonding:

- The previous MO diagram ignores π bonding. If the ligands possess orbitals of local πsymmetry then these can interact with the metal d-orbitals with the same symmetry (i.e. the t_{2g} set) to form new LGOs
- These ligand SALCs can act as electron donors (populated) or electron acceptors (vacant)





Pi (π) bonding:

- The previous MO diagram ignores π bonding. If the ligands possess orbitals of local πsymmetry then these can interact with the metal d-orbitals with the same symmetry (i.e. the t_{2g} set) to form new LGOs
- These ligand SALCs can act as electron donors (so populated) or electron acceptors (vacant)
- The nature of this secondary interaction will affect $\Delta_{o_{ML_e}}$













 t_{2g} and e_{g}

Pi (π) donor ligands: (aka π -bases)

Example Take [FeCl₆]³⁻

Cl can σ -bond through its lone pair AND π -bond through its p-orbitals



The Cl⁻ p orbitals can now interact with the Fe t_{2g} , which are destabilized

These complexes are now largely high spin











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Electronic Structure and Properties of Complexes: LFT Theory – Octahedral Complexes

t_{2g}

Pi (π) acceptor ligands: (aka π -acids)

Example Take $[Cr(CO)_6]$

CO can σ -bond through its lone pair on C AND π -bond through its p-orbitals AND its π^* orbitals can form bonding interactions with metal d orbitals







Electronic Structure and Properties of Complexes: Crystal Field Theory Limitations & MO (LFT) Theory

Summary: π -bonding and π -backbonding modulate the energy of the metal t_{2g} orbitals





The Law in Transition Metal Chemistry: The 18 electron Rule



It's like the octet rule for inorganic chemists As with many laws, not always obeyed

NEUTRAL (COVALENT) METHOD

- We remove all the ligands from the metal and associate the electrons of the bonds being broken to the ligands in order to make them neutral (So NMe₃ is a 2e⁻ donor and CH₃ is viewed as a radical 1e⁻ donor)
- 2. We count the d-electrons of the metal, taking into account which group it is in, plus the electrons for each of the ligands as well as the charge of the overall complex

IONIC METHOD (MY FAVOURITE)

- 1. We remove all the ligands from the metal and associate the electrons of the bonds being broken with the ligand (so CO and NMe₃ are a 2e⁻ donors, Cl⁻ is an ionic 2e⁻ donor)
- 2. We increase the oxidation of the metal to compensate for the added electrons in order to maintain charge neutrality
- 3. We count the d-electrons of the metal plus the electrons for each of the ligands as well as the charge of the overall complex



The Law in Transition Metal Chemistry: The 18 electron Rule - Examples

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2e

8e

<u>8e</u>

18

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The Law in Transition Metal Chemistry: The 18 electron Rule - Examples

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W(0)	d6
Cp ⁻	6e-
NO ⁺	2e-
PR ₃	2e-
<u>co</u>	<u>2e-</u>
Total	18 e-

 $[AuCl_2Ph_2]^- (Ph = C_6H_5)$ $Au(+3) \quad d8$ $2Ph^- \quad 4e 2Cl^- \quad 4e Total \quad 16 e-$


Descriptive Chemistry of Transition Elements

The Period 4 transition metals



Scandium, Sc; 3B(3)



Titanium, Ti; 4B(4)



Vanadium, V; 5B(5)



Chromium, Cr; 6B(6)



Manganese, Mn; 7B(7)



Iron, Fe; 8B(8)



Cobalt, Co; 8B(9)



Nickel, Ni; 8B(10)



Copper, Cu; 1B(11)



Zinc, Zn; 2B(12)

Descriptive Chemistry of Transition Elements



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titanium(IV) oxide sodium chromate

potassium nickel(II) nitrate zinc ferricyanide hexahydrate hepta

zinc sulfate heptahydrate







Decreasing enthalpy

Descriptive Chemistry of Transition Elements

Increasing electronegativity

f cation	21 S c	22 Ti	23 V	24 C r	25 Mn	26 Fe	27 C o	28 Ni	29 C u	30 Zn	
ation o	39 Y	40 Z r	41 Nb	42 Мо	43 Тс	44 Ru	45 Rh	46 P d	47 Ag	48 C d	
of hydr.	57 La	72 Hf	73 Ta	74 W	75 R e	76 Os	77 Ir	78 Pt	79 Au	80 Hg	

Decreasing enthalpy of hydration of cation

electronegativ

Increasing



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photocatalyst



Global market: > 5.1 M metric tonnes



Descriptive Chemistry of Transition Elements: Titanium (Ti)

 TiX_4 (X = F, Cl, Br, I)

Compound	Colour	Mp (°C)	Bp (°C)
TiF ₄	white	284	
TiCl ₄	colourless	-24	136.5
TiBr ₄	orange	38	233.5
Til ₄	violet black	155	377

These are very Lewis acidic tetrahedral d⁰ complexes Why is there colour?



LMCT from ligand p orbital to metal e^{*} orbital (d_{x2-y2} or d_{z2}) As this is a p \rightarrow d transition ($\Delta I = 1$) it is allowed and colour is intense





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 $\text{TiCl}_4 + 4 \text{ H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{ HCl}$





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Ti + HCl → $[TiCl_n(OH_2)_{6-n}]^{(3-n)+}$ average n ~3





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Ti^{IV}

Sharpless Asymmetric Epoxidation









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vanadinite, Pb₅[VO₄]₃Cl



Andrés Manuel del Río discovered vanadium in New Spain (Mexico), which he first named panchromium, then renamed erythronium, in 1801



World vanadium manufacturers produced around 61 000 tonnes in 2011 and rising at 3% pa









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oxo ligand good π donor

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3d⁰ but colour comes from LMCT



oxo ligand good π donor



³d⁰ but colour comes from LMCT

VIV

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The V=O bond is weakened by coordination of the pyridine because the higher electron density on the V atom reduces the extent of π -donation

VF₄ is stable, VBr₄ is stable <-20 °C VI₄ not known. VCl₄ covalent oil decomposes to VCl₃ + $\frac{1}{2}$ Cl₂







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VII

 $[V(OH_2)_6]^{2+}$ (3d³) strong enough reducing agent to reduce water to hydrogen, but slow.





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3d⁵4s¹ – Extra stability from half filled shell of d electrons

- Cr⁰ makes steel "stainless", which is its biggest application
- Cr is also combined with other metals to make them hard, shiny and chemically resistant

	In Acidic, solu	Aqueous tion	In Alkali Solution		
Oxidation State	Colour Ion		Colour	lon	
+2	Blue	Cr2+			
+3	Green	Cr ^a *	Green	[Cr(OH) ₆] ³	
+6	Orange	Cr ₂ O ₇ 2	Yellow	CrO4	



These colours arise mainly from Laporte allowed MLCT transitions





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Cr^{VI}

- Cr^{VI} (3d⁰) complexes are very strong oxidizing agents (Jones reagent $CrO_3 + H_2SO_4$)
- [Cr₂O₇]²⁻ oxidizes NH₄⁺ to NO₂ and H₂O with most of the O coming from the metal it is reduced to Cr³⁺.
- Cr^{VI} is extremely toxic (hexavalent chromium Erin Brockovitch)





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Cr^{III}

Cr^{III} (3d³) is usually found as green CrCl₃·6H₂O. This dissolves in water to give dark green solution, which slowly hydrolyses to a pale purple solution





OH₂

OH₂

/n/Hg H₂O.

 H_2O

blue

OH₂

12

 H_2O

H₂O

violet

2+

NaOAc

δ

 $\overline{\mathbf{o}}$

H₂O-Ci

red

d_{xv} from each orbital

2 x π d_{xz} or d_{yz} from each metal

dz2 from each metal







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Cr^{II}

• Very unusual but can be made by reduction of Cr^{VI} or Cr^{III}





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Cr⁰

3d⁶ complexes that are stabilized with good acceptor ligands and obey 18e⁻ rule
 [Cr(CO)₆] is very stable as is [Cr(C₆H₆)₂] and the piano stool complex [Cr(C₆H₆)CO₃]



 η^6 bonding!



3d⁵4S² with complexes exhibiting the widest range of oxidation states – Mn^{VII} – Mn^{-III} commonest are +7, +4 and +2.



Descriptive Chemistry of Transition Elements: Manganese (Mn)

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Mn^{VII} and Mn ^{VI}

MnO₄⁻ deep purple because of LMCT. Strong oxidizing agent



MnO₄⁻ Slowly decomposes in acid solution so fresh solutions must be made up for titrations
 4MnO₄⁻ + 4H⁺ → 3O₂ + 2H₂O + MnO₂

- Reacts with strong alkali $4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + H_2 + O_2$
- MnO_4^{2-} disproportionates in acid $3Mn^{VI}O_4^{2-} + 4H^+ \rightarrow 2Mn^{VII}O_4^{-} + Mn^{IV}O_2 + 2H_2O$









Descriptive Chemistry of Transition Elements: Manganese (Mn)²⁰⁸

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 Mn^{V} and Mn^{V}

- Mn^{V} is $3d^{2}$ is rare but stable form in fused NaOH. MnO_{4}^{3-} is blue
- Mn^{IV} is $3d^3$. MnO_2 is the most common oxide of Mn and is an oxidizing agent $MnO_2 + 4HCl \rightarrow [Mn(OH_2)_6]^{2+} + 2Cl^- + Cl_2 + H_2O$

Mn^{III} and Mn ^{II}

- Mn^{III} is 3d⁴ is rare and disproportionates to MnO₂ + Mn^{II}
 It can form in air: [Mn(OH₂)]²⁺ + 2OH⁻ → Mn(OH)₂ pink precipitate Mn(OH)₂ + O₂ → MnO(OH) brown (rapid)
- Mn^{II} is 3d⁵. Derives extra stability from half-filled shell

1 1absorptions are Laporte forbidden so are weak

No difference in CFSE for O_h or T_d
 e.g [Mn(DMSO)₆]²⁺[MnCl₄]²⁻





Low oxidation state Mn

Since Mn has an odd number of electrons, Mn(CO)_n cannot form as an 18e⁻ complex. • Stable carbonyl is $[Mn_2(CO)_{10}]$





Descriptive Chemistry of Transition Elements: Iron (Fe)

- Fe 3d⁶4s². Abundant (4th most) and cheap (though used to be 8x more than gold!)
- It has been used for more than 6000 years
- Has a wide number of oxidation states from Fe²⁻ to Fe⁶⁺



Heme



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Fe^{VI} and Fe^{III}

- Fe^{VI} 3d². [Fe^{VI}O₄]²⁻ + heat gives [Fe^VO₄]³⁻ + O₂, showing strongly oxidising nature of Fe^{VI}
- Fe^{III} 3d⁵. High spin complex. Weak absorption as $\Delta I = 0 [Fe(OH_2)_6]^{3+}$ is pale violet

















е



Descriptive Chemistry of Transition Elements: Cobalt (Co)

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Cobalt Demand Segments



Brazil: 4%

Canada: 13%

China: 17%


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Co^{III}

- 3d⁷4s². Co^{III} and Co^{II} are the only really important oxidation states (OS range from Co⁻³ Co⁴)
- Co^{III} is 3d⁶. [Co(OH₂)₆]³⁺ is a rare example of a low spin aqua complex in the 1st row. It oxidizes water slowly to O₂
- Co^{III} low spin complexes are generally inert due to high CFSE









Co^{II}

Co^{II} is 3d⁷. Tetrahedral complexes are quite common, especially [CoX₂]²⁻ (X = F, Cl, Br, I) as there is not such a big difference in CFSE between O_h and T_d

 $[\operatorname{Co}(\operatorname{OH}_2)_6]^{2+} + 4 \operatorname{Cl}^- \rightarrow [\operatorname{Co}\operatorname{Cl}_4]^{2-} + 6 \operatorname{H}_2\operatorname{O}$





In both cases there is an orbital contribution to μ due incompletely filled t_{2g} orbitals (Recall: μ_{S+L} = [4S(S+1) + L(L+1)]^{1/2})



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Co⁰

- Co⁰ is 3d⁹. Rare examples and formed with strong field π -acid ligands
- These can be used as catalysts for alkene hydroformylation or the Pauson Khand reactions





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- Ni 3d⁸4s². Second most abundant metal after Fe
- It is corrosion resistant and used in stainless steel



"kupfernickel" or "goblin's copper"



Estimated first use of nickel, 2013e





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Ni^{II}

- Ni^{II} is 3d⁸. Main oxidation state of Ni
- Octahedral: small weak field ligands, including water, usually pale green or blue 2 unpaired electrons μ_{eff} = 2.83
- Tetrahedral: large ligands especially negative, dark blue or green 2 unpaired electrons μ_{eff} = 3.05-4.00
- Square planar strong field ligands, usually yellow or red diamagnetic



[Ni(PPh₃)₂Br₂] green paramagnetic, tetrahedral

[Ni(PMe₃)₂Cl₂] red, diamagnetic, square planar

Square planar to tetrahedral

yellow

diamagnetic square planar





paramagnetic square pyramidal

blue

Square planar to octahedral

Can change geometry •

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Nill

Descriptive Chemistry of Transition Elements: Nickel (Ni)



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Ni⁰

- Ni⁰ is 3d¹⁰. [Ni(CO)₄] is tetrahedral
- It is an intermediate in the Mond process for the purification of Ni very toxic





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- Cu 3d¹⁰4S¹. People have been using copper for at least 11 000 years
- Cu is second to Ag in electrical conductance
- Very corrosion resistant
- Cu too soft so incorporate into alloys like brass (with Zn) or bronze (with Sn)







•

Cu^{ll} is 3d⁹. Jahn Teller distortion always occurs $[Cu(H_2O)_4]^{2+}$ OH_2 72+Cu(OH)₂ pale blue ______ $[Cu(H_2O)_2Cl_2]^{2+}$ ÔH₂ CuSO₄.Cu(OH)₂ $Cu(en)_2(H_2O)_2]^{2+}$ NH_{3(aq)} greeny blue [OH-] Cu in xs [Cu(H₂O)₆]²⁺ blue $[CuCl_4]^{2-}$ $CuI + \frac{1}{2}I_2$ [OH]xs Cl-Br-Cu(OH)₂ CNblue $[CuX_4]^{2-}$ yellow tetrahedral CN [Cu(CN)4]2-[Cu(CN)₄] Cu(CN)2 tetrahedral All 6 coordinate are Jahn-Teller NC-CN distorted

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Descriptive Chemistry of Transition Elements: Copper (Cu)

Cu^I

• Cu^l is 3d¹⁰. Complexes are often linear and usually colourless





Typical colours of transition metal salts in water

OS	Ti	V	Cr	Mn	Fe	Со	Ni	Cu
3	purple	green	Green	Brown	pale	brown		
				(MnOOH)	violet			
					or			
					brown			
2		lilac	royal blue	Colourless	pale	pink	Green	blue
				(v pale pink)	green		Red/	
							yellow	
Other	colourless	Pale	yellow	purple				Colourless
	(Ti ^{IV})	yellow	[Cr ^{VI} O ₄] ²⁻	[Mn ^{∨ii} O ₄]⁻				(Cu ⁱ)
		[V ^v O ₂] ⁺	orange	Green				
		royal	[Cr ^{VI} 2O7] ²⁻	[Mn ^{∨i} O₄]²⁻				
		blue		Blue				
		[V ^{IV} O] ²⁺		[Mn ^v O₄]³₋				
				Brown				
				MnO ₂				

For other oxidation states and geometries see notes on individual elements



Transition Metal Chemistry Revision Aid

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For a given complex work out d configuration – **ALL** outer electrons are in the d shell.

- **d**⁰ If coloured then from LMCT
- **d**¹ UV Vis explained by simple model. Unsymmetrically filled t_{2g} set. Orbital contribution
- **d**² UV Vis explained by simple model. Orbital contribution
- d³ Inert (high CFSE). O_h very much favoured over T_d (CFSE) relatively large metal centre and so very few tetrahedral compounds
- d⁴ High spin. Jahn Teller distortion easily oxidized to d³ or reduced to d⁵
 d⁴ Low spin. Orbital contribution relatively inert
- d⁵ High spin. Totally half-filled shell very stable. Very pale colour. CFSE = 0 for O_h and T_d Tetrahedral complexes are common

d⁵ – Low spin. Fairly inert (high CFSE) readily reduced to LS d⁶. Orbital contribution Very unusual electronic configuration. Needs strong field ligands or 2nd or 3rd row metals

- d⁶ High spin. Easily oxidized to HS d⁵. Orbital contribution.
 Rather unusual electronic configuration. Needs weak field ligands such as F⁻
 d⁶ Low spin. Very stable (totally filled sub-shell) and inert (very high CFSE).
- d⁷ High spin. CFSE_{oct} >> CFSE_{tet}, small ion. Orbital contribution.
 T_d complexes very common.
 - ${\bf d^7}$ Low spin. Jahn Teller distortion. Easily oxidized to LS d^6
- d⁸ CFSE_{oct} >> CFSE_{tet}. Usually O_h but with large ligands T_d dominates. Square planar for strong field ligands and for 2nd and 3rd row metal complexes
- d⁹ Jahn Teller distortion. Square planar for strong field ligands and for 2nd and 3rd row metal complexes. Very unusual electronic configuration
- **d**¹⁰ Often linear or tetrahedral. Usually colourless



Molecules in the Atmosphere





- The role of the atmosphere
- Structure of the atmosphere
- CFCs and the ozone layer
- Infrared absorption by gases (theory): the enhanced greenhouse effect and global warming
- Gaseous molecules involved in atmospheric pollution: acid rain (S-,N-oxides), photochemical smog
- Throughout: Molecular orbital (MO) theory of bonding in diatomics and in triatomics



The atmosphere, recycling of material, N₂ and O₂ bonding, photoprocesses in the upper atmosphere and aurora





Atmosphere cycles water, carbon, nitrogen and oxygen and partly S, P, and as salt spray NaCl





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Reservoir for O_2 , permitting respiration in animals





Natural greenhouse effect essential for life on Earth





Atmospheric molecules in upper atmosphere absorb harmful UVC radiation to undergo photochemistry





Temperature gradients from photochemistry give atmosphere a structure. And weather!



X-ray



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Formation of ozone layer in the stratosphere gives further protection from UVB and some UVA





Atmosphere as a Recycling Machine

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The atmosphere aids in the recycling of water, carbon, phosphorus, sulfur and nitrogen



The Water (Hydrological) Cycle

Nearly all of the water on the Earth is salty.

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The Water (Hydrological) Cycle

Nearly all of the water on the Earth is salty.



http://cnx.org/content/m45559/latest/?collection=col11487/latest



The Water (Hydrological) Cycle

Important processes: evaporation and sublimation; condensation and precipitation; subsurface water flow; snowmelt and surface runoff; streamflow

Residence time of water in atmosphere is short compared to mixing time, which is defined as the amount of water in atmosphere/amount entering (or leaving) and lasts for several years

Some stats to justify this claim:

7x10¹⁴ mol in atmosphere and approx. 9.5 x 10¹⁹ mol in seas/lakes! Rate of water evaporation: from oceans 2.2 x 10¹⁶ mol y⁻¹; Lakes and rivers 3.5 x 10¹⁵ mol y⁻¹ Rate of precipitation: oceans 1.9 x 10¹⁶ mol y⁻¹; Land 5.5 x 10¹⁵ mol y⁻¹

So residence time is 11 days: Residence time = $7x10^{14}$ mol / (1.9 x 10^{16} + 5.5 x 10^{15}) mol y⁻¹= 0.03 y = 11 days Short compared to mixing time



The Carbon Cycle

Biological processes very important for rapid carbon cycling while geological processes are important for long-term carbon cycling.





The Carbon Cycle

Using solar energy atmospheric CO₂ or dissolved HCO₃⁻ is converted into high-energy compounds such as glucose by autotrophs

Important biological Processes:

Plants

Day time – photosynthesis to carbohydrates (sugars, starch) $6 CO_2 + 6H_2O + hv \rightarrow C_6H_{12}O_6 + 6O_2$ Night time – respiration $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Animals – respiration only



Excrement and rotting dead organic plant and animal matter return nutrients to land (not via atmosphere)

- > Note human sewage washed to sea disrupts natural cycles for recycling nutrients
- Human behaviour also disrupts natural return of minerals and carbon content to biosphere (e.g., the raising of livestock)





The Carbon Cycle

University St Andrews Using solar energy atmospheric CO_2 or dissolved HCO_3^- is converted into high-energy CH2501 compounds such as glucose by autotrophs

Carbon is stored for long periods of times in carbon reservoirs

On land, carbon is stored within organic compounds as the result of decomposition of organisms (fossil fuels) or the weathering of carbon-containing minerals

In the atmosphere, carbon is stored primarily as $CO_2(g)$. The amount of atmospheric CO_2 is dependent on the amount of dissolved CO_2 in the oceans, which itself is reactive and sensitive to pH and ion concentration in the oceans (e.g., $CaCO_3$). The largest carbon reservoirs on Earth are the limestone deposits.

Carbon can also enter the atmosphere through volcanic eruption









The Carbon Cycle

Humans have made significant contributions to CO₂ levels.

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The Nitrogen Cycle

University St Andrews Unlike carbon and oxygen, most living organisms are not equipped to directly use CH2501 atmospheric nitrogen (BDE = 945 kJ mol⁻¹)





The Nitrogen Cycle

^{University} St Andrews Unlike carbon and oxygen, most living organisms are not equipped to directly use CH2501 atmospheric nitrogen (BDE = 945 kJ mol⁻¹)

Nitrogen is incorporated into living organisms through nitrogen fixation processes mediated by bacteria wherein $N_2(g)$ is converted first into NH_4^+ (ammonification), which is then oxidized into NO_2^- (nitrification) and NO_3^- . The cycle is completed when nitrates are converted to N_2 (denitrification).

Humans release nitrogen into the atmosphere through:

- Combustion of fossil fuels (nitrogen oxides)
- The use of fertilizers

Other sources of atmospheric nitrogen include acid rain (HNO₃) and greenhouse gases (N₂O)







The Phosphorus Cycle

Phosphorus, essential for living processes and biomacromolecules, naturally occurs as PO_4^{3-}




The Phosphorus Cycle

Phosphorus, essential for living processes and biomacromolecules, naturally occurs as PO₄³⁻

Phosphate runoff due to human activity (fertilizers and sewage) and weathering from rocks and minerals are two main sources of phosphorus in the environment

Volcanic ash is also high in phosphates as is ocean sediment.

Average oceanic residence time ranges from 20 000 to 100 000 y.



Excess phosphorus (and nitrogen) result in algae blooms, which deplete oxygen and lead to aquatic dead zones.





http://cnx.org/content/m45559/latest/?collection=col11487/latest



The Sulfur Cycle

Sulfur is also an essential element due to its presence in the amino acid cysteine

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The Sulfur Cycle



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Sulfur is also an essential element due to its presence in the amino acid cysteine

Atmospheric sulfur is found in the form of SO₂ which when combined with rain forms H₂SO₄

SO₂ enters the atmosphere through:

- \blacktriangleright Decomposition of organic matter (released at H₂S)
- Volcanic activity (fallout)
- \succ Burning of fossil fuels (released as H₂S, especially coal)



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Essential Elements for Humans

Element	Body level/ppm	Recycled by atmosphere?
0	6.5 x 10 ⁵	Respiration,
С	1.8 x 10 ⁵	photosynthesis, Rain
Н	1x10 ⁵	Rain
Ν	3x10 ⁴	Nitrogen cycle
Ca	1.5x10 ⁴	No
Р	1.0x10 ⁴	Partly PO ₄ ³⁻
S	2.5x10 ³	Partly Me_2S , H_2S
К	2x10 ³	No
Cl	1.5x 10 ³	Partly (wind-borne sea
Na	1.5x10 ³	water)
Fe,Zn,Si,Cu,I,Mn,V,Co,Mo	Varies < 60	Νο





Chemistry in the Upper Atmosphere: Photochemistry

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Photodissociation: Energy to reach dissociation limit (homolytic bond cleavage)

➢ e.g., N₂ + hv → 2N ΔH^Q +945 kJ mol⁻¹ Molecule must be able to absorb light at these wavelengths i.e. have an absorption band at the right energy. N₂ does not have strong absorption bands in UVC and so it is difficult to photodissociate

Another possibility is **photoionisation**:

- > Of the atoms $O + hv \rightarrow O^+$ and $N + hv \rightarrow N^+$
- > Or molecules: N_2 to N_2^+ or O_2 molecules to O_2^+ Photoionisation results in the ejection of electrons from atoms, ions or molecules. This occurs in the ionosphere

Molecule does not need an absorption band in this case





How to Calculate Threshold Energies for Photodissociation

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Photodissociation: Energy to reach dissociation limit (homolytic bond cleavage)

- \succ e.g., N₂ + hν → 2N ΔH^o +945 kJ mol⁻¹
- This calculation is based on the Conservation of Energy
- The energy of the photon used MUST be greater than this threshold energy (BDE)
- This reaction is always exothermic and kinetic energy is always released
- In photochemistry only 1 photon is absorbed per molecule
- So for N₂ each photon must have energy $\Delta H^{\circ} / N_{A} = 945,000 / 6.02 \times 10^{23} = 1.57 \times 10^{-18} J$
- Now photons of wavelength λ have energy E= hv = hc/ λ and so λ = hc/E
- So in this case $\lambda = hc/E = 6.6 \times 10^{-34} \times 3 \times 10^8 / 1.57 \times 10^{-18} = 126 \text{ nm} \text{ in the UVC region}$

For $O_2 \Delta H^{\circ} = +498 \text{ kJ mol}^{-1}$ which corresponds to **240 nm** in the UVC



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How to Calculate Threshold Energies for Photoionization

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Photoionization: Energy necessary to eject an electron from an atom, ion or molecule

- ➢ e.g., A + h_V → A⁺ + e-
- This calculation is based on the Conservation of Energy So: E(A) + hv = E(A⁺) + E (e⁻)
- Since the e⁻ possesses only kinetic energy: $KE=hv [E(A^+) E(A)] = hv BE$ where BE is the binding energy. This equation is known as the Einstein equation
- BE is usually measured in eV : 1 eV is one electron moved through one volt = $1.6 \times 10^{-19} \text{ J}$





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Photoionization: Energy necessary to eject an electron from an atom, ion or molecule

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- Since the e⁻ possesses only kinetic energy: $KE=hv [E(A^+) E(A)] = hv BE$ where BE is the binding energy. This equation is known as the Einstein equation
- BE is usually measured in eV : 1 eV is one electron moved through one volt = 1.6 x 10⁻¹⁹ J
- The threshold energy occurs when KE=0 and hv = BEFor O₂ the BE of the highest orbital electron energy is 12 eV, So 12 eV x $1.6x10^{-19}$ J·eV-¹= $1.92x 10^{-18}$ J, So the max wavelength $\lambda = hc/BE = 6.6 \times 10^{-34}$ J·s x $3x10^8$ m·s⁻¹/ $1.92x 10^{-18}$ J= **103 nm**

Thresholds for O atom and N₂ molecule are at **91.1 nm and 79.6 nm**, respectively. Most O₂ dissociated in upper atmosphere, so O₂⁺ only formed by O⁺ + O₂ \rightarrow O + O₂⁺ and N₂⁺ + O₂ \rightarrow N₂⁺ + O₂⁺

Photoionization is integral to Photoelectron spectroscopy (PES) where the KE is measured to determine the binding energies of the electrons in atoms and molecules



Reactions to Give NO⁺

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$O^+ + N_2 \rightarrow$	$NO^{+} + O_{2}^{+}$
$N_2^+ + O \rightarrow$	NO ⁺ + N
$O_2^+ + N \rightarrow$	$NO^+ + O$



So NO, which is regenerated in the 3rd step can assist in the destruction of many ozone molecules.





Photoionization and Photoelectron Spectroscopy

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Photoionization: Energy necessary to eject an electron from an atom, ion or molecule The IE shown is the $[E(A^+) - E(A)]$ taken from the photon energy hv

The Franck-Condon principle states that electrons move faster than nuclei

- So the nuclei do not move when the electron is ejected,
- So changes in energy take place vertically on the energy-distance diagram (arrow)

This means that, since the H_2^+ ion is more weakly bound (BO: 0.5) and has therefore a longer equilibrium H-H bond length, its potential well is displaced and the ion is formed in **a vibrationally excited state**

This gives rise to spacing between lines of emitted electron energies of the H-H frequency in H_2^+

→ H-H stretch in H_2^+ is lower (2200 cm⁻¹ vs 4000 cm⁻¹ in H_2) as we have a weaker H-H bond 0 -





Photoelectron Spectroscopy of O₂

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- Photoelectron spectroscopy of O₂ has three peaks corresponding to ionisation to give ions with electrons lost from σ_g , $1\pi_u$, $1\pi_g$
- The lowest energy line shows vibrational fine structure with v(O-O)
 (O-O stretching frequency 1868 cm⁻¹) higher (more widely spaced peaks) than that of neutral O₂ (1580 cm⁻¹), indicating bond is stronger in O₂⁺ (BO=2.5 compared to 2.0 in O₂)
- This confirms HOMO in O₂ (and F₂) is anti-bonding (π_g) because removal of an electron from this orbital leads to a stronger bond





The Auroras

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- The Auroras are caused when high-energy particles from Solar flares collide with O and N atoms in the thermosphere resulting in an excited state.
- O emits red (630 nm) in the upper atmosphere or yellow-green (558 nm) in the lower atmosphere
- N₂ emits in the red (661-686 nm)
- N₂⁺ emits in blue and purple (391-470 nm) in the lower atmosphere (60-90 Km)





St Andrews, Nov. 20, 2003

Aurora Australis



The Auroras





Structure of the Atmosphere and The Ozone Layer









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100,000 km Space Shuttl	Stru	cture of the	Atmosphere	100,000 km
600 km	Exosphere			600 km
		Pressure	Mass	Temperature
Aurora Boreali	is			-90 to 1500+ ≅C
_85 km	Thermosphere	.001 mb		85 km
Meteor Shower	Mesosphere	.01 mb .1 mb		0 to -90 ±C
50 km		l mb	About 19% of mass is in stratosphere	50 km
Ozone Layer	Stratosphere	10 mb.	•	3 -50 to 0 ≅C
10 km	Troposphere	100 mb	80% of mass is in troposphere	10 km
ATEN GLOBA	1 km = .62 mile	mb = millibar 1000 mb = 14.7 pounds/in²	Total mass = 5 quintillion kg (5.1 × 10 ¹⁸ kg)	-60 -40 -20 _{2C} 0 20 40











01 100,000 km Space	e Shuttle Stru	Structure of the Atmosphere		100,000 km	
And a second sec	Exosphere				
600 km				600 km	
		Pressure	Mass	Temperature	
Aurore	a Borealis			-90 to 1500+ ≌C	
	Thermosphere	.001 mb			
85 km		Mesopa	use		
Meteor Shower	Mesosphere	.01 mb .1 mb		0 to -90 ≅C	
50 km		1 mb		50 km	
	Stratosphere	1 mb	About 19% of mass is in stratosphere	J -50 to 0 ≅C	
Ozone Layer 10 km		100 mb		10 km	
Mt. E	Everest Troposphere	1000 mb 🥌	80% of mass is in troposphere	16 to -55 S	
ATTEN GLOBA	1 km = .62 mile	mb = millibar 1000 mb = 14.7 pounds/in²	Total mass = 5 quintillion kg (5.1 x 10 ¹⁸ kg)	-60 -40 -20 ₂₀ 0 20 40	



















Chemistry in the Thermosphere





The lonosphere











Guiglielmo Marconi (1874– 20 July 1937)





















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Chemistry in the Mesosphere and Stratosphere





Chemistry in the Mesosphere and Stratosphere





Chemistry in the Ozone Layer

H2501	100,000 km Space Shutt	Structure of the Atmosphere		. 100,000 km	
	***	Exosphere	•		
	- 600 km	•			600 km
			Pressure	Mass	Temperature
	Aurora Borea	lis			-90 to 1500+ ≌C
	_ 85 km	Thermosphere	.001 mb		85 km
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	Mt. Everest	Troposphere	1000 mb	80% of mass is in troposphere	▶ 16 to -55 °c
	AT NOR INSTITUT	1 km = .62 mile	nio = militoar 1000 mb = 14.7 pounds/in ²	(5.1 x 10 ¹⁸ kg)	-60 -40 -20 ±C 20 40



Chemistry in the Ozone Layer






Chemistry in the Ozone Layer











Chemistry in the Ozone Layer: The Chapman Mechanism

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Recall that O₂ molecule can absorb only the very high energy UV light (UVC) to give oxygen atoms: O₂ + hv (<240 nm) \rightarrow 20 Δ H^o: +495 – E(photon) kJ mol⁻¹

Now these O atoms can participate in chemistry. When they react with O_2 they give O_3

- $0 + 0_2 \rightarrow 0_3^*$
- $O_3^* + M \rightarrow O_3 + M^* \Delta H^{\circ} 105 \text{ kJ mol}^{-1}$ \therefore heat is evolved

Due to its larger π -system, O₃ can absorb light between 240-320 nm Ozone destruction passes through one of two routes:

- $O_3 + hv (<320 \text{ nm}) \rightarrow O + O_2 \Delta H^{\circ}: +105 E(\text{photon}) \text{ kJ mol}^{-1}$ $O + O_3 \rightarrow 2 O_2 \Delta H^{\circ}: -389 \text{ kJ mol}^{-1}$



Ozone can reform, leading to a steady-state concentration of ozone, known as the ozone layer. This layer protects the Earth's surface from harmful UV radiation.





Why is Ozone Formed as a Layer?





Why is Ozone Formed as a Layer?

The ozone layer resides much lower (25-30 km altitude) than the point of maximum O_3 production (at the temperature maximum, the stratopause, at 50 km)







This is due to Brewer-Dobson circulation, which transports ozone-rich air from the area of the stratopause lying over the tropics to the lower levels of the atmosphere







The Brewer-Dobson circulation is also responsible for maximising the ozone concentration over mid-latitudes, rather than the tropics where light intensity is highest







Complex circulation also causes ozone peaking in **Spring** not summer and lowest in **Autumn** not winter at latitudes other than tropics





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100-280 nm 280-315 nm 315-400 nm



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Summary of Absorption of UV Light as a Function of Altitude

UVC absorbed by atomic & molecular N_2 and O_2 ; UVB and some UVA absorbed by O_3





Summary of Absorption of UV Light as a Function of Altitude

UVC absorbed by atomic & molecular N_2 and $O_2;$ UVB and some UVA absorbed by O_3

Energy Spectrum of Sunlight





















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Chemistry in the Ozone Layer

100,000 km Space Shuttle Structure of the Atmosphere					
A CONTRACT OF A	Exosphere			· .	
600 km				600 km	
		Pressure	Mass	Temperature	
Aurora Borea	lis			-90 to 1500+ ≅C	
· ·	Thermosphere	.001 mb			
85 km Meteor Shower		.01 mb		85 km	
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Ozone Layer	Stratosphere	Ozone La	yer		
10 km	Troposphere	1000 mb	80% of mass is in troposphere	10 km	
SHEEN GLOHA	1 km = .62 mile	mb = millibar 1000 mb = 14.7 pounds/in²	Total mass = 5 quintillion kg (5.1 x 10 ¹⁸ kg)	-60 -40 -20 ₂₀ 20 40	



Chemistry in the Ozone Layer





Why is Ozone Formed as a Layer?













Sunscreen

СООН

 $\dot{N}H_2$

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In the past PABA was used as a suncreen as it absorbs UVB light (290-320 nm) However, as it discoloured clothing and was linked in some studies to cellular UV damage it has been largely discontinued.



To protect against both UVA and UBC mixtures of absorbing molecules are used in modern sunscreens



Sun **P**rotection **F**actor (SPF) is a measurement of UVB protection. The number refers to the ratio of amount of sunlight necessary to induce redness in skin protected by sunscreen to bare skin.



Ozone Depletion





Ozone Depletion – Chapman Mechanism

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There was a problem with the Chapman theory. In the 1960s it was realised that the loss of ozone given by:

 $O + O_3 \rightarrow 2O_2$ was too slow.

Other species, destroying O₃ faster, had to be responsible

 $X + O_3 \rightarrow XO + O_2$ $O_3 + hv \rightarrow O + O_2$ to generate O for the next reaction $XO + O \rightarrow X + O_2$

 $2O_3 \rightarrow 3O_2 - \text{net effect}$

X = NO (from N₂O), OH and H are naturally occurring X = Cl and Br are manmade!





Ozone Depletion

Mountain of refigerators





Thomas Midgley Jr.

1920's – invention of CFCs as coolants in refrigerators



Ozone Depletion



1920's – invention of CFCs as coolants in refrigerators

CFCs are 10 900x worse than CO_2 as a Greenhouse gas and have a $t_{1/2}$ of ca. 100 y.

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Ozone Depletion



1920's – invention of CFCs as coolants in refrigerators

CFCs are 10 900x worse than CO_2 as a Greenhouse gas and have a $t_{1/2}$ of ca. 100 y.



Ozone Depletion – Radical Chemistry



Polar Weather



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[O₃] ↓

From May-Sept During the winter polar night, sunlight does not reach the south pole. A strong circumpolar wind develops in the middle to lower stratosphere (16 Km altitude). These strong winds are known as the 'polar vortex'. This has the effect of isolating the air over the polar region.



34316

May

June

July

August

Antarctic Winter

Sep

Oct



How HCl and ClONO₂ Generate Cl₂ on the PSC Ice Particles in the Dark Antarctic Winter



Recipe for O₃ loss

- 1. Polar winter → polar vortex → isolation of air
- 2. T↓ (<197 K) and persist, Polar Stratospheric Clouds (PSC), which are formed of HNO₃·3H₂O, contribute to [O₃]↓



nacreous or "mother of pearl" clouds over Montrose Basin, 02/94317



How Chlorine Destroys Ozone in the Spring Over Antarctica: More Complex than the "X" Mechanism

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Recall:

 $Cl \bullet + CH_4 \rightarrow HCl + CH_3 \bullet$ $Cl \bullet + O_3 \rightarrow ClO \bullet + O_2$ (here the radical is on chlorine) $ClO \bullet + NO_2 \rightarrow ClONO_2$ (reversed by sunlight) So HCl "stores" damaging Cl • and ClONO₂ "stores" damaging ClO •

But at the low T in the stratosphere 2 ClO• \rightarrow ClOOCl Once Sun shines then ClOOCl +hv \rightarrow Cl• + ClOO• and then ClOO• + M \rightarrow O₂ + Cl• Each Cl atom destroys up to 100 000 O₃ molecules! Cycle 1





nacreous or "mother of pearl" clouds over Montrose Basin, 02/94318



How Chlorine Destroys Ozone in the Spring Over Antarctica: More Complex than the "X" Mechanism

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Recall:

 $CI \bullet + CH_4 \rightarrow HCI + CH_3 \bullet$ $CI \bullet + O_3 \rightarrow CIO \bullet + O_2$ (here the radical is on chlorine) $CIO \bullet + NO_2 \rightarrow CIONO_2$ (reversed by sunlight) So HCI "stores" damaging CI \bullet and CIONO₂ "stores" damaging CIO \bullet

But at the low T in the stratosphere 2 ClO• \rightarrow ClOOCl Once Sun shines then ClOOCl +hv \rightarrow Cl• + ClOO• and then ClOO• + M \rightarrow O₂ + Cl• Each Cl atom destroys up to 100 000 O₃ molecules!





The COMET Program nacreous or "mother of pearl" clouds over Montrose Basin, 02/94319



The Unfortunate Role of Nitric Acid: Denoxification

- The HNO $_3$ formed in the PSC accumulates over the winter and the [NO $_x$] f I
- The result of this is that the rate of removal of CIO• decreases (CIO• + $NO_2 \rightarrow CIONO_2$) AND
 - NO₂ + O₃ → NO₃ + O₂
 NO₂ + NO₃ → N₂O₅
 Both reactions reversible and so do not remove NO₂
 - $NO_2 + NO_3 \rightarrow N_2O_5$ BUT
 - $N_2O_5 + H_2O$ (droplets) $\rightarrow 2HNO_3$





Mid-Latitude Ozone Destruction

- Not cold enough for ice particles
- Suggest cold liquid droplets of sulfuric acid (H₂SO₄) act in similar way
 - Small natural background amounts
 - Large amounts from volcanoes Pinatubo eruption helps explain big ozone loss in early 90s
- These take up HCl and ClONO₂, playing a similar role to the PSC ice crystals to produce Cl₂ and hence damaging Cl• and ClO•





Ozone Depletion Potentials Table (ODP)

Substance	Chemical formula	ODP values
CFCs CFC-11 CFC-12 CFC-113 CFC-115 Other CFCs	$CFCI_3$ CF_2CI_2 $C_2F_3CI_3$ C_2F_5CI -	1.0 1.0 0.8 0.6 -
Tetrachloromethane	CCI ₄	1.1
1,1,1-trichloroethane	CH ₃ CCl ₃	0.1
Halons Halon-1301 Halon-1211 Halon-2402	CF_3Br CF_2BrCl CF_2BrCF_2Br	10 3 6
Methyl bromide	CH₃Br	0.6 (1)
HCFCs HCFC-22 HCFC-123 HCFC-141b HCFC-142b	$CHF_{2}CI$ $C_{2}HCL_{2}F_{3}$ $C_{2}H_{3}FCI_{2}$ $C_{2}H_{3}F_{2}CI$	0.055 0.02 0.11 0.065



The Result: 1987 – The Montreal Protocol

- Ban all chlorofluorocarbons, carbon tetrachloride, methyl chloroform, and halons in developed countries as of January 1996 and in developing countries by 2010
- Control measures for other halocarbons, such as methyl bromide and the transitional CFC replacement, hydrochlorofluorocarbons HCFCs
 - 2013 : freeze the consumption and production of HCFCs
 - ✓ 2015: reduce consumption and production in 2015





Long Term CFC Replacement: HFC's

- Replacement chemicals should contain no Br or Cl in structure
- C-F bonds are OK as they are stronger and do not photodissociate BUT their half lives are extremely long and are greenhouse gasses
- ✓ HFCs can be destroyed in the troposphere due to C-H bond e.g., OH + CF₃CH₂F (HFC-134a) → H₂O + CF₃CHF which can be readily attacked by O₂
- ✓ HFC-134a shows a good vapour pressure match with the most widely used refrigerant CFC-12 and also has a low toxicity

Nomenclature: take number and add 90. The number tells the mol. Formula as digits C, H, F e.g., 134+90 = 224 \rightarrow C₂H₂F₄ HFC-134a; 11+90 = 101 \rightarrow C₂H₀F₁Cl₃ CFC-11




And What About the Halons and MeBr

325

- Halons are bromine-containing chemicals that are used as fire retardants
- C-Br bonds are weaker than C-Cl bonds and give Br radicals, which persist in the atmosphere and destroy ozone.
- **Nomenclature:** Halon 1301 (H1301) → C₁F₃Cl₀Br₁



Halon-1301, CBrF₃





The Goal is to Return to Pre-Hole Cl Level of 2 ppbv

Not gonna happen anytime soon





Is the Montreal Protocol Working?

- The average size of the ozone hole in 2012 was 17.9 x10⁶ Km², 2nd smallest in 20 year.
- The minimum value of total ozone in the ozone hole reached 124 DU (Dobson Units), the second highest in 20 years
- **Recall:** When no ozone hole, total ozone ranges from 240-500 DU





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Effective chlorine



Ozone Depletion: Perhaps Healing

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For the first time, scientists report that the protective ozone layer over Antarctica is showing signs of healing (Science, **2016**, DOI: 10.1126/science.aae0061).

Closure

The seasonal Antarctic ozone hole, shown here in October 2015, is gradually shrinking.



Learning Outcomes

- To be able to explain the influence of the weather conditions at the Antarctic on the production of Cl₂ from the reservoir compounds HCl and ClONO₂
- To be able to write down the simple, and the ClOOCI mechanism for destruction of the ozone layer by Cl atoms
- To know about CFCs and their replacements





Global Warming: Managing Earth's Energy Balance

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Earth's Energy Balance

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Incoming:

- Total solar irradiation (TSI) output varies by approximately 0.1% or about 1.3 W/m² peak-to-trough of the 11 year sunspot cycle.
- The Earth collects TSI=1366 W m⁻² from its projected disk area ($A=\pi R_e^2$) reduced to one-quarter (340 W m⁻²) when averaged over the whole surface ($4\pi R_e^2$) over a day of Earth complete revolution
- 20% absorbed (UV by O₂ and IR by CO₂ and water)
- 30% reflected back to space (albedo)

Outgoing:

- If outgoing heat less than incoming Earth gets warmer
- A warmer Earth will then emit more energy
- Only when the rate of warming (energy in) is equal to the rate of cooling will a steady temperature be achieved and Energy Balance be maintained





Earth's Energy Balance: Incoming Radiation from the Sun

- Wien's Law for "black body" radiation gives the peak wavelength:
 - **λ**_{max}=2897/T Sun (5800 K) emits visible light; Earth (300K) emits infra-red
- Boltzmann's Law for "black body" radiation gives total energy $\mathbf{E} = \mathbf{\sigma}\mathbf{T}^4$ where T is in Kelvin (T in °C = T in K + 273) where σ is Boltzmann's constant at 5.67 x 10⁻⁸
- Energy reaching the surface of the Earth is 340 W m⁻²
- Of this 100 W m⁻² is reflected back out into space (albedo, 30%), which leaves 240 W m⁻²
- For Earth to be at an energy balance 240 W m⁻² = σT^4 ; \therefore T = 255 K or -18 °C
- To explain this discrepancy, we invoke a Greenhouse effect (ε) that results in a rate of cooling on Earth that is lower than that for a black body (atmospheric insulation)
- So the Greenhouse cooling rate = $\varepsilon \sigma T^4$ and ε = 0.615 for right temperature (T = 288 K = 15 °C)





Earth's Energy Balance: Incoming Radiation from the Sun

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Earth's Energy Balance: Incoming Radiation from the Sun

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Natural Greenhouse Effect

Energy reflected by the Earth gets reabsorbed by gases in the atmosphere and re-radiated back

- Water vapour counts for 2/3 of the effect (cold desert nights); counts for a 1/4 of the effect.
- Natural process keeps Earth's average surface temperature near +15 °C. If absent then –18 °C!





Natural Greenhouse Effect

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Natural process – keeps Earth's average surface temperature near +15 °C. If absent then –18 °C!





The Physics Behind Energy Absorption by Gas Molecules





The Physics Behind Energy Absorption by Gas Molecules

University St Andrews CH2501 Radiation interacts with matter through one of several processes: scattering, absorption & emission Absorption is a process where by the energy of the photon is taken up by the matter

- UV radiation has enough energy to ionize electrons (i.e. eject them from atoms)
- Visible radiation has enough energy to excite electrons (i.e. induce an electron transition)
- IR radiation has enough energy to excite vibrational and rotational states of a molecule

For a molecule to absorb IR radiation there must be a match between the change in dipole moment as a function of vibrations and rotations with the energy of the radiation.

Upon absorption there will be a change in the amplitude of the molecular vibration. This is what is observed in an IR spectrum



E	Before absorption	During absorption	After absorption	
Î				Vibrational energy states of an excited electronic energy level
	ννν Incident photon ħω	~~~	Molecule in excited state	
			<u> </u>	Vibrational energy states of the ground state electronic energy level
	Molecule in ground state	****		341

Type of Molecular Vibration

Remember: For a molecule to absorb IR radiation there must be a match between the change in dipole moment due to vibrations and rotations with the energy of the radiation.

Stretch: change in bond length	Bend: change in bond angle
Stretch symmetric	scissoring
Stretch asymmetric	wagging
	rocking
	twisting/torsion

e.g., H₂O



All vibrational motions change the molecular dipole moment, so all are infrared active, or electric-dipole allowed transitions.

Type of Molecular Vibration

Remember: For a molecule to absorb IR radiation there must be a match between the change in dipole moment due to vibrations and rotations with the energy of the radiation.



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CO₂ and H₂O – Major Greenhouse Gases

O-H stretching, CO₂ antisymmetric stretch , O-H bend+rotational structure, CO₂ bend





CO₂ and H₂O – Major Greenhouse Gases

O-H stretching, CO₂ antisymmetric stretch , O-H bend+rotational structure, CO₂ bend



Wavelength (µm)

Figure 2-13 The absorptivity of selected gases of the atmosphere and the atmosphere as a whole. (From R. G. Fleagle and J. A. Businger, An introduction to Atmospheric Physics. © 1963 by Academic Press; reprinted by permission of the publisher)



CO₂ and H₂O – Major Greenhouse Gases

Water in atmosphere will **1** ÃĐĆ CBÃB ÇÅAZE Đ ẢÇà ǰ ĊC Đ ẢZE**1** greenhouse effect But will also give more

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Recent History of CO₂ in Atmosphere





Recent History of CO₂ in Atmosphere

 CO_2 has increased by one- third since 1800 (measured by CO_2 bubbles trapped in ice cores)





The Future for CO₂ in Atmosphere



Predicted Temperature Increase Across the United States

By 2100

t Si Cl



These calculations by Climate Central are based on projections by the <u>World Climate Research Programine</u> that assume that greenhouse gas emission trends will continue unabated through 2100. Daily maximum values for the average of the years 1991 to 2010 are based on <u>meteorological data</u> compiled by Ed Maurer at Santa Clara University. See: http://www.nytimes.com/interactive/2016/08/20/sunday-review/climate-change-hot-future.html



The Oceans Are Acting as a Heat Sink

Where the Oceans Have Been Colder and Hotter Than Average



Average temperatures from each decade compared with the 20th-century average. See: http://www.nytimes.com/interactive/2016/09/12/science/earth/ocean-warming-climate-change.html



The Oceans Are Acting as a Heat Sink



Amounts in zettajoules, or sextillions of joules, relative to 1971 levels. See: http://www.nytimes.com/interactive/2016/09/12/science/earth/ocean-warming-climate-change.html



The Future for CO₂ in Atmosphere

Observed and Predicted Global Temperature vs CO2 Projection and IPCC A1B Scenario 415 CO2 concentration [ppm] ΔT [*C] (1961-1990 Basel) observed observed (ex post) 0,8 MMM predicted (most likely) IPCC A1B Scenario CO2 0,6 375 365 n 🤉 080 090 091 020 0.93 96 96 0 16 0 80 80 ä 0 345 335 ©2011 KnowledgeMiner Software



Other Culprits



IPCC Conclusions



IPCC Conclusions





IPCC Conclusions: Confidence

The global mean radiative forcing of the climate system for the year 2000, relative to 1750



Level of Scientific Understanding





Other GHGs U.S. Greenhouse Gas Emissions 2010

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In 2010, the United States emitted over 6.8 billion metric tons of greenhouse gases

Atmospheric Lifetime of Different Greenhouse Gases



Methane

_10%


The Main Greenhouse Gases U.S. Greenhouse Gas Emissions 2010

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In 2010, the United States emitted over 6.8 billion metric tons of greenhouse gases

Greenhouse gases	Chemical formula	Pre-industrial concentration	Concentration in 1994	Atmospheric lifetime (years)***	Anthropogenic sources	Global warming potential (GWP) *
Carbon-dioxide	CO ⁵	278 000 ppbv	358 000 ppbv	Variable	Fossil fuel combustion Land use conversion Cement production	1
Methane	CH4	700 ppbv	1721 ppbv	12,2 +/- 3	Fossil fuels Rice paddies Waste dumps Livestock	21**
Nitrous oxide	N ₂ O	275 ppbv	311 ppbv	120	Fertilizer industrial processes combustion	310
CFC-12	CCl ₂ F ₂	0	0,503 ppbv	102	Liquid coolants. Foams	6200-7100 ****
HCFC-22	CHCIF ₂	0	0,105 ppbv	12,1	Liquid coolants	1300-1400 ****
Perfluoromethane	CF4	0	0,070 ppbv	50 000	Production of aluminium	6 500
Sulphur hexa-fluoride	SF6	0	0,032 ppbv	3 200	Dielectric fluid	23 900

Note : pptv= 1 part per trillion by volume; ppbv= 1 part per billion by volume, ppmv= 1 part per million by volume

* GWP for 100 year time horizon. ** Includes indirect effects of troposphericozoue production and stratospheric water vapour production. *** On page 15 of the IPCC SAR. No single lifetime for CO₂ can be defined because of the different rates of uptake by different sink processes.**** Net global warming potential (i.e., including the indirect effect due to ozone depletion).



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Important Points

- To know what is meant by the Earth's energy balance
 - Energy balance equation and Stefan's Law
 - Factors affecting incoming solar radiation
 - Albedo (reflection coefficient)
- Correction for Natural Greenhouse Effect
- To know about one-dimensional energy balance models
- To know Infra-red absorption by greenhouse gases is converted to vibrational energy
- Concept of radiative forcing
- Greenhouse gases compared by lifetime in atmosphere and global warming potential (GWP)
- Natural greenhouse gases other than CO₂ and water:
 - Ozone, nitrous oxide (N₂O) and methane
- Man-made greenhouse gases:
 - Refrigerants: CFCs, HCFCs, HFCs
 - Fire retardants: halons

