Advanced Glass Science
(4016101)

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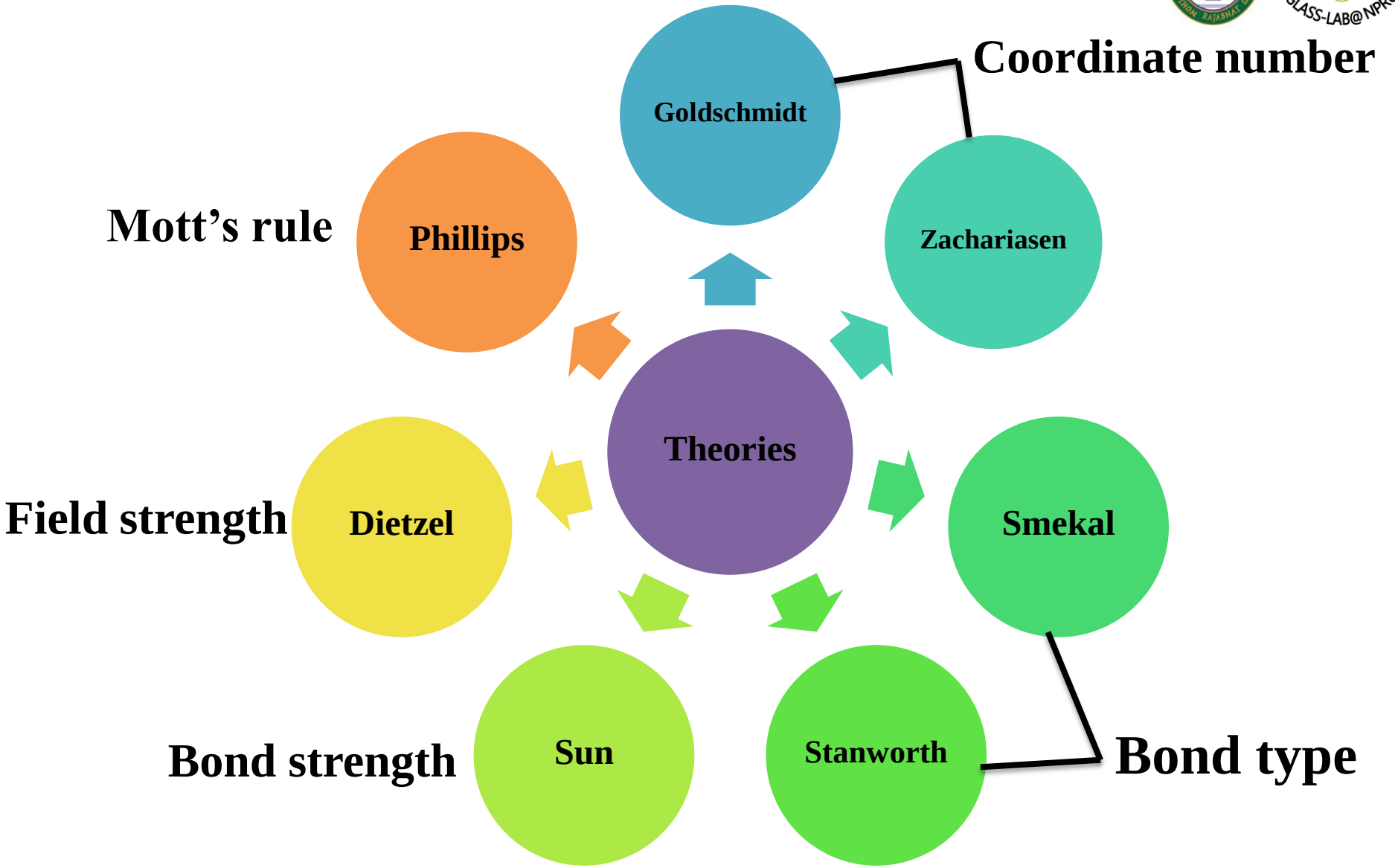
Course Outine:

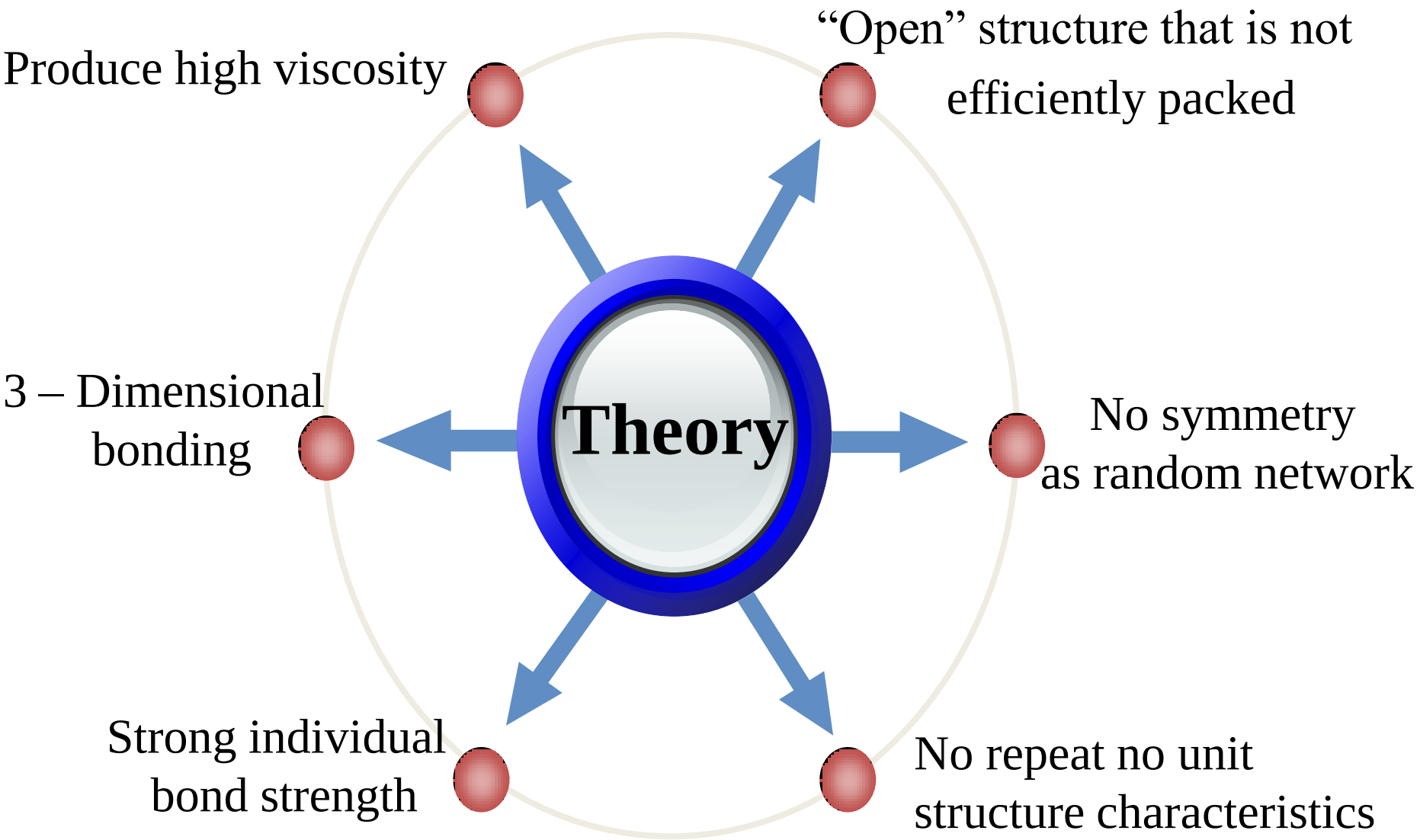
Week 2: Glass formation principles
- Zachariasen's random network theory
- Sun's single bond strength criterion
- Dietzel's field strength criterion

Book: Arun K. Varshneya. Fundamentals of inorganic glasses

Structural theories of glass formation



Zachariasen's random network theory



Zachariasen's random network theory

1. An oxygen atom is linked to no more than two atom of A.
2. The oxygen coordination around A is small, say 3 or 4.
3. The cation polyhedra share corners, not edges, not face.
4. At least three corners are shared.

The table here summarizes the **cation to anion radius ratios, Rx/Rz,** for various coordination numbers and gives the name of the coordination polyhedron for each coordination number.

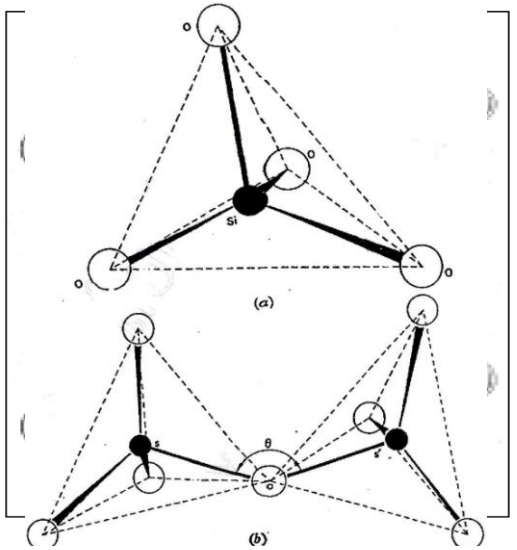
Rx/Rz	C.N.	Type
1.0	12	Hexagonal or Cubic Closest Packing
0.732 - 1.0	8	Cubic
0.414 - 0.732	6	Octahedral
0.225 - 0.414	4	Tetrahedral
0.155 - 0.225	3	Triangular
0.155>	2	Linear

Zachariasen's random network theory

1. Consider Silica
   - covalent Si-O bond
   - tetrahedral bond
   solve by Pauling's packing rule:

$$\frac{r(Si^{4+})}{r(O^{2-})} = \frac{0.40}{1.40} \approx 0.29$$

➡ Satisfies Zachariasen's rule #2

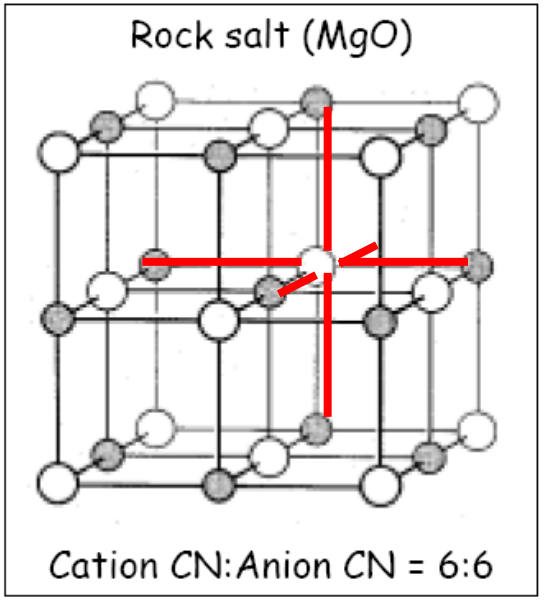


r_{cation}/r_{anion} = 0·225 (tetrahedral) 0.414 (octahedral) 0.73 (cubic)

2. Consider Magnesia (MgO) :
   - Ionic Mg-O bond

$$\frac{r(Mg^{2+})}{r(O^{2})} = \frac{0.72}{1.40} \approx 0.51$$

➡ Violates Zachariasen's rule #2.



r_{cation}/r_{anion} = 0·225 (tetrahedral) 0.414 (octahedral) 0.73 (cubic)

Sun's single bond strength criterion

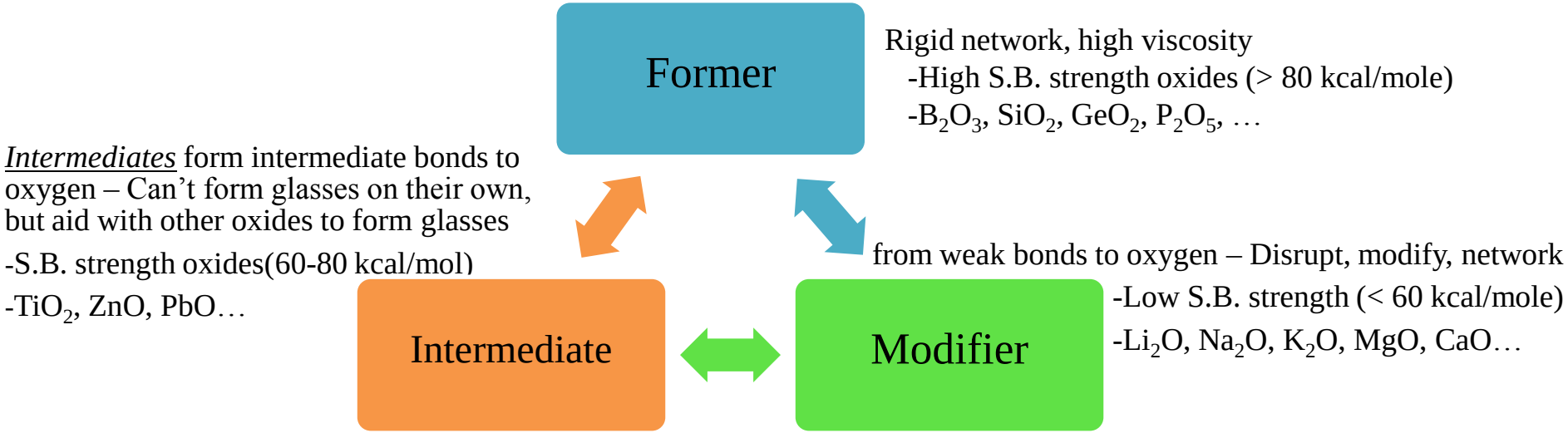
Consider a single bond strength approach:

Dissociation energy for a molecule, E_d: $\mathbf{A_xO_y \rightarrow xA + yO}$

Single bond (S.B.) ~ E_d/C.N.

Glass Formation is brought about by both:

- *Connectivity of Bridge Bonds*
- *Strong Bonds between atoms (ions)*



Sun's single bond strength criterion

Function in glass structure	M in MO_x	Valence	Dissociation energy E_d per MO_x (kcal)	Coordination number	Single-bond strength (kcals)
Glass Formers	B	3	356	3	119
	Si	4	424	4	106
	Ge	4	431	4	108
	Al	3	302-317	4	79-101
	B	3	356	4	89
	P	5	442	4	88-111
	Sb	5	339	4	68-85
	Zr	4	485	6	81
Intermediates	Ti	4	435	6	73
	Zn	2	144	2	72
	Pb	2	145	2	73
	Al	3	317-402	6	53-67
	Th	4	516	8	64
	Be	2	250	4	63
	Zr	4	485	8	61
	Cd	2	119	2	60
Modifiers	Sc	3	362	6	60
	La	3	406	7	58
	Y	3	399	8	50
	Sn	4	278	6	46
	Ga	3	267	6	45
	In	3	259	6	43
	Th	4	516	12	43
	Pb	4	232	6	39

Dietzel's field strength criterion

Dietzel examined direct Coulombic interactions:

$$\text{Attractive force} = \frac{(Z_c e)(Z_a e)}{(r_c + r_a)^2}$$

Let $a = (r_c + r_a)$

$z_a = -2$ for oxide

Then Dietzel categorized cations using: $\text{Field strength (F.S.)} = \frac{z_c}{a^2}$

High F. S. cations → high cation-oxygen bond energy:

Classify	**Z_c/a^2**
Former	> 1.3
Intermediate	0.4 < F.S. < 1.3
Modifier	< 0.4

More factors are important than just bond strength

Small cations with high charge – ***glass formers***

Large cations with small charge – ***modifiers***

Medium sized cations with medium charge ***-intermediates***

Dietzel's field strength criterion

Function in glass structure	Element	Valence, Z^-	Ionic radius (for CN = 6) r in Å	Most frequent coordination number, CN	Ionic distance for oxides a in Å	Field strength at distance of O^{2-} ions Z/a^2
Modofier	K	1	1.33	8	2.77	0.13
	Na	1	0.98	6	2.30	0.19
	Li	1	0.78	6	2.10	0.23
	Ba	2	1.43	8	2.86	0.24
	Pb	2	1.32	8	2.74	0.27
	Sr	2	1.27	8	2.69	0.28
	Ca	2	1.06	8	2.48	0.33
	Mn	2	0.91	6	2.23	0.40
	Fe	2	0.83	6	2.15	0.43
Intermediate	Mg	2	0.78	6	2.10	0.45
				4	1.96	0.53
	Zr	4	0.87	8	2.28	0.77
	Be	2	0.34	4	1.53	0.86
	Fe	3	0.67	6	1.99	0.76
				4	1.88	0.85
	Al	3	0.57	6	1.89	0.84
				4	1.77	0.96
	Ti	4	0.64	6	1.96	1.04
Network Former	B	3	0.20	4	1.50	1.34
	Ge	4	0.44	4	1.66	1.45
	Si	4	0.39	4	1.60	1.57
	P	5	0.34	4	1.55	2.10
	B	3	0.20	3	1.36	1.63

Next week

Course Outine:

Week 3: Physical properties and measurement/calculate

- Density
- Other
- *Case studies from international publications*

Structural properties, advanced measurement/calculation analysis

- XRD
- Molar volume
- FTIR

Case studies from international publications