Precursor Methods

Intimate mixing of components in solution, precipitation, filtration, washing, drying, calcination

- 💣 **High degree of homogenization**
- 💣 **Large contact area**
- 💣 **Reduction of diffusion distances**
- 💣 **Faster reaction rates**
- 💣 **Lower reaction temperatures**
- 💣 **Metastable phases, smaller grain size, larger surface area**

Coprecipitation Method

Coprecipitation applicable to nitrates, acetates, oxalates, hydroxides, alkoxides, beta-diketonates

Requires: **similar salt solubilities**
                       similar precipitation rates
                       no supersaturation

Washing: **water, organic solvents**

Drying: **evaporation**
                       azeotropic distillation
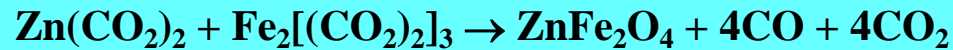   **freeze-drying**

Disadvantage: difficult to prepare high purity, accurate stoichiometric phases if solubilities do not match
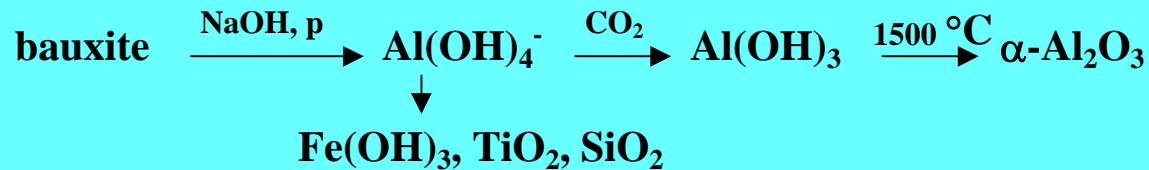
Coprecipitation Method

Spinels

oxalates: $Zn(CO_2)_2$/$Fe_2[(CO_2)_2]_3$/H_2O 1 : 1 mixing, H_2O evaporation, salts coprecipitation
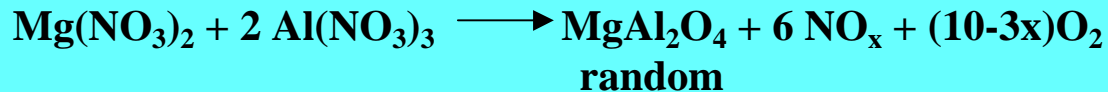**Solid-solution mixing on atomic scale, filter, calcine in air**

$$Zn(CO_2)_2 + Fe_2[(CO_2)_2]_3 \rightarrow ZnFe_2O_4 + 4CO + 4CO_2$$

Al_2O_3 Bayer Process

$$\text{bauxite} \xrightarrow{\text{NaOH, p}} Al(OH)_4^- \xrightarrow{CO_2} Al(OH)_3 \xrightarrow{1500\ °C} \alpha\text{-}Al_2O_3$$

$$\downarrow$$

$$Fe(OH)_3, TiO_2, SiO_2$$

$BaTiO_3$
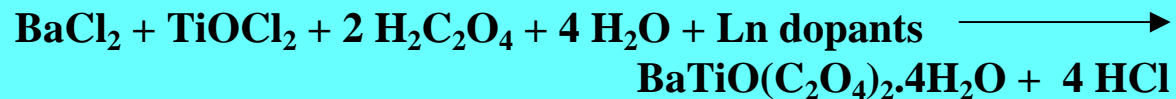
$BaCl_2 + TiOCl_2 + 2\ H_2C_2O_4 + 4\ H_2O + Ln\ dopants \longrightarrow$
$$BaTiO(C_2O_4)_2.4H_2O +\ 4\ HCl$$
filtration, washing, drying, calcination @ 730 °C

Coprecipitation Method

Spinel

$Al(NO_3)_3 + Mg(NO_3)_2 + H_2O$ **freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T**

$$Mg(NO_3)_2 + 2\ Al(NO_3)_3 \longrightarrow MgAl_2O_4 + 6\ NO_x + (10-3x)O_2$$
random

Ruby
Ion exchange
$$Al(NO_3)_3 + Cr(NO_3)_3 \longrightarrow Al(OH)_3 + Cr(OH)_3\ \text{sol}$$
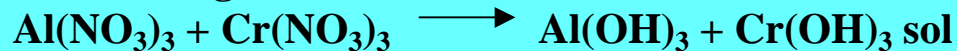
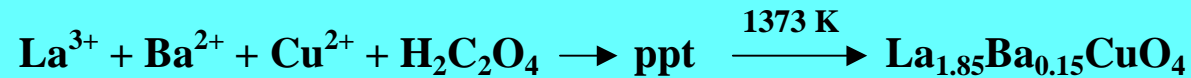**freeze drying gives solid (Al/Cr)(OH)$_3$ @ LN$_2$ temperature, 5 Pa anealing @ 950 °C for 2.5 h gives solid solution $Al_{2-x}Cr_xO_3$**

Zirconia

$$ZrSiO_4(\text{zircon}) + NaOH \longrightarrow Na_2ZrO_3 + Na_2SiO_3 \xrightarrow{HCl}$$

$$ZrOCl_2 \xrightarrow{OH^-,\ YCl_3} Zr(OH)_4 / Y(OH)_3 \xrightarrow[\text{calcination}]{\text{azeot. dist.}} \text{nano-Y/ZrO}_2$$

4
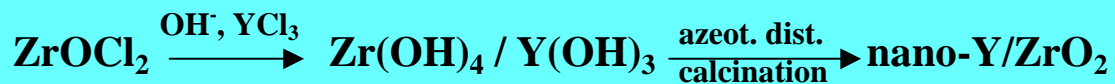
Coprecipitation Method

High-T_c Superconductors

$$La^{3+} + Ba^{2+} + Cu^{2+} + H_2C_2O_4 \longrightarrow ppt \xrightarrow{\text{1373 K}} La_{1.85}Ba_{0.15}CuO_4$$

Magnetic garnets, tunable magnetic materials

$$Y(NO_3)_3 + Gd(NO_3)_3 + FeCl_3 + NaOH \rightarrow Y_xGd_{3-x}Fe_5O_{12}$$
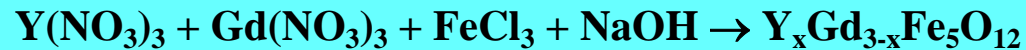
Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes $REFeO_3$ perovskite impurity
Isomorphous replacement of Y^{3+} for Gd^{3+} on dodecahedral sites, solid solution, similar rare earth ionic radii
complete family accessible, $0 < x < 3$, $2Fe^{3+}$ O_h sites, $3Fe^{3+}$ T_d sites, $3RE^{3+}$ dodecahedral sites

Pechini and Citrate Gel Method

Aqueous solution of metal ions

Chelate formation with citric acid
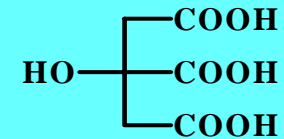
Polyesterification with polyfunctional alcohol on heating

further heating leads to resin, transparent glassy gel
calcination provides oxide powder

control of stoichiometry by initial reagent ratio

complex compositions, mixture of metal ions
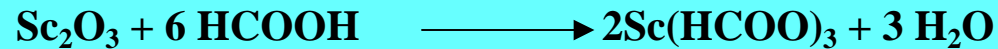
good homogeneity, mixing at the molecular level

low firing temperatures

HO——————COOH
 ————COOH
 ————COOH

6

Pechini and Citrate Gel Method

$BaTiO_3$
by conventional powder method at 1200 °C

Ba^{2+} + $Ti(O^iPr)_4$ + citric acid at 650 °C

$$Sc_2O_3 + 6\ HCOOH \longrightarrow 2Sc(HCOO)_3 + 3\ H_2O$$
$$MnCO_3 + 2\ HCOOH \longrightarrow Mn(HCOO)_2 + CO_2 + H_2O$$

added to citric acid, water removal, calcination @ 690 °C gives
$ScMnO_3$
without citric acid only mixture of Sc_2O_3 and Mn_2O_3 is formed

Double Salt Precursors

Double salts of known and controlled stoichiometry such as:
$Ni_3Fe_6(CH_3COO)_{17}O_3(OH).12Py$

Burn off organics 200-300 ºC, then 1000 ºC in air for 2-3 days
Product highly crystalline phase pure $NiFe_2O_4$ spinel
**Good way to make chromite spinels, important tunable magnetic materials**
Juggling the electronic-magnetic properties of the O_h and T_d ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, ºC
$MgCr_2O_4$	$(NH_4)_2Mg(CrO_4)_2.6H_2O$	1100-1200
$NiCr_2O_4$	$(NH_4)_2Ni(CrO_4)_2.6H_2O$	1100
$MnCr_2O_4$	$MnCr_2O_7.4C_5H_5N$	1100
$CoCr_2O_4$	$CoCr_2O_7.4C_5H_5N$	1200
$CuCr_2O_4$	$(NH_4)_2Cu(CrO_4)_2.2NH_3$	700-800
$ZnCr_2O_4$	$(NH_4)_2Zn(CrO_4)_2. 2NH_3$	1400
$FeCr_2O_4$	$(NH_4)_2Fe(CrO_4)_2$	1150

Single Source Precursor

Compounds containing desired elements in a proper stoichiometric ratio

Easy chemical pathway for ligand removal

$$M-O-Si(O...)_3 \longrightarrow H_2O \; + \; (M-O-SiO_3)_x$$
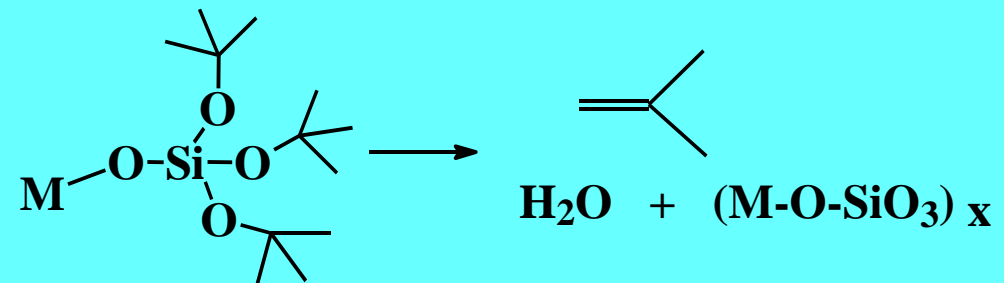
Vegard's Law

Vegard law behavior:

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

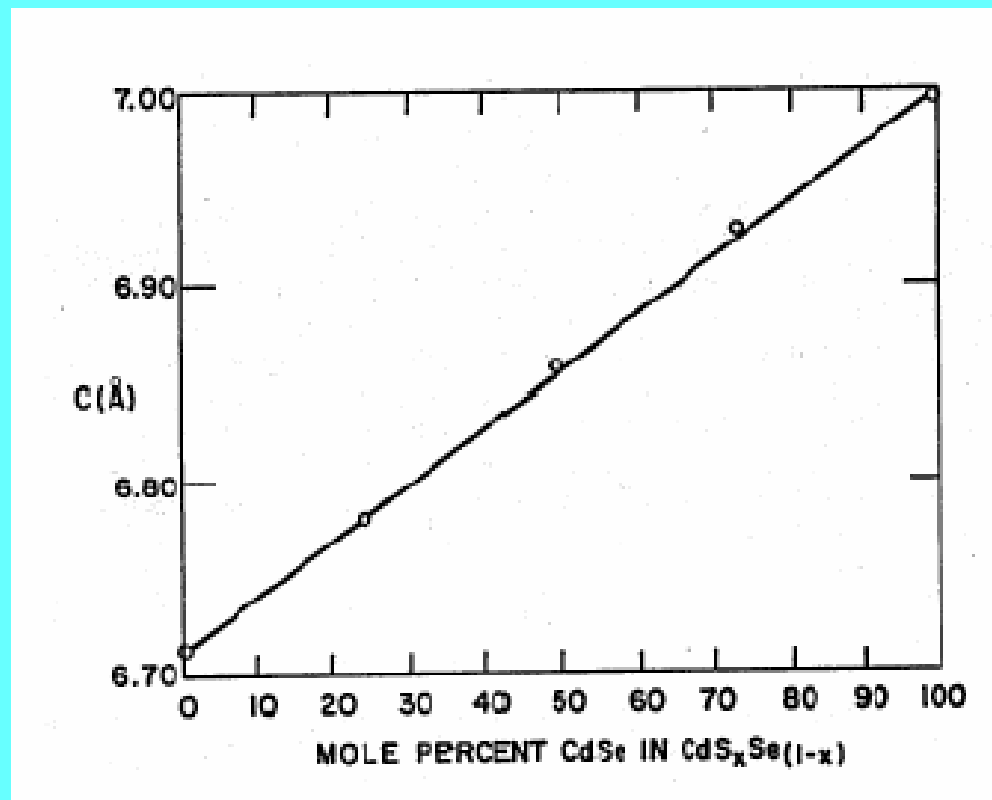**The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard's law**

The lattice parameter of a solid solution alloy will be given by a linear dependence of lattice parameter on composition:

$a(A_{1-x}B_x) = x\, a(B) + (1-x)\, a(A)$

Vegard's Law

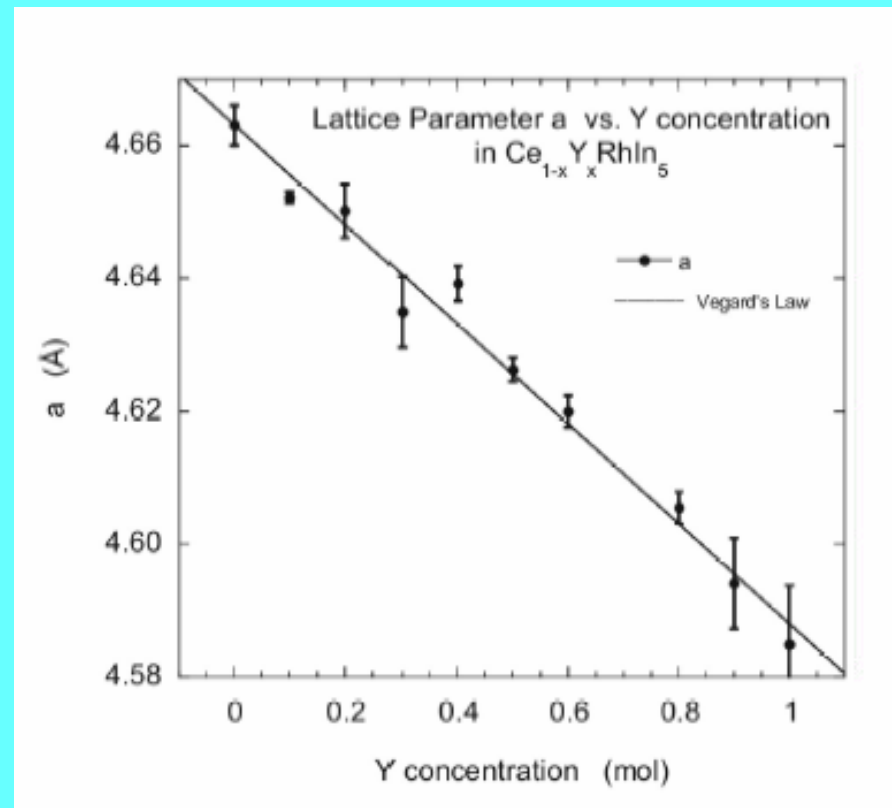$$c(CdSe_{1-x}S_x) = x\ c(CdS) + (1-x)\ c(CdSe)$$

Vegard's Law

$$P\ (Y_xCe_{1-x}RhIn_5) = x\ P\ (Y_xCe_{1-x}RhIn_5) + (1-x)\ P\ (Y_xCe_{1-x}RhIn_5)$$

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

Tetragonal lattice constant a
as a function of
Y concentration x
for the $Ce_{1-x}Y_xRhIn_5$ system

Lattice Parameter a vs. Y concentration in $Ce_{1-x}Y_xRhIn_5$

Vegard's Law

A linear relationship exists between the concentration of the substitute element and the size of the lattice parameters

The direction of the linear relationship, increasing or decreasing, depends upon the system being analyzed

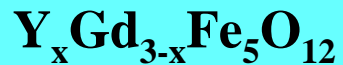As the concentration of Y is increased, lattice constant a decreases, implying the cell is contracting along the a axis

Vegard's Law

Vegard law behavior:

$$P\ (Y_xGd_{3-x}Fe_5O_{12}) = x/3\ P\ (Y_3Fe_5O_{12}) + (3-x)/3\ P\ (Gd_3Fe_5O_{12})$$

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

Tunable magnetic properties by tuning the x value in the binary garnet
$Y_xGd_{3-x}Fe_5O_{12}$
3 T_d Fe^{3+} sites, 5 UPEs
2 O_h Fe^{3+} sites, 5UPEs
Ferrimagnetically coupled material, oppositely aligned electron spins
on the T_d and O_h Fe^{3+} magnetic sublattices
Counting spins $Y_3Fe_5O_{12}$ ferrimagnetic at low T: 3 x 5 - 2 x 5 = 5UPEs
Counting spins $Gd_3Fe_5O_{12}$ ferrimagnetic at low T: 3 x 7 - 3 x 5 + 2 x 5 = 16 UPEs
$Y_xGd_{3-x}Fe_5O_{12}$ creates a tunable magnetic garnet that is strongly
temperature and composition dependent,
applications in permanent magnets, magnetic recording media,
magnetic bubble memories and so forth, similar concepts apply to
magnetic spinels

Flux Method

Molten salts (inert or reactive), oxides, metals
MNO_3, MOH, (M = alkali metal)
FLINAK: LiF-NaF-KF
M_2Q_x (M = alkali metal, Q = S, Se, Te)

molten salts ionic, low mp, eutectics, completely ionized
act as solvents or reactants, T = 250-550 °C
enhanced diffusion, reduced reaction temperatures in comparison with
powder method

products finely divided solids, high surface area (SA)
slow cooling to grow crystals
separation of water insoluble product from a water soluble flux

incorporation of the molten salt ions in product prevented by using
salts with ions of much different sizes than the ones in the product
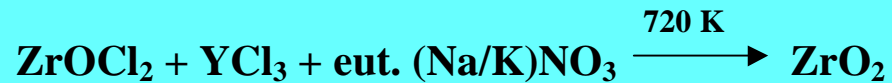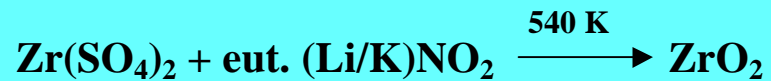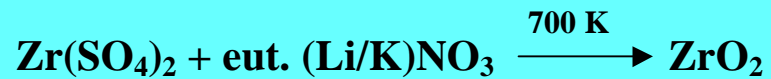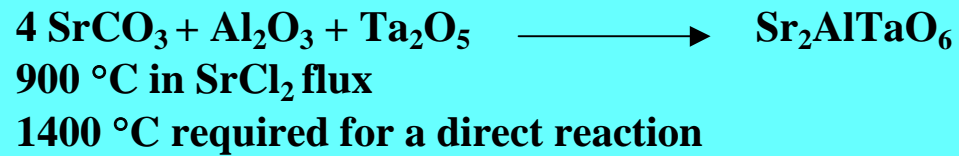($PbZrO_3$ in a B_2O_3 flux)

Flux Method

Lux-Flood formalism
oxide = strong base
acid = oxide acceptor
base = oxide donor

$$A + OB \longrightarrow AO + B$$

$$Zr(SO_4)_2 + eut. \ (Li/K)NO_3 \xrightarrow{700 \ K} ZrO_2$$

$$Zr(SO_4)_2 + eut. \ (Li/K)NO_2 \xrightarrow{540 \ K} ZrO_2$$

$$ZrOCl_2 + eut. \ (Na/K)NO_3 \xrightarrow{520 \ K} ZrO_2 \ amorph. \longrightarrow t\text{-} ZrO_2$$

$$ZrOCl_2 + YCl_3 + eut. \ (Na/K)NO_3 \xrightarrow{720 \ K} ZrO_2$$

$$BaCO_3 + SrCO_3 + TiO_2 + eut. \ (Na/K)OH$$

$$\xrightarrow{570 \ K} cubic\text{-}Ba_{0.75} Sr_{0.25}TiO_3$$

Flux Method

fly ash (aluminosilicates)

NaOH, NH_4F, $NaNO_3$ $\longrightarrow$ zeolites (sodalite, cancrinite)

$NH_4H_2PO_4$ + (Na/K)NO_3 + M(NO$_3$)$_2$ $\longrightarrow$ (Na/K)MPO$_4$

4 $SrCO_3$ + Al_2O_3 + Ta_2O_5 $\longrightarrow$ Sr_2AlTaO_6
900 °C in $SrCl_2$ flux
1400 °C required for a direct reaction

K_2Te_x + Cu $\longrightarrow$ $K_2Cu_5Te_5$ K_2Te_x reactive flux, 350 °C

Flux Method

Electrolysis in molten salts

Reduction of TiO_2 pellets to Ti sponge in a $CaCl_2$ melt at 950 °C

O^{2-} dissolves in $CaCl_2$, diffuses to the graphite anode
insulating $TiO_2 \longrightarrow TiO_{2-x}$ conductive
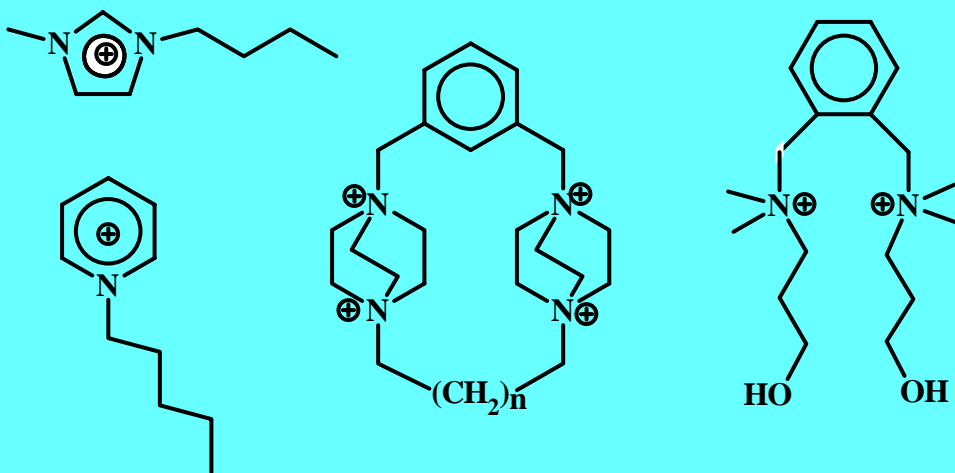
graphite anode
anodic oxidation $2\ O^{2-} \longrightarrow O_2\ + 4\ e^-$
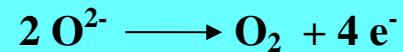
cathode TiO_2 pellet
cathodic reduction $Ti^{4+}\ + 4\ e^- \longrightarrow Ti$
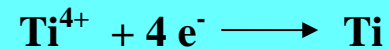
Ionic Liquids

Organic cations (containing N, P)

Inorganic anions: Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, PF_6^-, $SnCl_3^-$, BCl_3^-, BF_4^-, NO_3^-, $OSO_2CF_3^-$ (triflate), $CH_3C_6H_4SO_3^-$, $N(SO_2CF_3)_2^-$, PO_4^{3-}
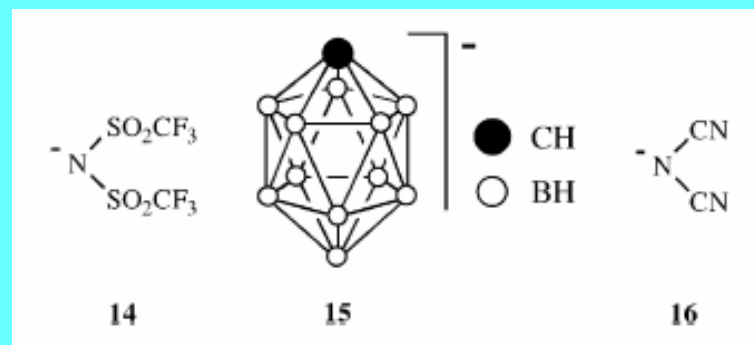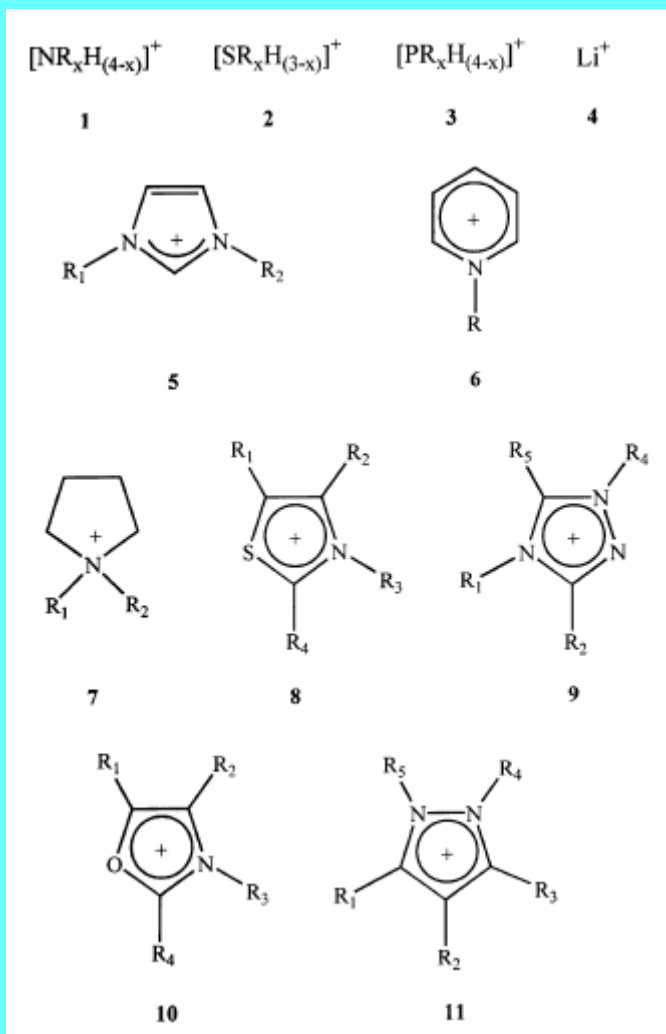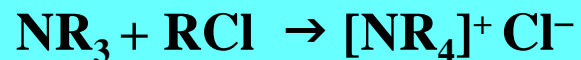
Ionic Liquids

Oldest known (1914) : $EtNH_3^+NO_3^-$ mp 12 °C

➔ Liquids at room temperature or low mp

➔ Thermal operating range from -40 °C to 400 °C

➔ Higly polar, noncoordinating, completely ionized

➔ Nonvolatile – no detectable vapor pressure

➔ Nonflamable, nonexplosive, nonoxidizing, high thermal stability

➔ Electrochemical window > 4V (not oxidized or reduced)

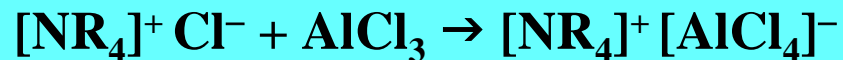➔ Immiscible with organic solvents

➔ Hydrophobic IL immiscible with water

Ionic Liquids

Synthesis of Ionic Liquids

$NR_3 + RCl \rightarrow [NR_4]^+ Cl^-$

Aluminates
$[NR_4]^+ Cl^- + AlCl_3 \rightarrow [NR_4]^+ [AlCl_4]^-$

Metal halide elimination
$[NR_4]^+ Cl^- + MA \rightarrow MCl + [NR_4]^+ A^-$

Reaction with an acid
$[NR_4]^+ Cl^- + HA \rightarrow HCl + [NR_4]^+ A^-$

Ion exchange
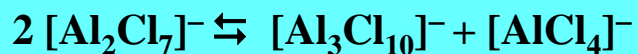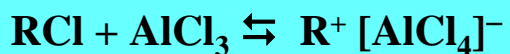$[NR_4]^+ Cl^- + Ion\ exchanger\ A \rightarrow [NR_4]^+ A^-$

23

Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

High sensitivity to moisture – handling under vacuum
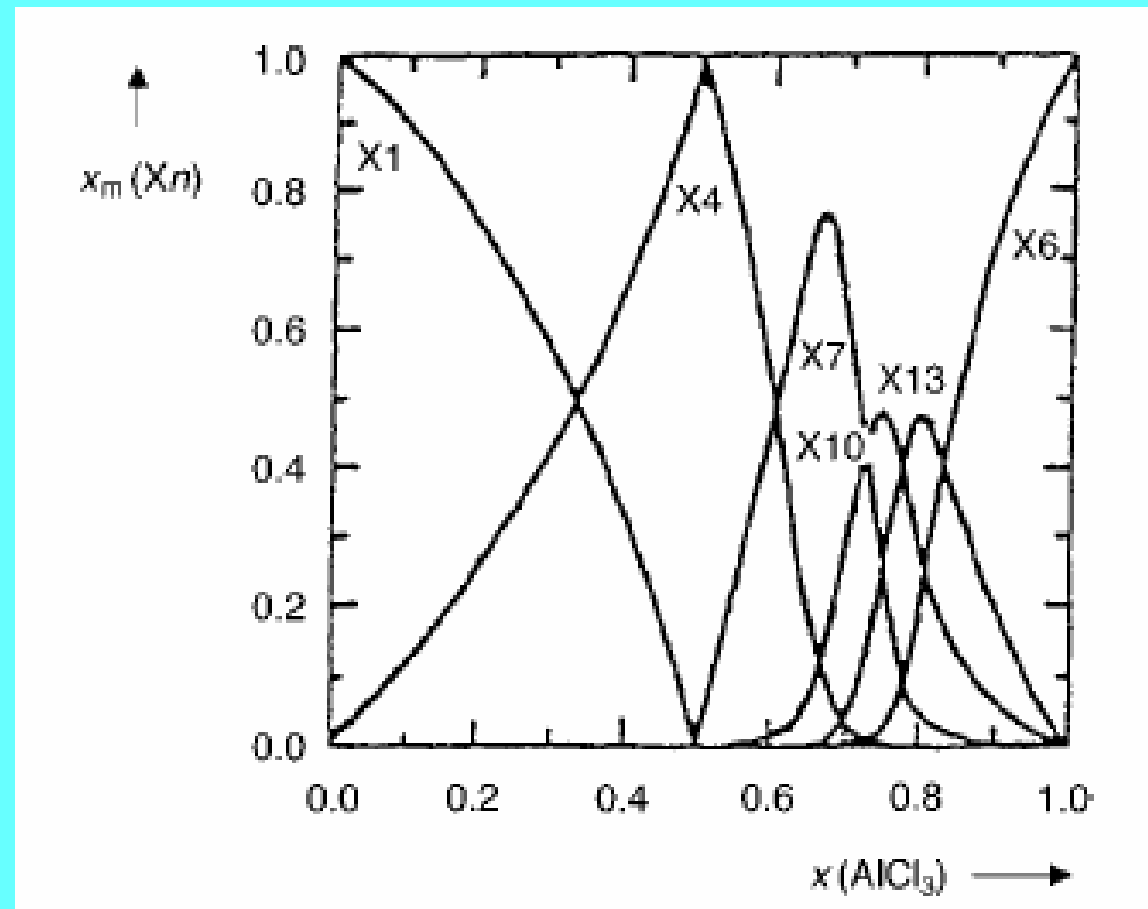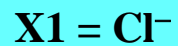**or inert atmosphere in glass/teflon**

$RCl + AlCl_3 \leftrightarrows R^+ [AlCl_4]^-$

$2\ [AlCl_4]^- \leftrightarrows [Al_2Cl_7]^- + Cl^-$ autosolvolysis $K_{eq} = 10^{-16}$ to 10^{-17} at 40 ºC

$2\ [Al_2Cl_7]^- \leftrightarrows [Al_3Cl_{10}]^- + [AlCl_4]^-$

Acidic: excess of $AlCl_3$ as $[Al_2Cl_7]^-$ **$x(AlCl_3) > 0.5$**

Basic: excess of Cl^-   **$x(AlCl_3) < 0.5$**

Neutral: $[AlCl_4]^-$ **$x(AlCl_3) = 0.5$**
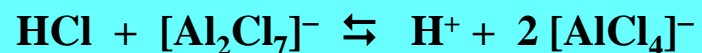
Equilibria in Halogenoaluminate(III) IL
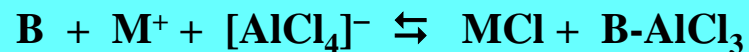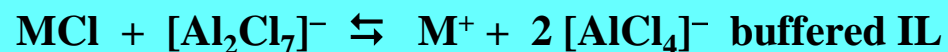
Equilibria in IL

X1 = Cl^-
X4 = $[AlCl_4]^-$
X7 = $[Al_2Cl_7]^-$
X10 = $[Al_3Cl_{10}]^-$
X13 = $[Al_4Cl_{13}]^-$
X6 = Al_2Cl_6

Halogenoaluminate(III) Ionic Liquids

$2\,[AlCl_4]^- \rightleftharpoons [Al_2Cl_7]^- + Cl^-$ autosolvolysis $K_{eq} = 10^{-16}$ to 10^{-17} at 40 ºC

Acidic IL with an excess of $AlCl_3$

$HCl + [Al_2Cl_7]^- \rightleftharpoons H^+ + 2\,[AlCl_4]^-$

Proton extremely poorly solvated = high reactivity

Superacid   [EMIM]Cl/$AlCl_3$/HCl $H_0 = -19$ (HSO$_3$F: $H_0 = -15$)

Latent acidity

$MCl + [Al_2Cl_7]^- \rightleftharpoons M^+ + 2\,[AlCl_4]^-$ **buffered IL**

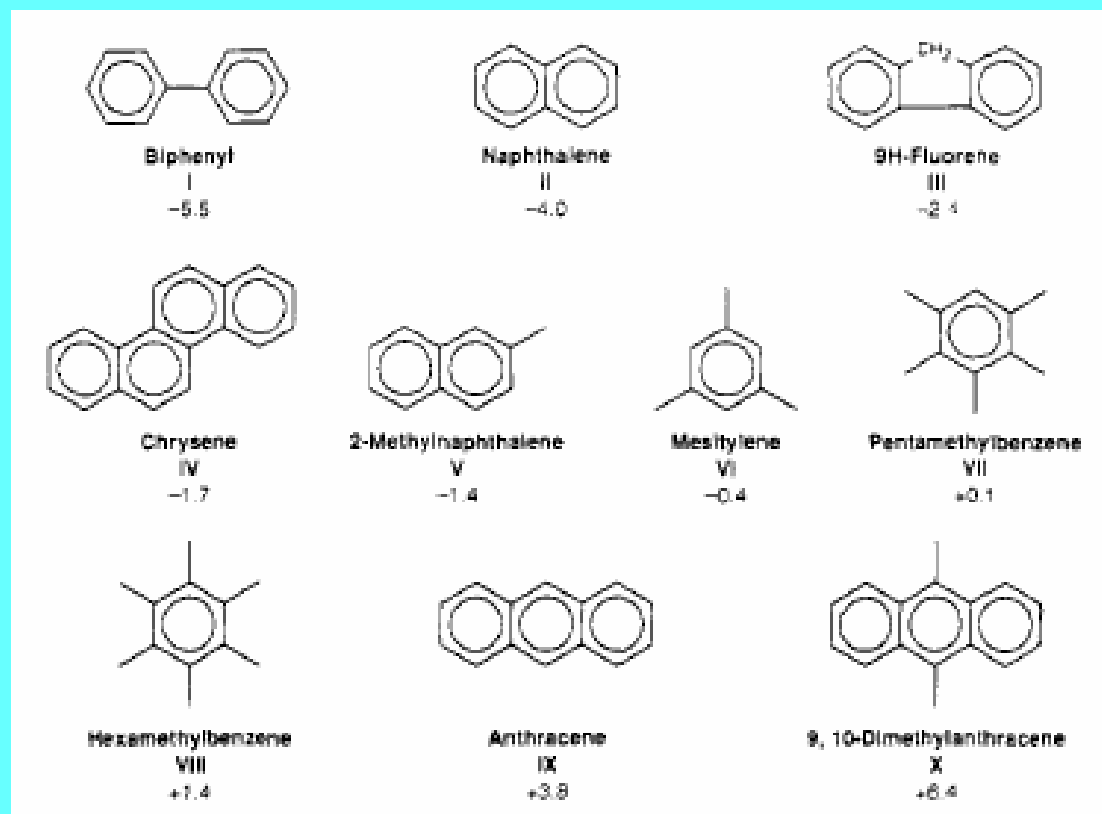$B + M^+ + [AlCl_4]^- \rightleftharpoons MCl + B\text{-}AlCl_3$
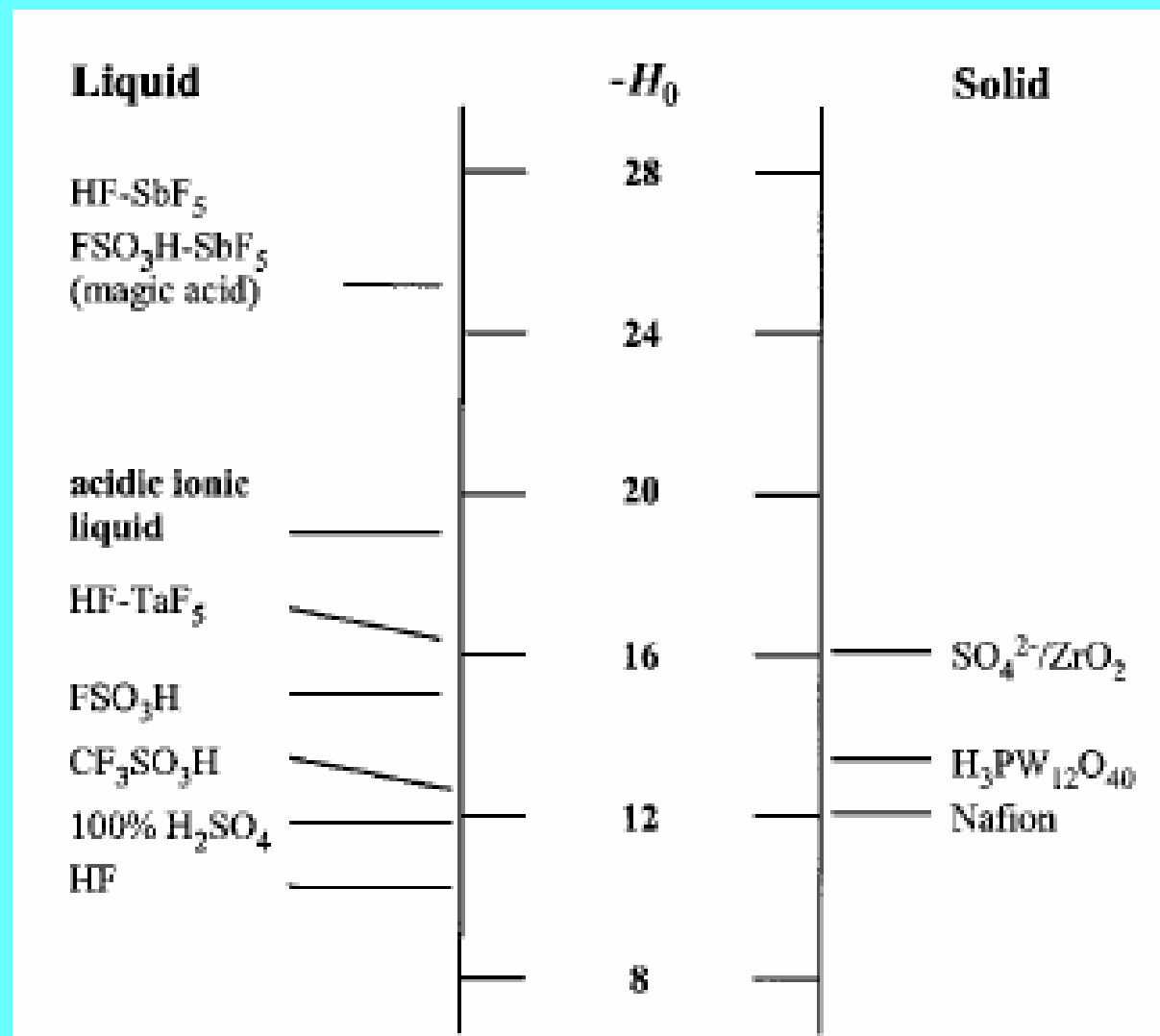
Superacidity

Superacidic [EMIM]Cl/AlCl$_3$/HCl

I = not protonated
II = slightly protonated
III and IV = 10-20 %
V = 75-90%
VI-VIII = nearly completely
IX and X = completely

log K$_b$ in HF

Ionic Liquids

Completely inorganic ionic liquids

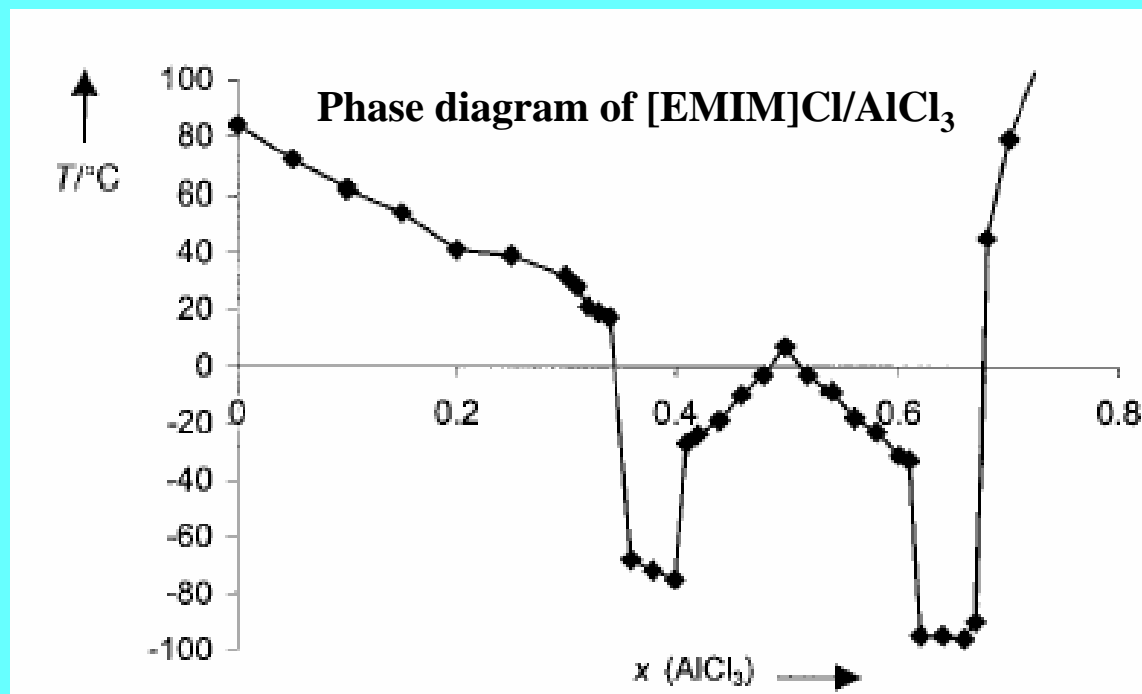| Compound	mp (K)	Compound	mp (K)
$Na_{13}[La(TiW_{11}O_{39})_2]$	253.0	$Na_{13}[Tm(TiW_{11}O_{39})_2]$	260.2
$Na_{13}[Ce(TiW_{11}O_{39})_2]$	263.0	$Na_{13}[Yb(TiW_{11}O_{39})_2]$	267.2
$Na_{13}[Pr(TiW_{11}O_{39})_2]$	253.0	$Na_5[CrTiW_{11}O_{39}]$	261.5
$Na_{13}[Sm(TiW_{11}O_{39})_2]$	256.0	$Na_5[MnTiW_{11}O_{39}]$	253.0
$Na_{13}[Gd(TiW_{11}O_{39})_2]$	265.1	$Na_5[FeTiW_{11}O_{39}]$	257.6
$Na_{13}[Dy(TiW_{11}O_{39})_2]$	265.2	$Na_6[ZnTiW_{11}O_{39}]$	257.4
$Na_{13}[Er(TiW_{11}O_{39})_2]$	261.0		

Melting Point of Ionic Liquids

Melting point is influenced by:

Cation – low symmetry, weak imtermolecular interactions, good distribution of charge
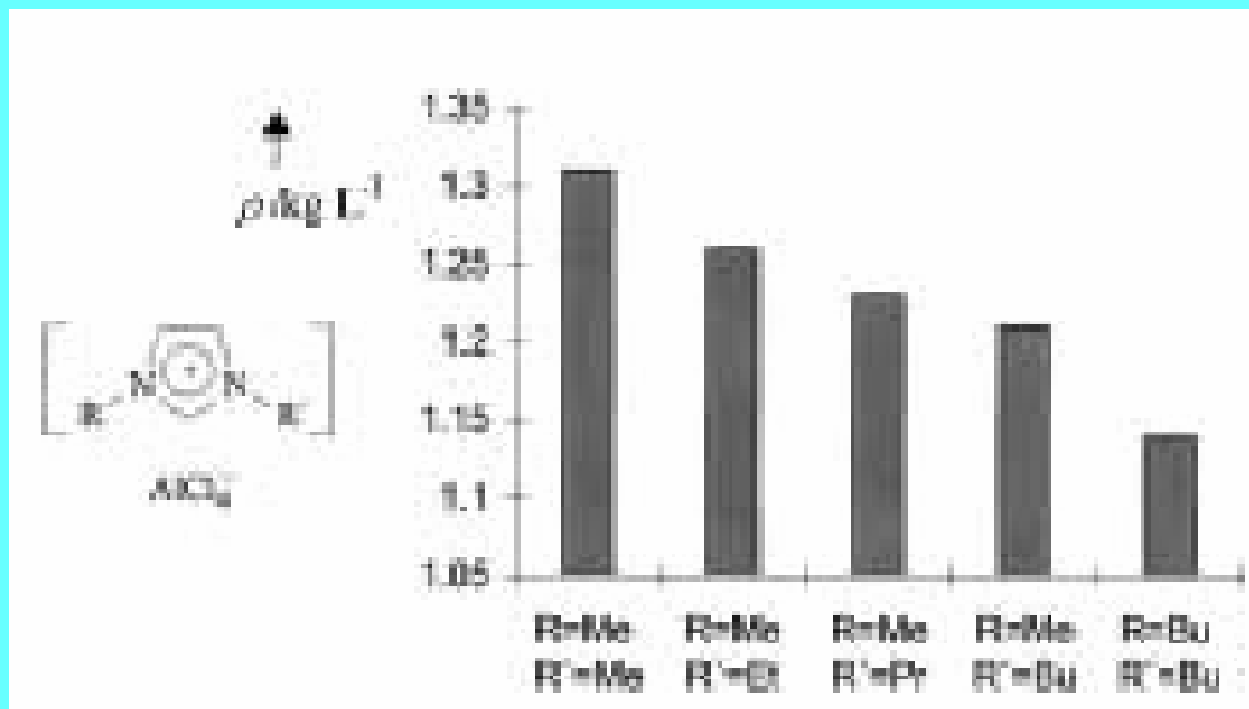**Anion – increasing size leads to lower mp**
Composition – Phase diagram

Phase diagram of [EMIM]Cl/AlCl$_3$

Melting Point of Ionic Liquids

R	X	mp/°C
Me	Cl	125
Et	Cl	87
n-Bu	Cl	65
Et	NO_3	38
Et	$AlCl_4$	7
Et	BF_4	6
Et	CF_3SO_3	−9
Et	$(CF_3SO_3)_2N$	−3
Et	CF_3CO_2	−14
n-Bu	CF_3SO_3	16

Density of Ionic Liquids

The density of IL decreases as the bulkiness of the organic cation increases:

Viscosity of Ionic Liquids

The viscosity of IL depends on:

van der Waals interactions

H-bonding

Anion $[A]^-$	η [cP]
$CF_3SO_3^-$	90
$n\text{-}C_4F_9SO_3^-$	373
CF_3COO^-	73
$n\text{-}C_3F_7COO^-$	182
$(CF_3SO_2)_2N^-$	52

Solubility in/of Ionic Liquids

Variation of the alkyl group
Increasing nonpolar character of the cation increases solubility of
nonpolar solutes.

Water solubility depends on the anion
water-soluble [BMIM] Br, CF_3COO, CF_3SO_3
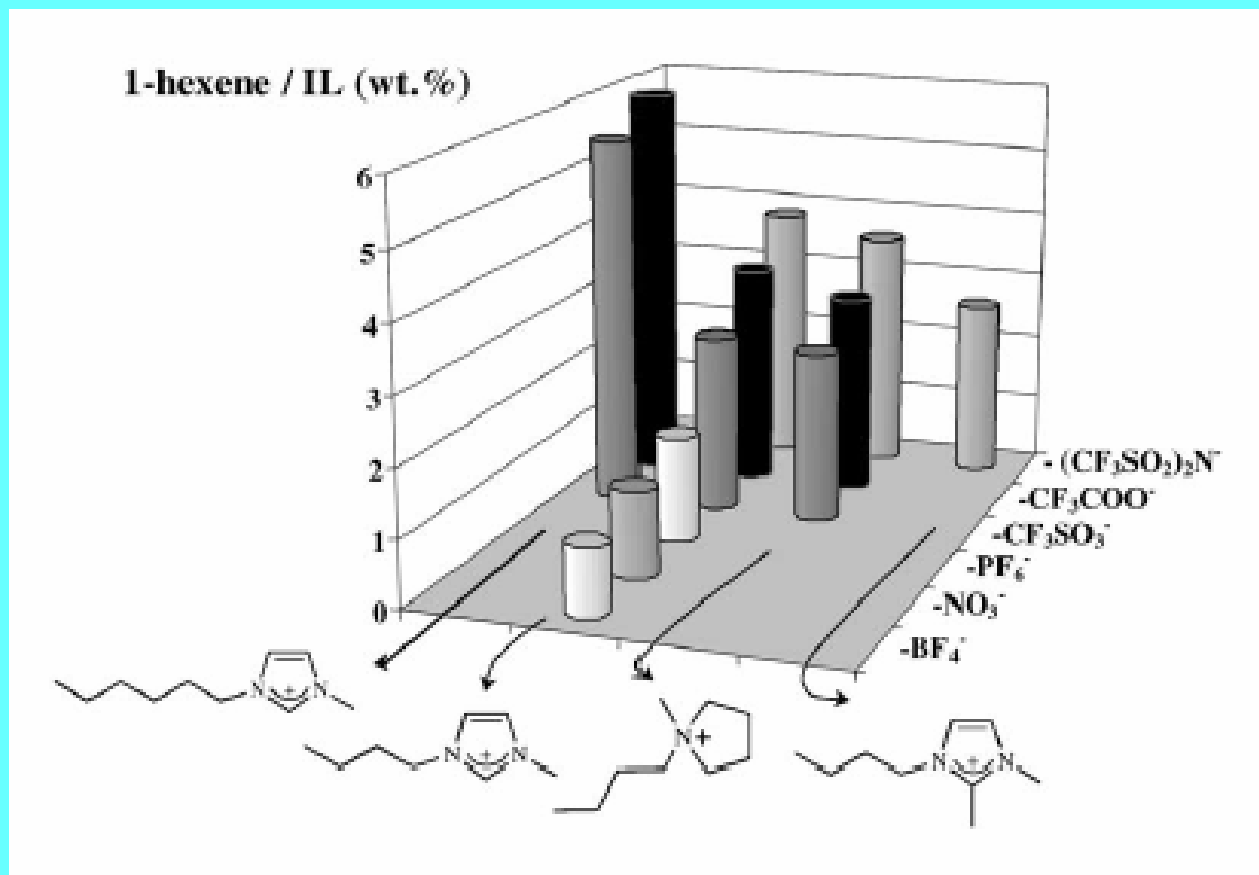Water-immiscilble [BMIM] PF_6 $(CF_3SO_2)_2N$

IL miscible with organic solvent IF their dielectric constant is above a
certain limit given by the cation/anion combination

Polarity by $E_{(T)}(30)$ scale

[EtNH$_3$][NO$_3$]   0.95   between CF_3CH_2OH and water

[BMIM] PF_6 as methanol

Solubility in/of Ionic Liquids

Applications of Ionic Liquids

Electrodeposition of metals and alloys (also nanoscopic)

Al, $CoAl_x$, $CuAl_x$, $FeAl_x$, $AlTi_x$

Semiconductors Si, Ge, GaAs, InSb, CdTe

Electrodeposition of a Bi-Sr-Ca-Cu alloy (precursor to SC oxides)

Melt of MeEtImCl at 120 °C

$BiCl_3$, $SrCl_2$, $CaCl_2$, $CuCl_2$ dissolve well

Constituent	$BiCl_3$	$SrCl_2$	$CaCl_2$	$CuCl_2$
Concentration ($mol\ kg^{-1}$ MeEtImCl)	0.068	0.50	0.18	0.050

Substrate Al
-1.72 V vs the Ag/Ag^+ reference electrode

Applications of Ionic Liquids

Biphasic solvent systems

Preparation of aerogels

$$2\ HCOOH\ +\ Si(OMe)_4\ \longrightarrow\ ag\text{-}SiO_2\ +\ 2\ MeOH\ +\ 2\ HCOOMe$$

Natural gas sweetening (H_2S, CO_2 removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U^{4+} oxidized to U^{6+})

Extraction

Enyzme activity

Applications of Ionic Liquids

Olefin polymerization

Ethene + $TiCl_4$ + $AlEtCl_2$ in acidic IL

Ethene + Cp_2TiCl_2 + $Al_2Me_3Cl_3$ in acidic IL

$$Cp_2TiCl_2 + [cation]^+[Al_2Cl_7]^- \rightleftharpoons [Cp_2TiCl]^+ + [cation]^+ + 2[AlCl_4]^-$$

Olefin hydrogenation

Cyclohexene + H_2 + $[RhCl(PPh_3)_3]$ (Wilkinson's catalyst)

Sound

Sound = pressure wave, periodic compression/expansion cycles traveling through a medium possessing elastic properties (gas, liqud, solid)

Liquids and gases – longitudinal pressure waves – compression/rarefaction
Solids – longitudinal and transverse waves

The energy is propagated as deformations in the media

The molecules oscillate about their original positions and are not propagated

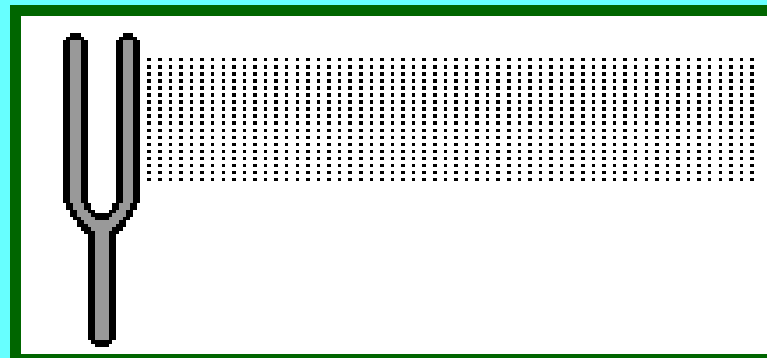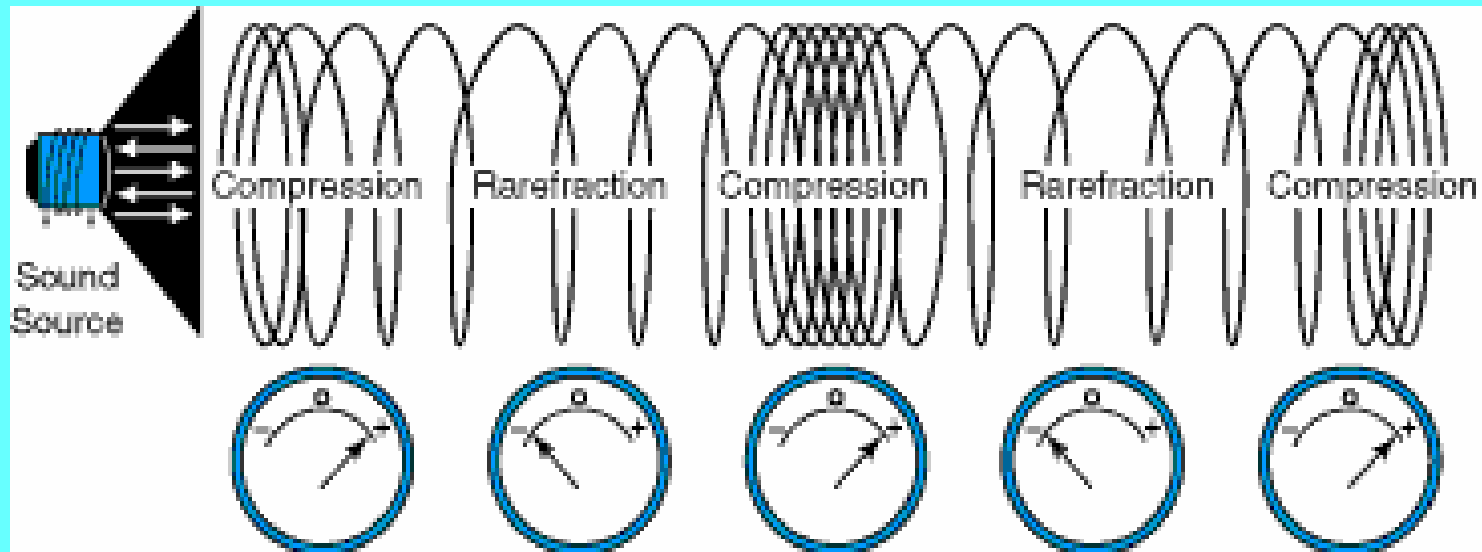The propagation of a sound wave = the transfer of vibrations from one molecule to another
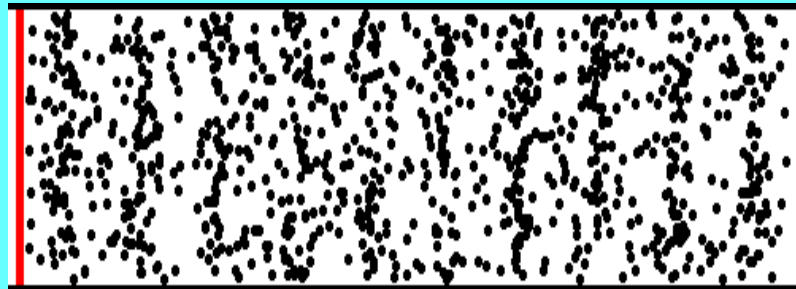
Sound

In a typical liquid, the speed of sound decreases as the temperature increases, at all temperatures.

The speed of sound in water is almost five times greater than that in air (340 m s^{-1})

Longitudinal Pressure Waves

Acoustic Pressure

$$P_a = P_A \sin 2\pi f t$$

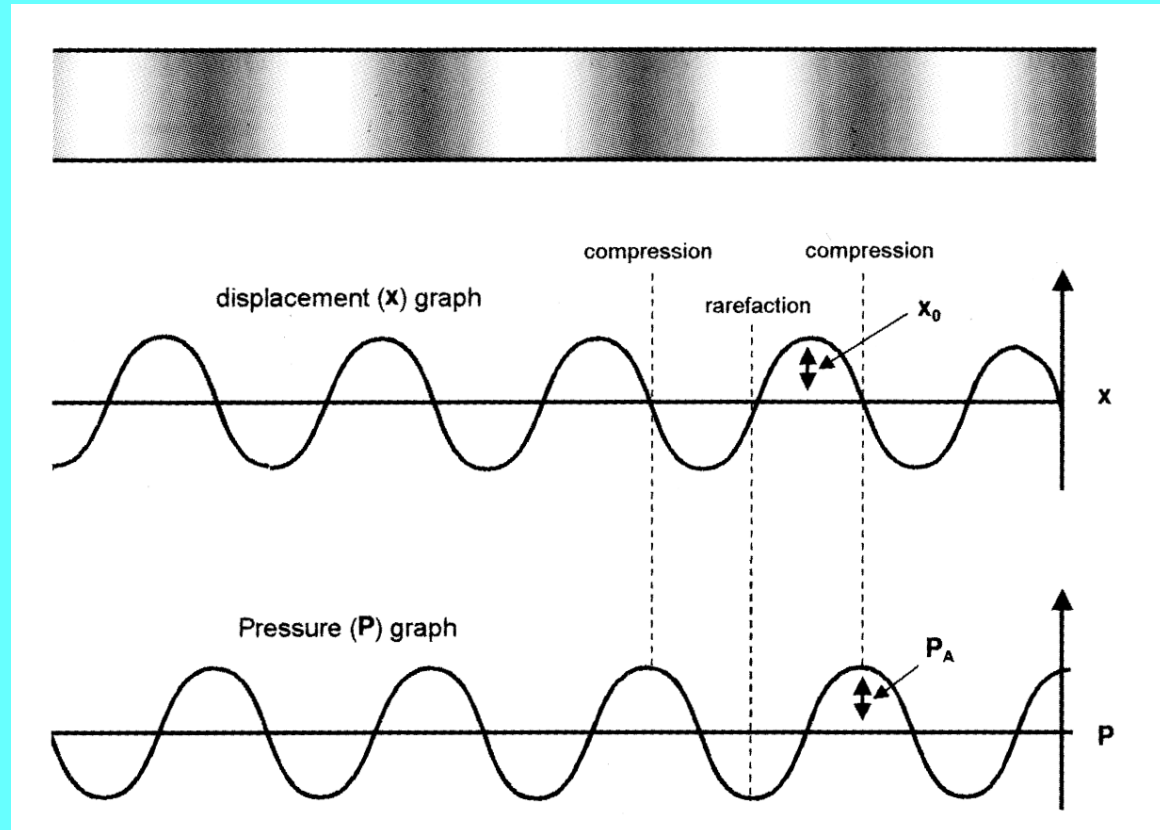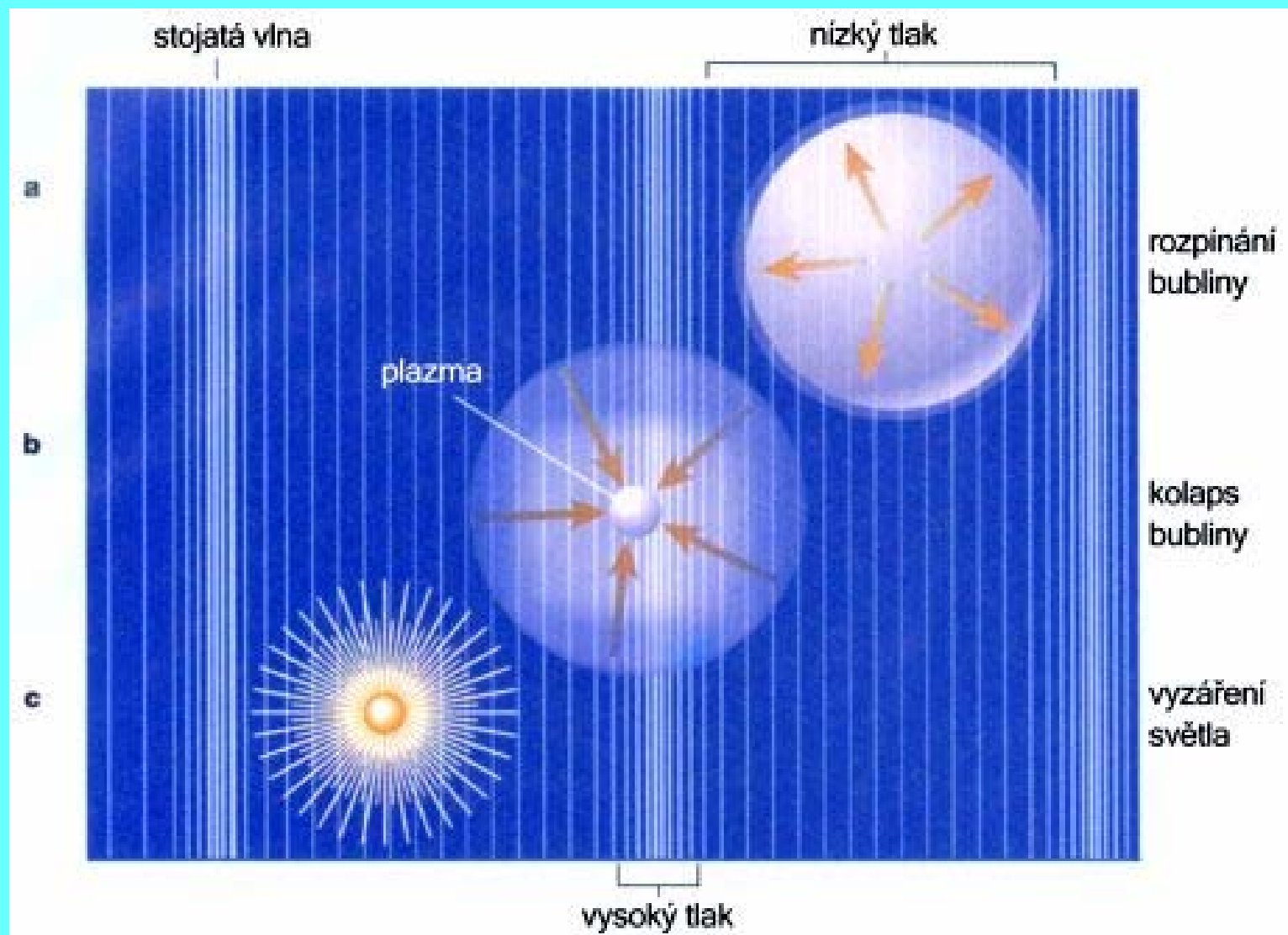P_a acoustic pressure

P_A pressure amplitude

f sound frequency

$c = \lambda f$

(for 20 kHz, $\lambda = 7.5$ cm)

$$P_{total} = P_a + P_h$$

P_h hydrostatic pressure

42

stojatá vlna

nízký tlak

a

rozpínání bubliny

plazma

b

kolaps bubliny

c

vyzáření světla

vysoký tlak

43

Acoustic Pressure

$$P_A = \sqrt{2I\rho c}$$

P_A = driving pressure amplitude [Pa]

I = irradiation intensity [W m^{-2}]

ρ = liquid density [kg m^{-3}]

c = sound velocity in liquid [m s^{-1}]

(Water 1482 m s^{-1})

Speed of Sound

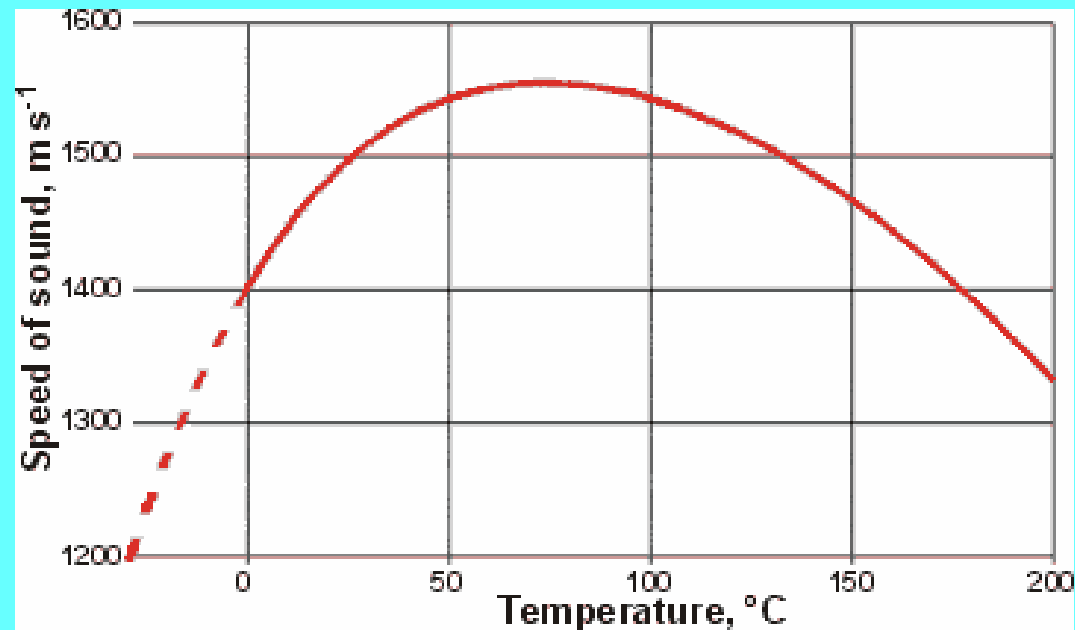| Substance	Speed of sound $[\text{m s}^{-1}]$
Air	343
Helium	965
Water	1482
Lead	1960
Steel	5960
Granite	6000

The speed of sound

The speed of sound (u)

$$u^2 = 1/\kappa_S\rho = [\partial P/\partial \rho]_S \sim 1/(<(\P V)2>)$$

where κ_S is the adiabatic compressibility
ρ is the density and P the pressure.

Sound Intensity

$$\text{Sound Intensity} = \text{Power} / \text{area} = \text{Watts/m}^2$$

Source of Sound	Intensity (W/m2)	Sound level (dB)
Jet Airplane 30 m away	10^2	140
Air-raid Siren, nearby	1	120
Threshold of Pain	10^{-1}	120
Concert	$\sim 10^{-1}$	115
Riveter	10^{-3}	100
Busy Traffic	10^{-5}	70
Normal Conversations	10^{-6}	60
Whisper	10^{-10}	20
Threshold of Hearing	10^{-12}	0

0 dB (10^{-12} W/m^2)

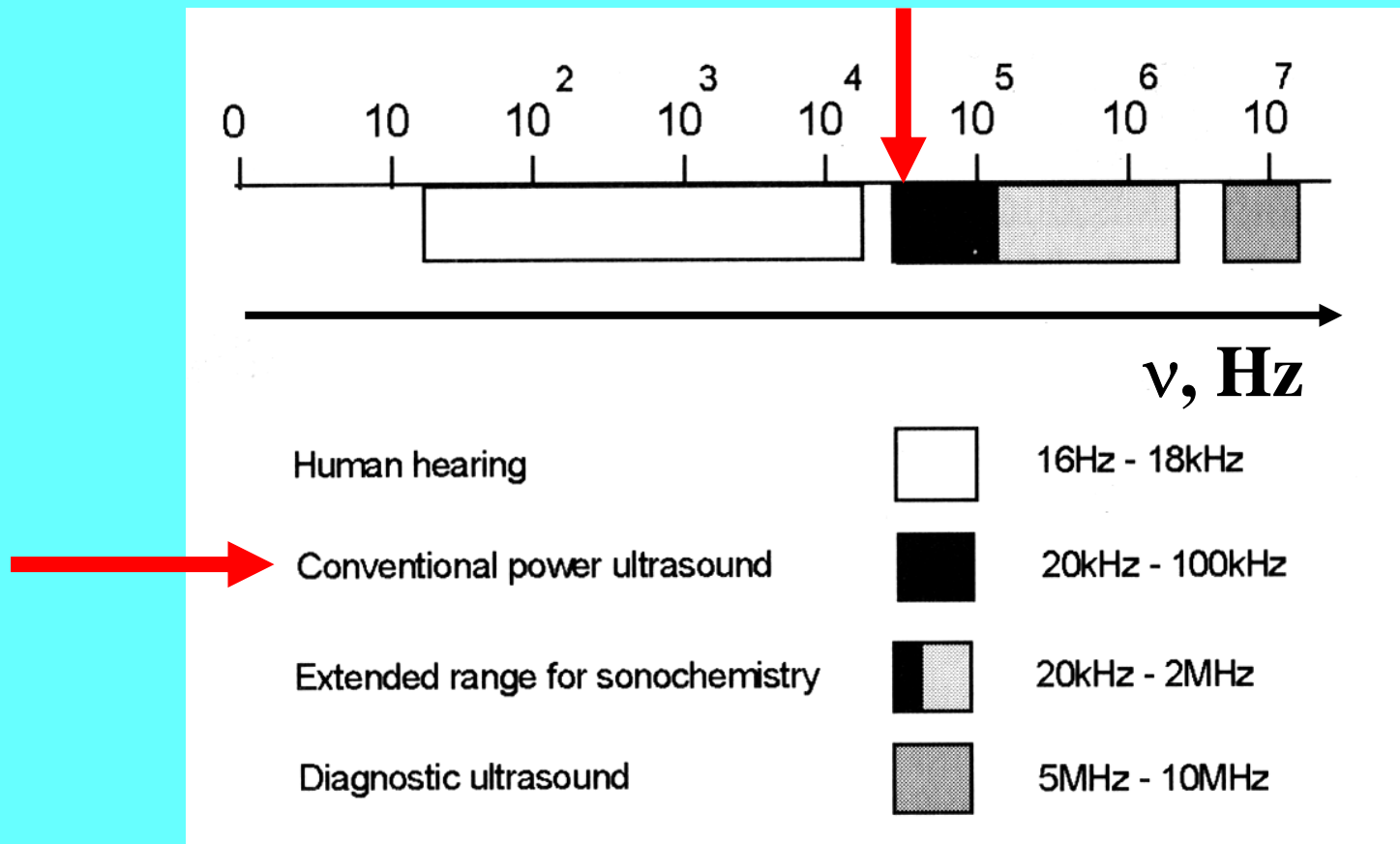10 dB = 10 as intense

20 dB = 10^2 as intense

30 dB = 10^3 as intense

120 dB = 10^{12} as intense

Ultrasound

Frequencies from 20 kHz to 50 MHz

Sonochemistry

Suslick, K. S.; Price, J. P. *Ann. Rev. Mater. Sci.* 1999, *29*, 295–326.

Mason, T. J.; Lorimer, J. P. *Applied Sonochemistry,* Wiley-VCH, Weinheim, 2002.

Gedanken, A. *Ultrason. Sonochem.* 2004, *11*, 47–55.

Mastai, Y.; Gedanken, A. In: Rao, C.N.R.; Mueller, A.; Cheetham, A. K. (Eds.), *The Chemistry of Nanomaterials*, Wiley-VCH, NY, 2004, 113–169.

Sonochemical Reactions

No direct interaction of US field with molecules

Liquid phase reactions – chemical reactions driven by cavitation effects

Solid state reactions – introduction of defects = speeding up diffusion

Hydrodynamic Cavitation

the passage of liquid through (an orifice plate)

the kinetic energy/velocity of the liquid increases at the expense of the pressure

throttling causes the pressure to fall below the threshold
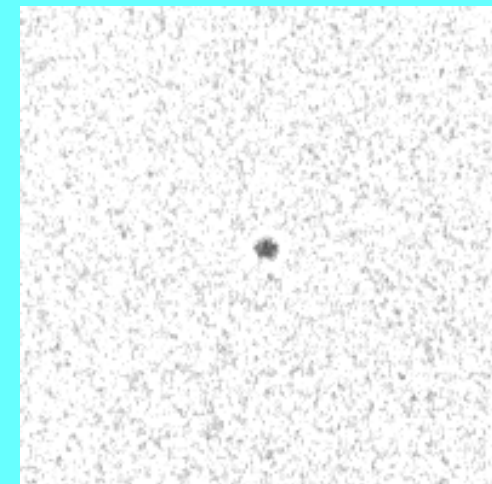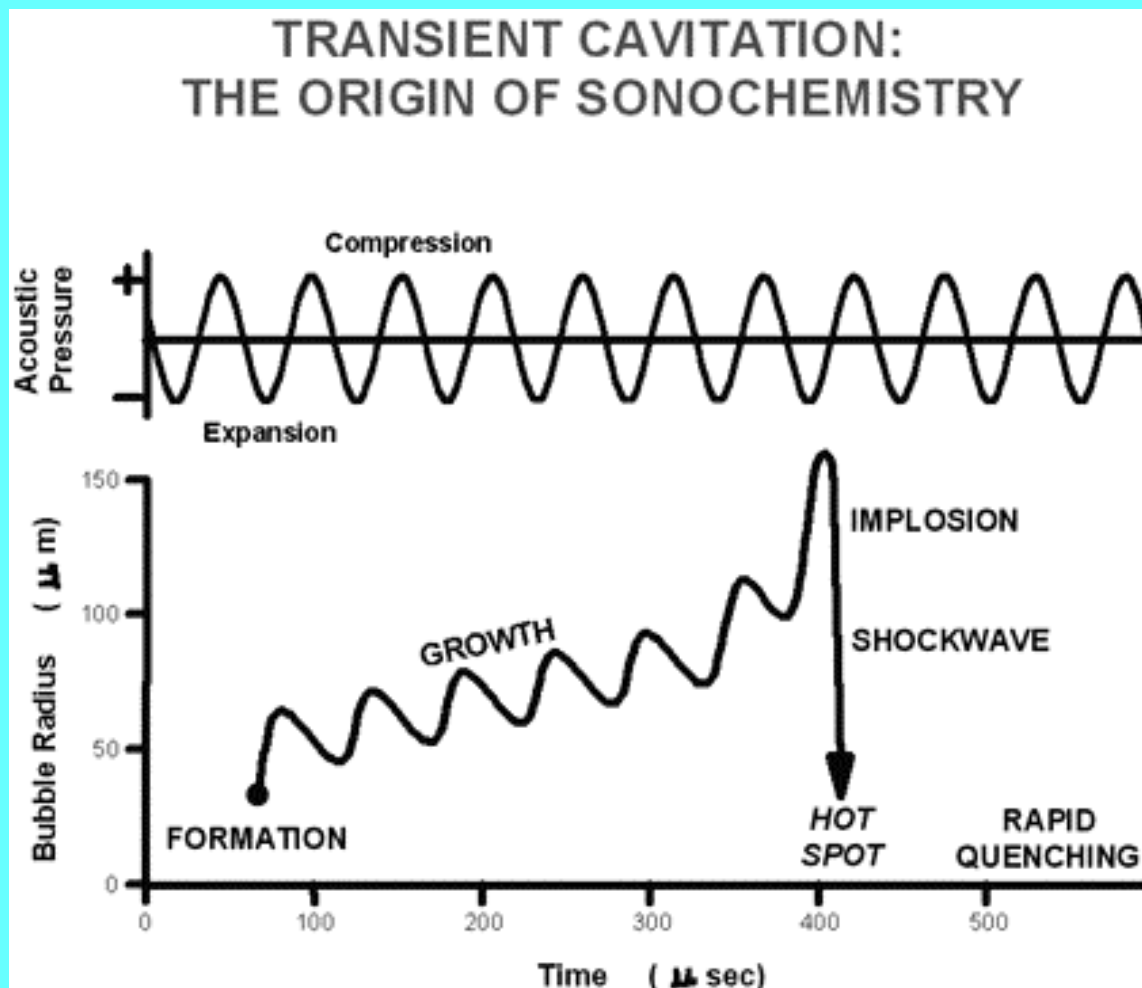pressure for cavitation (vapor pressure)

cavities are generated

the liquid jet expands, the pressure recovers

the collapse of the cavities

Acoustic Cavitation
Cavitation effects = creation, growth, and implosive collapse of bubbles in a liquid

TRANSIENT CAVITATION: THE ORIGIN OF SONOCHEMISTRY

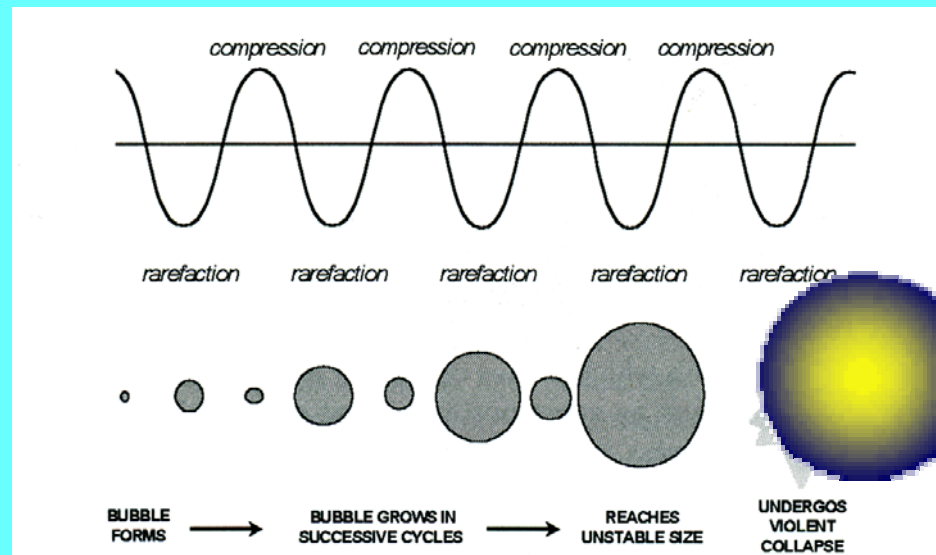stable cavitation - bubbles oscillate for many cycles

transient cavitation - transient cavities expand rapidly collapse violently

52

Acoustic Cavitation

Bubble formation = overcoming tensile strength of the liquid (pure water 1500 bar, only 50 bar available)

Weak spots = dissolved gas molecules, solid particles, trapped gases
slow bubble growth (300 μs), energy absorption, size oscillations
critical size (170-300 μm) = most efficient energy absorption, rapid growth, inefficient energy absorption, collapse

compression   compression   compression   compression

rarefaction   rarefaction   rarefaction   rarefaction   rarefaction

BUBBLE FORMS → BUBBLE GROWS IN SUCCESSIVE CYCLES → REACHES UNSTABLE SIZE → UNDERGOS VIOLENT COLLAPSE

Cavitation

Bubble collapse = implosion (1 ns)

• HOMOGENEOUS
liquid: spherically symmetrical implosion, shear forces

Hot spots = adiabatic compression, life time 2 µs
temperature of the gas inside bubble 5 000 – 20 000 °C,
surrounding liquid layer 2000 °C
pressure 500 – 1000 bar
cooling rate 10^{10} K s^{-1}

red hot steel poured into water 2500 K s^{-1}
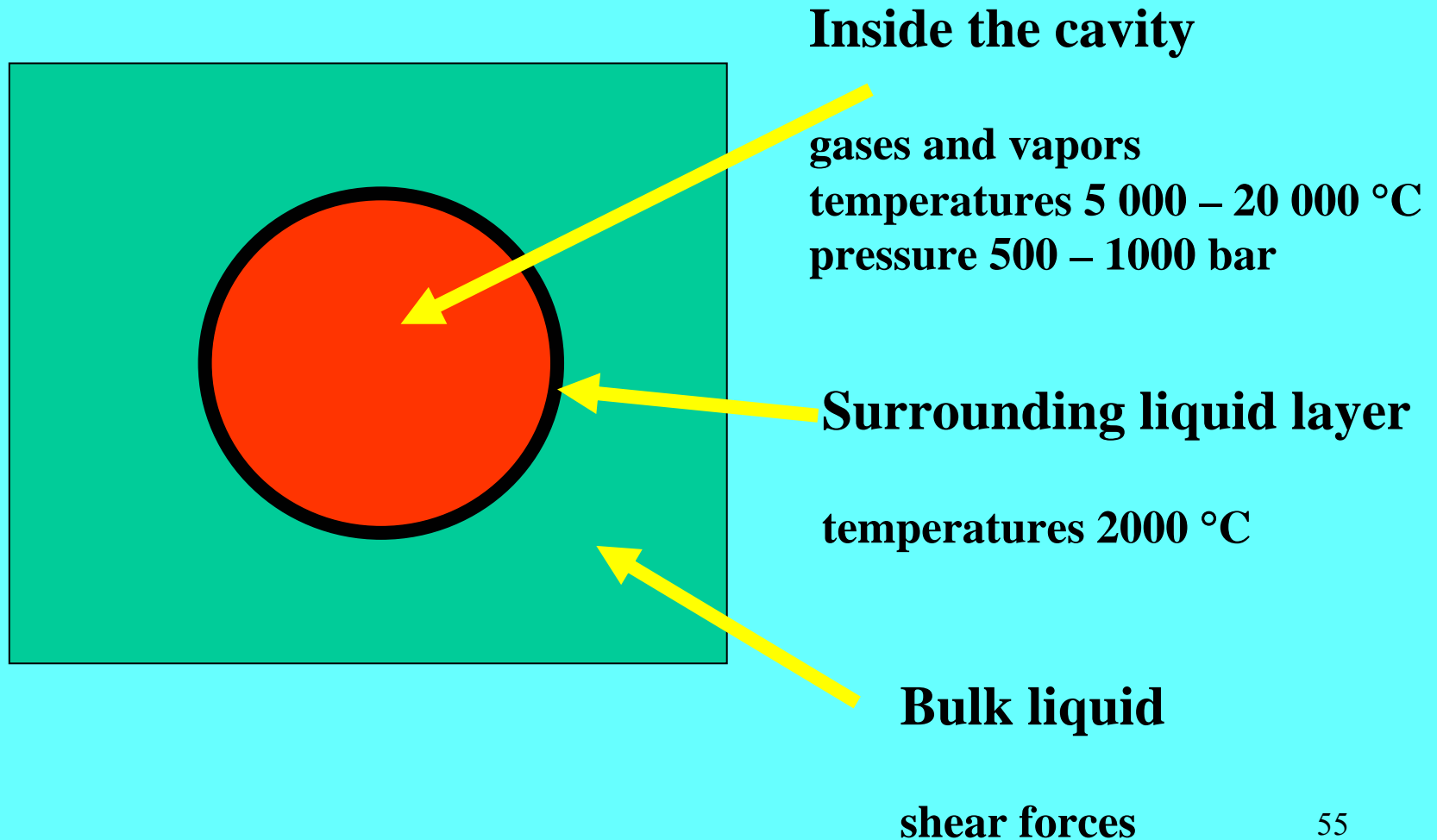
• HETEROGENEOUS
liquid-solid interface: asymmetrical implosion,
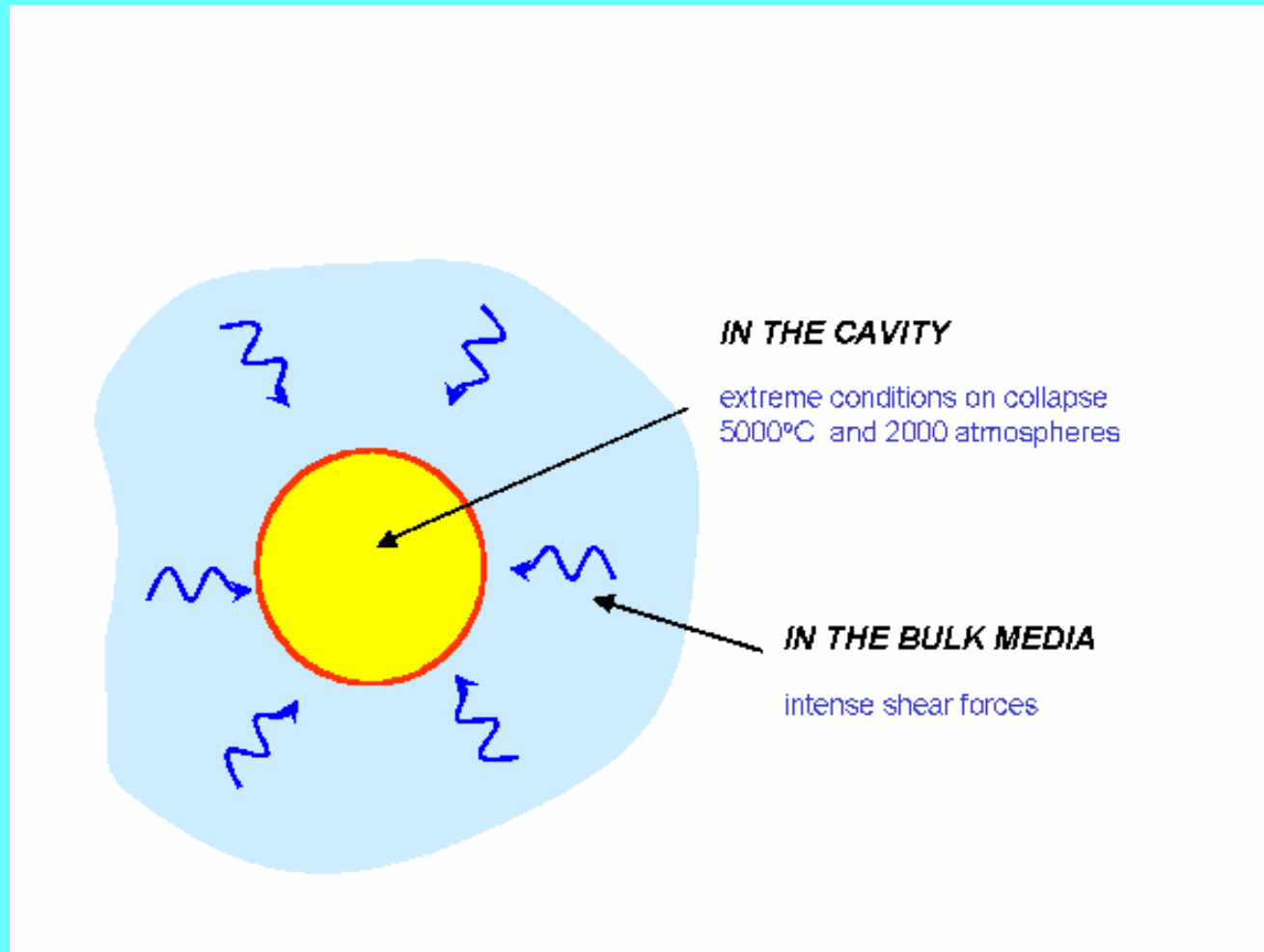**high speed microjets of liquid (400 km h^{-1})**

Microjet - bubble implosion

Homogeneous Sonochemistry
Two-Site Mechanism

Inside the cavity

gases and vapors
temperatures 5 000 – 20 000 °C
pressure 500 – 1000 bar

Surrounding liquid layer

temperatures 2000 °C

Bulk liquid

shear forces

55

Two-site Mechanism

IN THE CAVITY

extreme conditions on collapse
5000°C and 2000 atmospheres

IN THE BULK MEDIA

intense shear forces

Heterogeneous Sonochemistry

Solid surfaces = implosion, microjets, shock waves
200 μm minimum particle size at 20 kHz for microjets

surface erosion
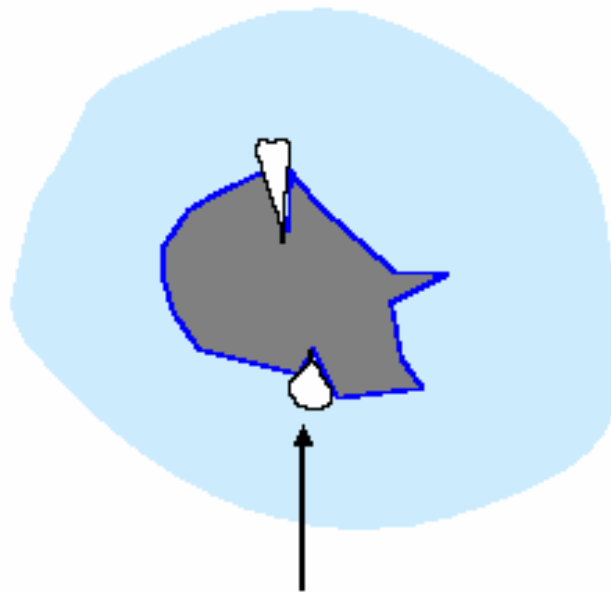removal of unreactive coatings (oxides, nitrides, carbonaceous)
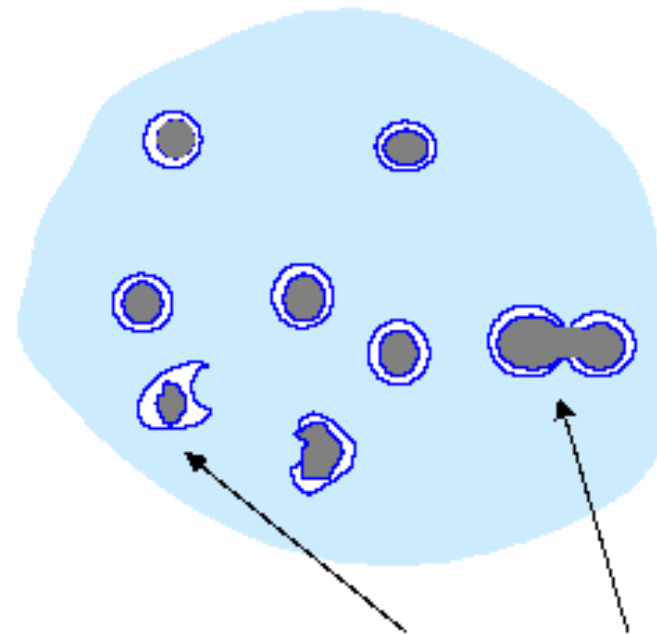fragmentation of brittle materials, increased surface area

Heterogeneous Sonochemistry

LARGE PARTICLES

SMALL PARTICLES

surface cavitation due to defects leading to **fragmentation**

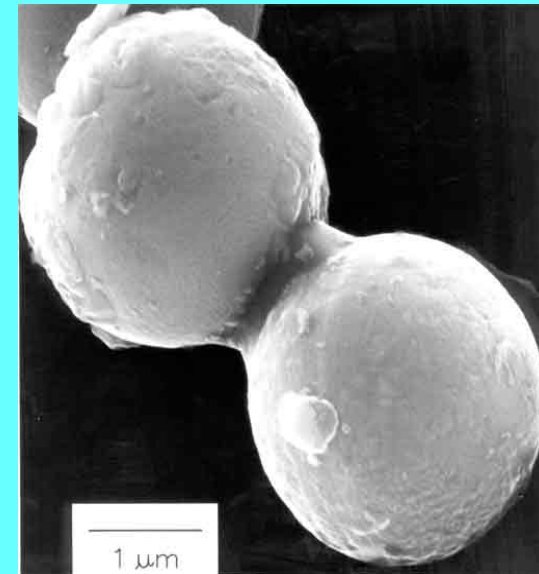collision can lead to **surface erosion** or **fusion**

Heterogeneous Sonochemistry

Solid particles in liquid = shock waves

high speed interparticle collisions (500 km/s)

surface smoothing, surface coating removal

localized melting of metal particles at the impact point fragmentation, increased surface area intercalation rates enhanced

1 μm

SONOCHEMICAL METHOD

◆ **Solid particles in liquid = shock waves, high speed interparticle collisions (500 km/s)**

surface smoothing, surface coating removal
Ni catalytic activity in hydrogenation increased 10^5 fold by NiO removal
localized melting of metal particles at the impact point
fragmentation, increased surface area
intercalation rates enhanced 200 fold in layered oxides and sulfides (V_2O_5, MoO_3, MoS_2, ZrS_2, TaS_2)
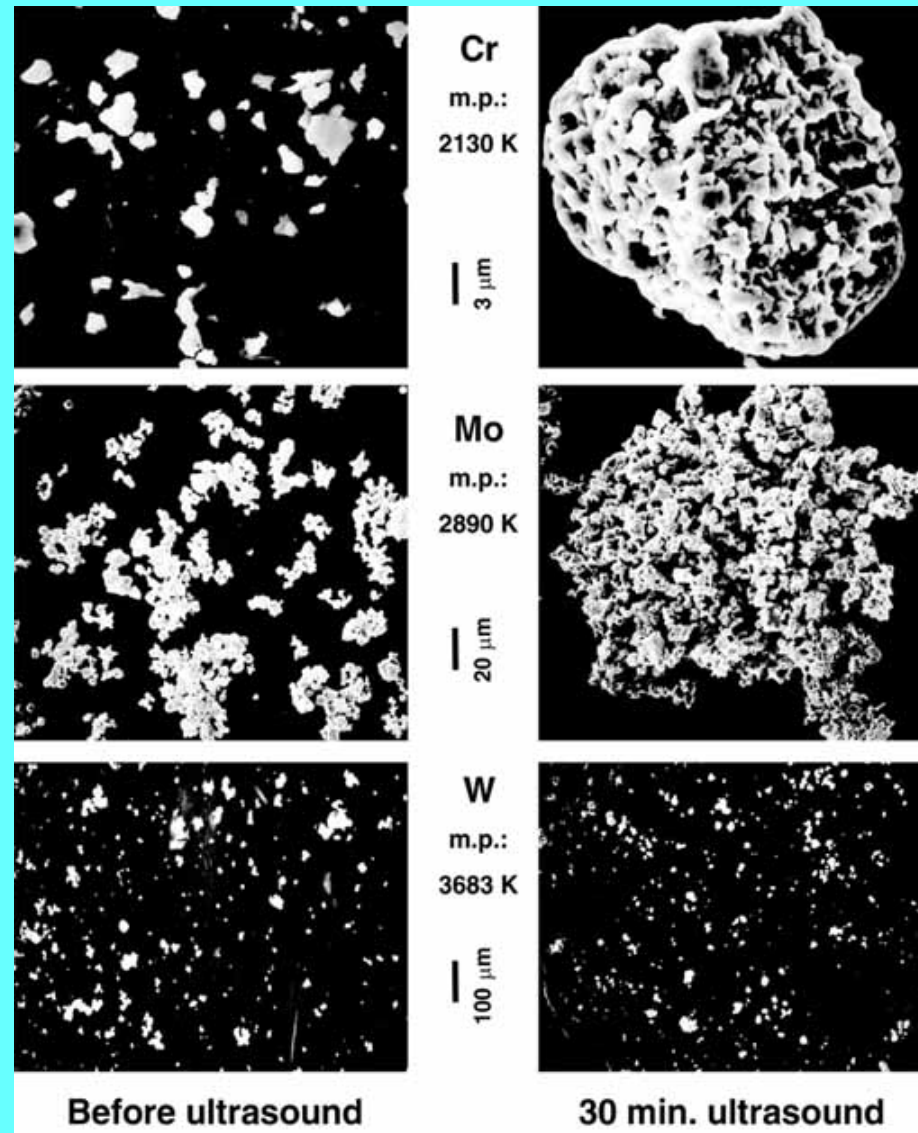

1 μm
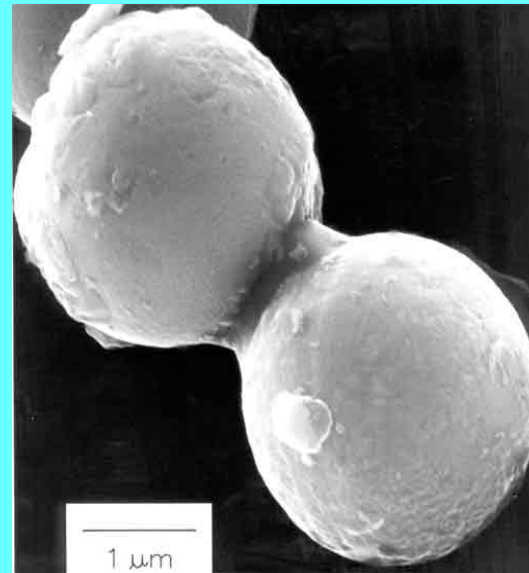
Heterogeneous Sonochemistry

Metal powders

Cr (mp 2130 K) and Mo (mp 2890 K) agglomerate

W (mp 3683 K) does not

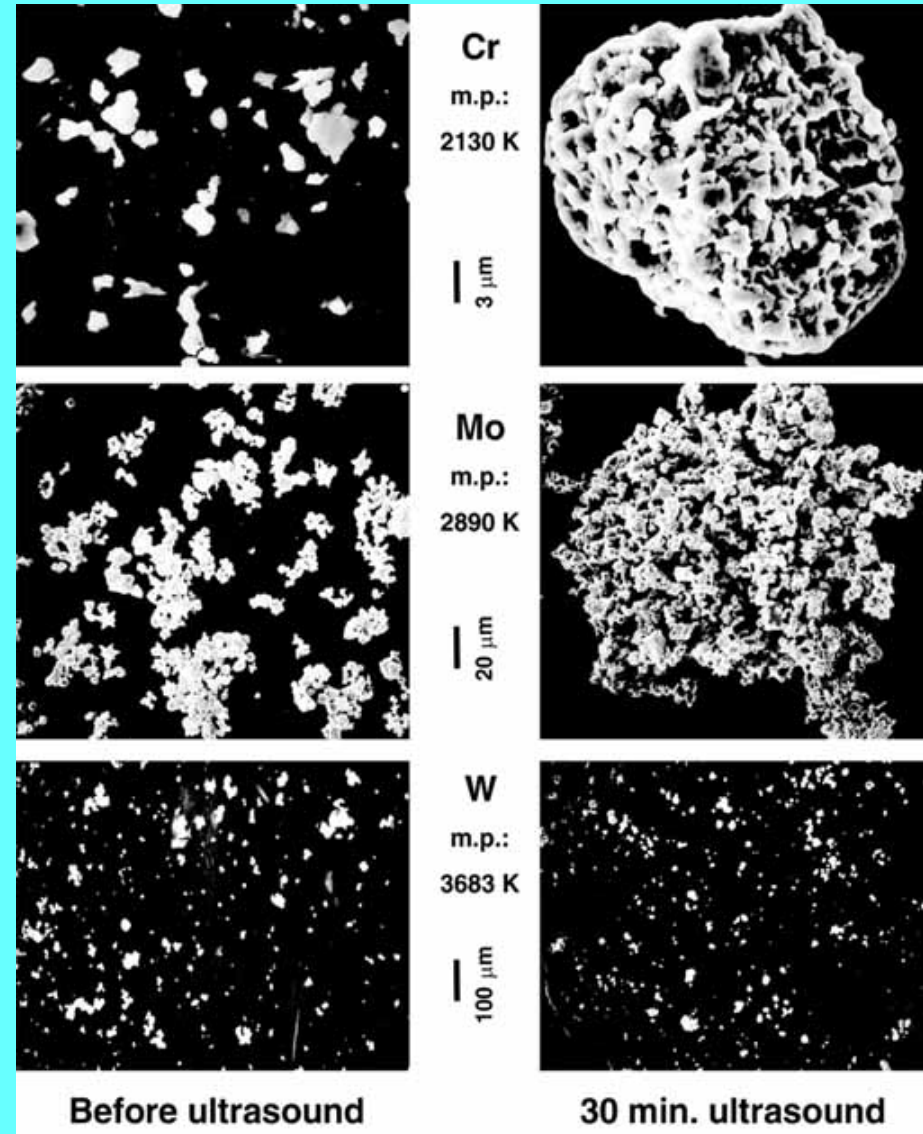temperature at the point of impact ~ 3000 °C

SONOCHEMICAL METHOD

Metal powders

Cr (mp 2130 K) and Mo (mp 2890 K) agglomerate
W (mp 3683 K) does not

temperature at the point of impact ~ 3000 °C

Cr m.p.: 2130 K — 3 μm

Mo m.p.: 2890 K — 20 μm

W m.p.: 3683 K — 100 μm

Before ultrasound   30 min. ultrasound

Cavitational Corrosion of the Tip

Control of sonochemical reactions

■frequency 20-40 kHz, the higher the frequency, the higher power needed to actuate cavitation, rarefaction phase shortens at high freq.

■volatile reactants, primary reaction site inside the bubbles, diameter 200 μm, 5000 °C, easier bubble formation, more vapors inside bubbles, but the cavitation is cushioned

■nonvolatile reactants, reaction in the thin layer (200 nm) surrounding the bubble, 2000 °C, less cushioning, more energetic cavitation (collapse)
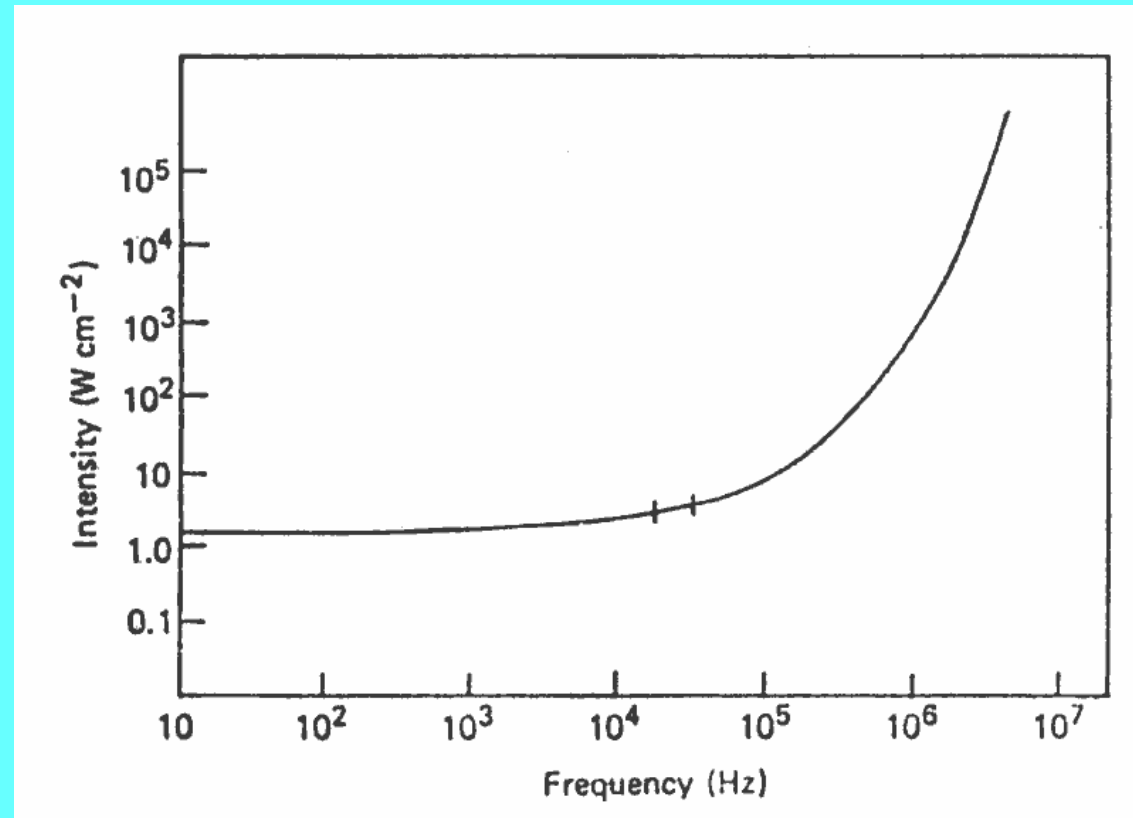
■use high boiling solvents, high vapor pressure inside the bubble cushions the implosion

■less cavitation in viscous liquids, viscosity resists shear forces

■reaction rates decrease with increasing temperature, more vapors in bubbles

■ low surface tension facilitates cavitation, in water add surfactants

Cavitation in Water

The frequency dependence of the intensity required to produce cavitation for degassed water at room temperature. The intensity required to produce vaporous cavitation above the frequency of 100 kHz rises rapidly.

The effect of temperature on cavitation
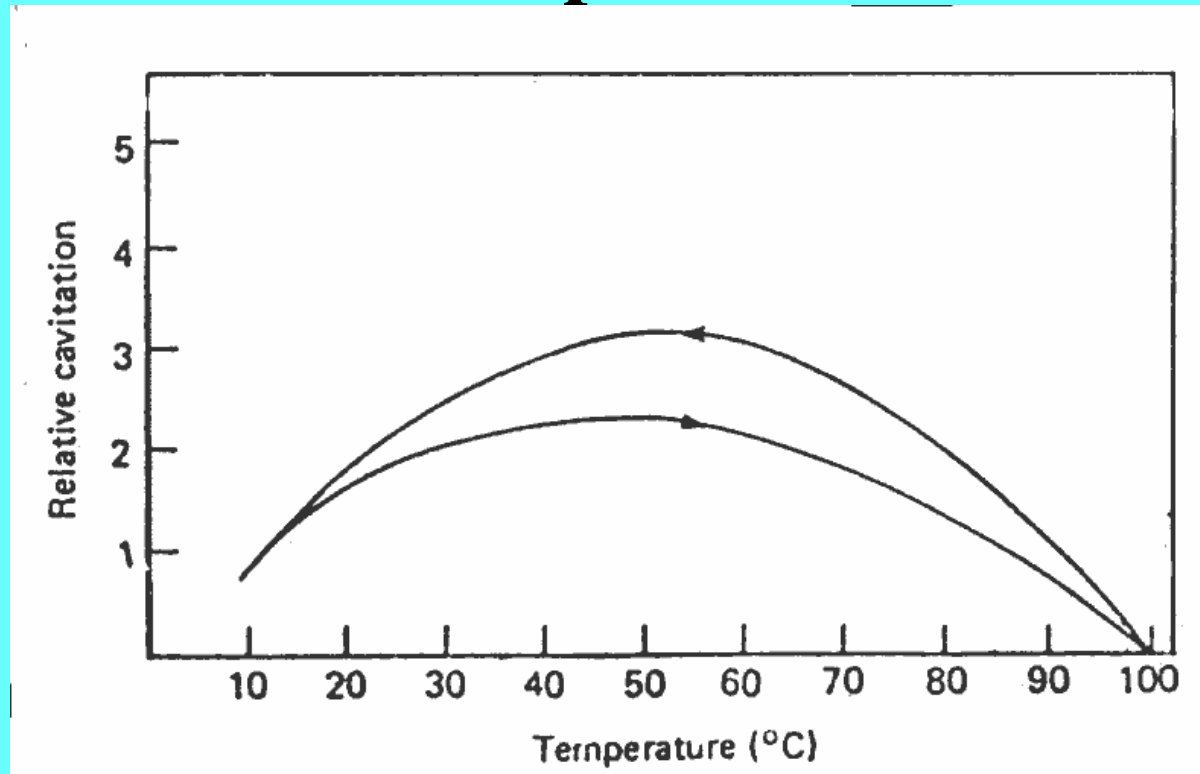
The effect of temperature on cavitation and its associated hysteresis effect for tap water. The increase in intensity as the temperature is increased can be observed before it falls away at the boiling point. When the temperature is allowed to fall an increase in intensity is found in the region of 50-60 °C. This is quite a significant effect and appears to occur in all liquids.

66

Control of sonochemical reactions

■ **ambient gas important**
energy developed on bubble collapse:
monoatomic (Ar) > diatomic (N_2) > triatomic (CO_2)
Xe: low thermal conductivity, heat of the collapsing cavity retained
He: high thermal conductivity, heat of the collapsing cavity dissipitated, no reaction

■**external pressure, higher pressure suppresses bubble formation but makes cavitation more energetic, optimum pressure for given frequency**

■**temperature, higher temperature increases vapor pressure of a medium, lowers viscosity and surface tension, many bubbles formed at temps. close to solvent boiling point, a barrier to sound transmission**

■**intensity, minimum intensity for cavitation threshold, depends on freq., optimum intensity for given reaction conditions, at high powers great number of bubbles hinder sound transmission, decoupling of a liquid from the source, breakdown of transducer material**

■ **sound attenuation is proportional to the frequency, more power needed at high freq.**

Generation of Ultrasound

a transducer - device converting one type of energy into other

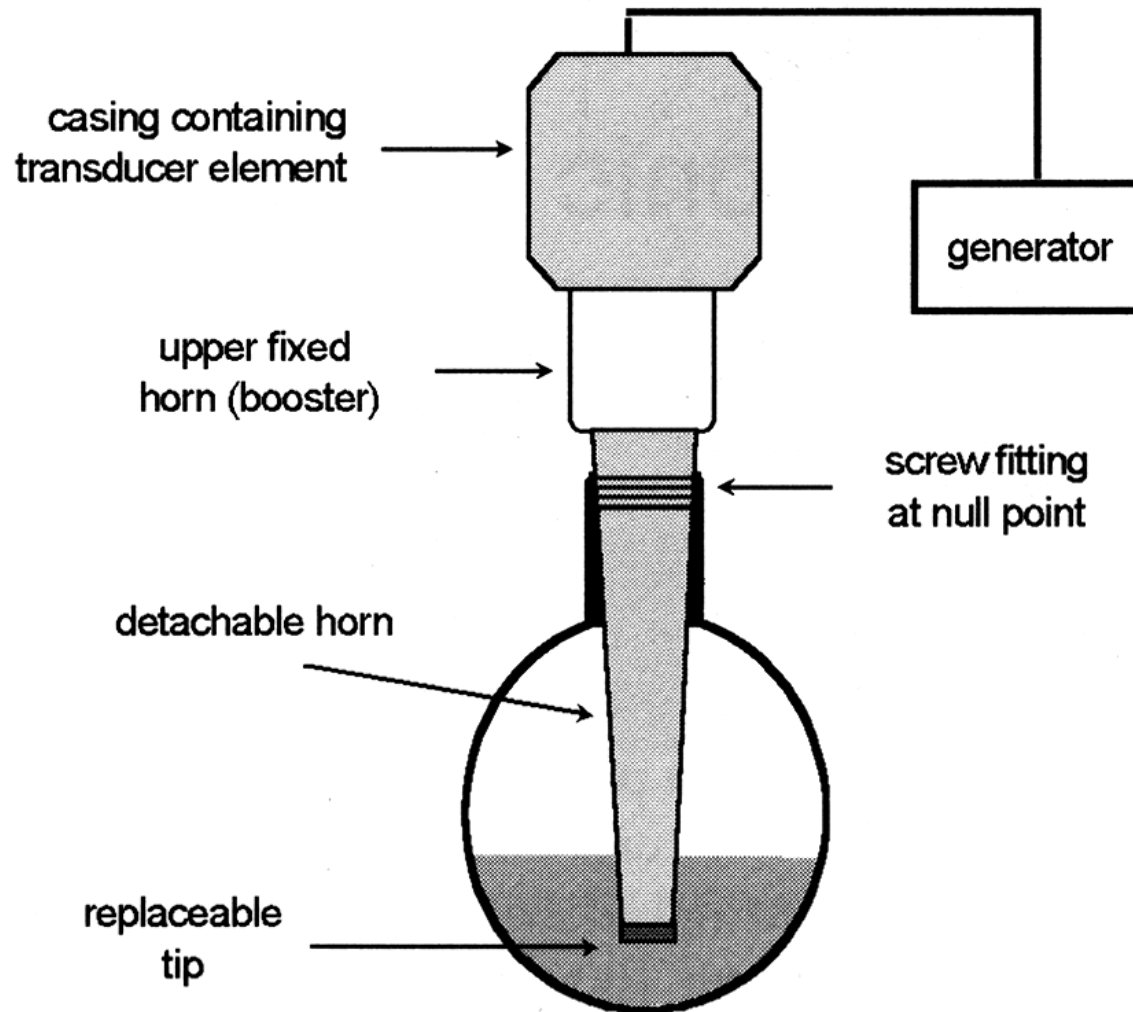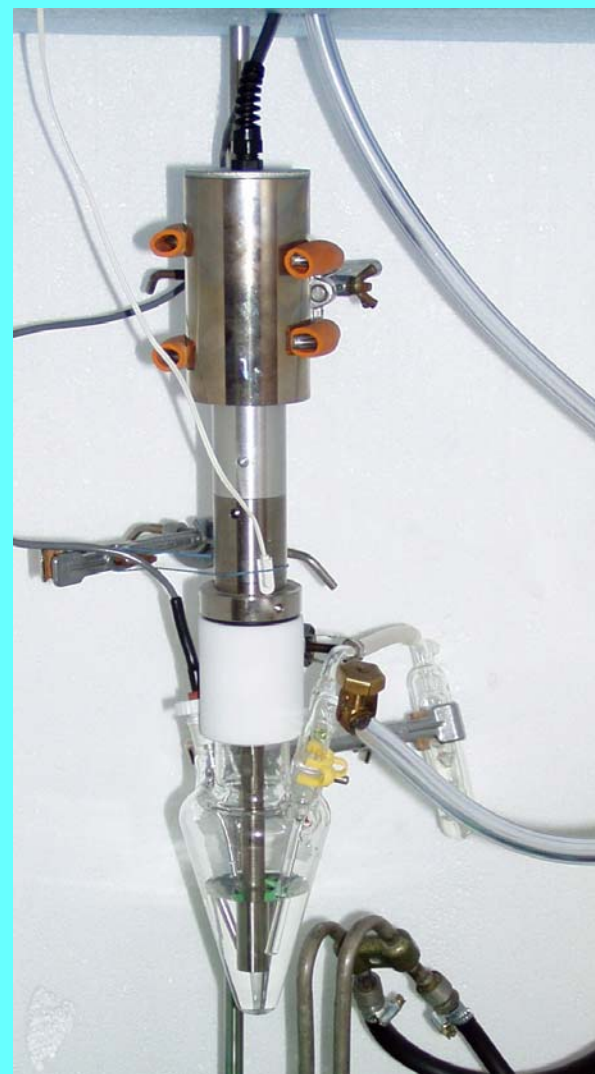|	
gas driven	**whistle (F. Galton), liquid atomizer**
	siren
liquid driven	**liquid whistle homogeniser, a jet of liquid passed through an orifice on a thin metal blade, vibrations, cavitation, mixing of immiscible liquids, ketchup, mayonnaise**
electromechanical	**magnetostrictive, Ni, Co/Fe, Al/Fe, Tb/Dy/Fe alloys shrink when placed in mg. field, solenoid, pulses, upper limit 100 kHz, cooling**
	piezoelectric, oposite charges applied on crystal sides, contraction/expansion, quartz, $Pb(Zr/Ti)O_3$ ceramics (PZT), up to MHz

68

Generation of Ultrasound

casing containing transducer element

upper fixed horn (booster)

detachable horn

replaceable tip

generator

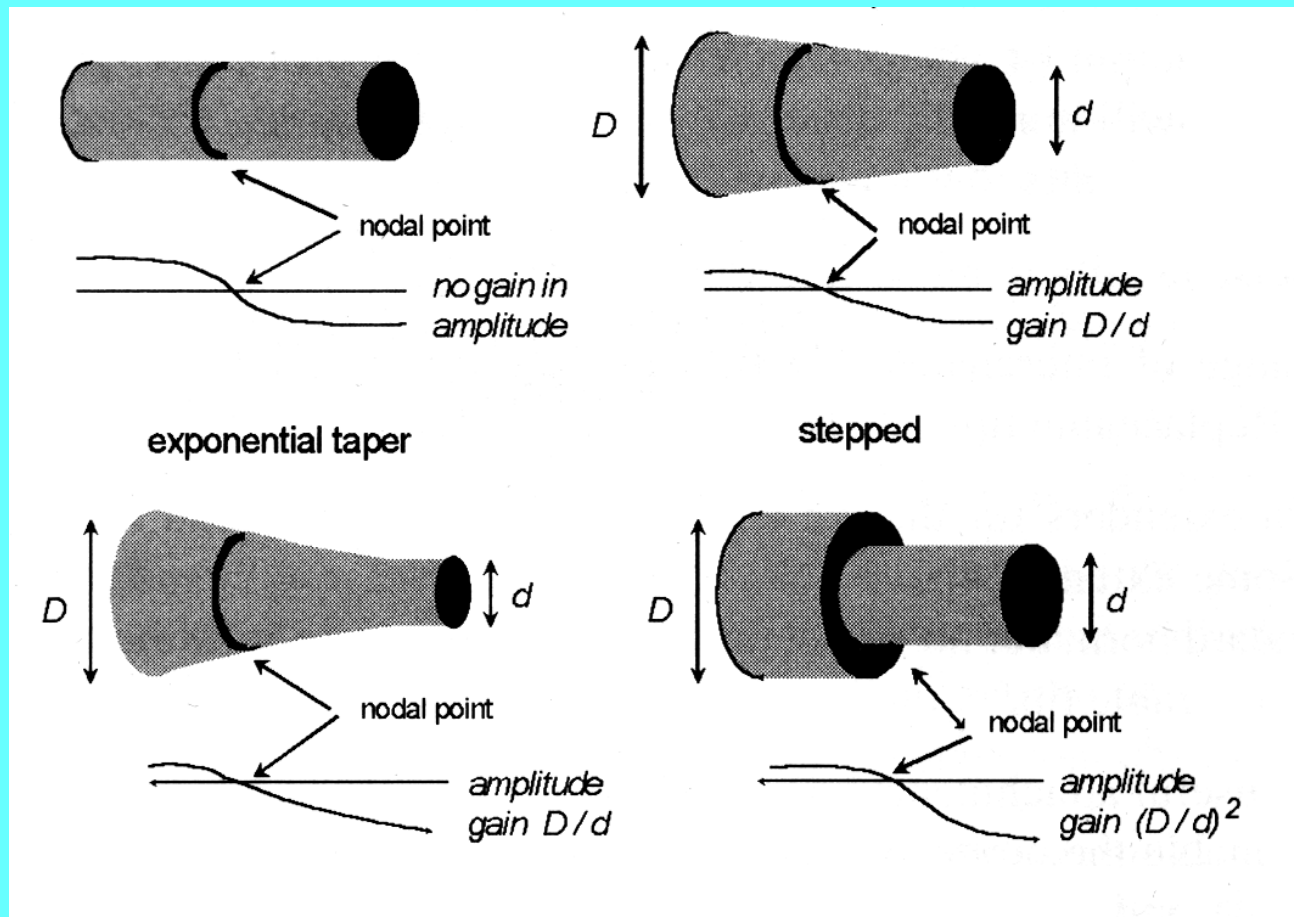screw fitting at null point

69

Sonochemical Reactor
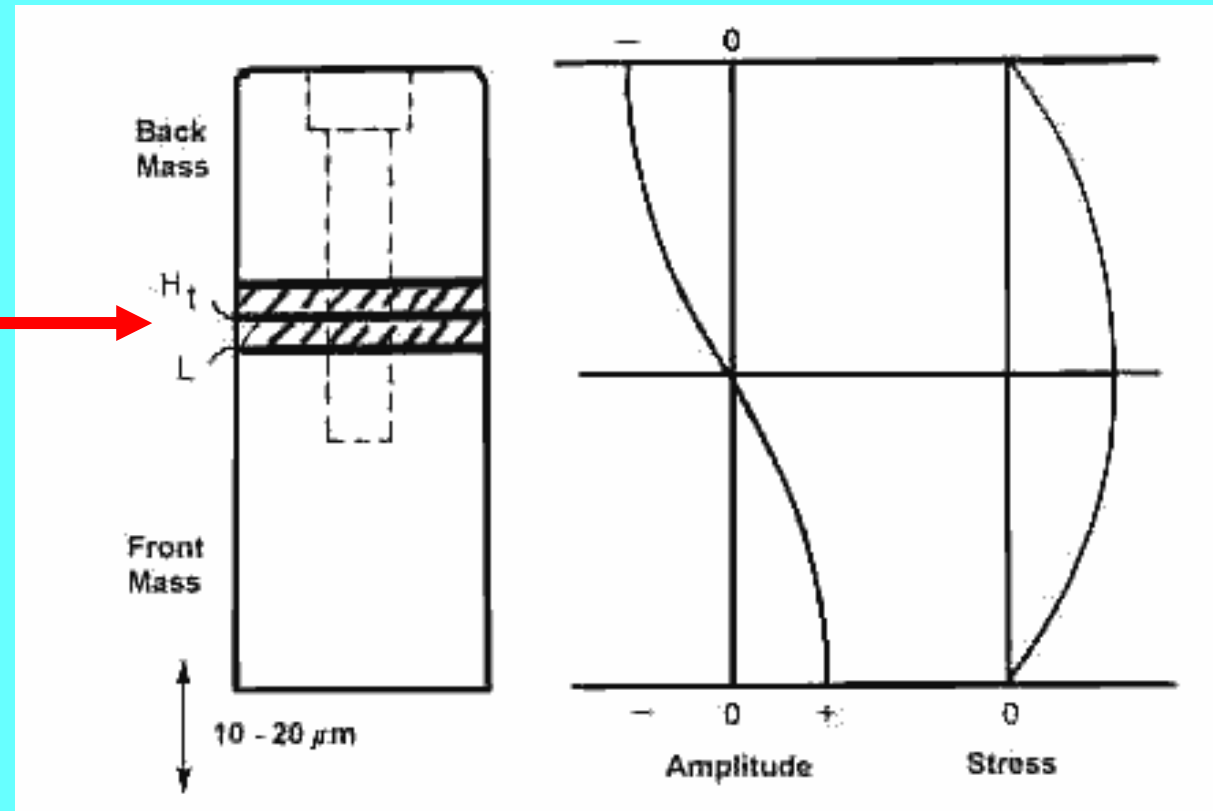
SONOCHEMICAL METHOD

Ti alloy horn, minimum lenght is a half-wavelength of sound in a material, 26 cm for 20 kHz in Ti, multiples of 13 cm

vibration amplitude 5 - 50 μm

Sandwich transducer operating at 1-200 kHz

PZT wafers

Sonochemical Reactor

Ultrasound Processor VCX 500 W

Frequency 20 kHz

0 to 40 °C

Argon (flow rate 62 cm^3 min^{-1})

TIME of ultrasound treatment
PULSE irradiation and a dwell time 2:2
TEMP maximum temperature 50 °C
AMPL amplitude 50 %

SONOCHEMICAL METHOD

◆ **Liquids = heating/cooling by cavity implosions**

$$H_2O \longrightarrow H^. + OH^. \longrightarrow H_2 + H_2O_2$$

precursor decomposition:
metals $\qquad$ $Fe(CO)_5 \longrightarrow Fe + 5\ CO$
oxides $\qquad$ $Ga^{3+} + H_2O \longrightarrow Ga(O)(OH)$, **diaspore**
nitrides, carbides, sulfides

alkane cracking
polymer degradation, lower MW, surface modification
emulsification of immiscible liquids (oil-water, Hg-organics, polymer-inorganics)
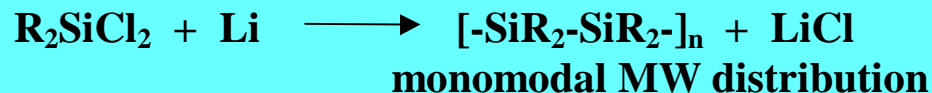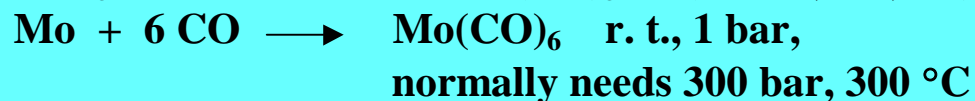
SONOCHEMICAL METHOD

♦ **Solid surfaces = implosion, microjets, shock waves**

200 μm minimum particle size at 20 kHz for microjets
surface erosion
removal of unreactive coatings (oxides, nitrides, carbonaceous)
fragmentation of brittle materials, increased surface area

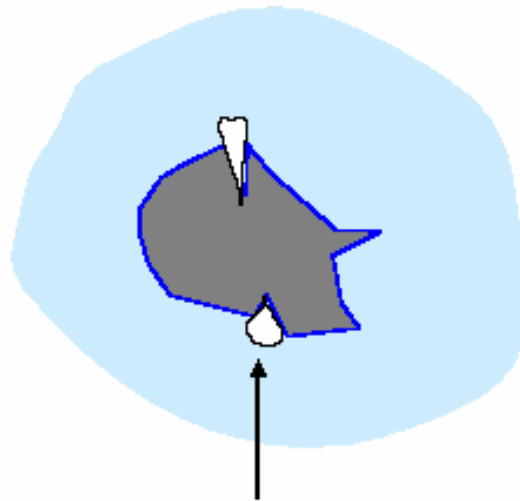**Li, Mg, Zn, Al, Cu react at room temperature**

$$MCl_5 + Na + CO \longrightarrow M(CO)_5^- \quad (M = V, Nb, Ta)$$
$$Mo + 6 CO \longrightarrow Mo(CO)_6 \quad \text{r. t., 1 bar,}$$
normally needs 300 bar, 300 °C
$$R_2SiCl_2 + Li \longrightarrow [-SiR_2-SiR_2-]_n + LiCl$$
monomodal MW distribution

Protein microspheres
diameter 2 μm, hollow
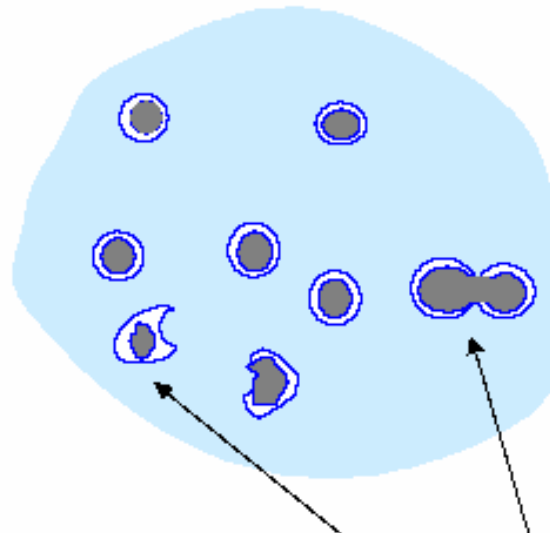**emulsification, crosslinking cysteine -S-S- by superoxide**

SONOCHEMICAL METHOD

LARGE PARTICLES

SMALL PARTICLES

surface cavitation due to defects leading to **fragmentation**

collision can lead to **surface erosion** or **fusion**