

Precursor Methods

Goals – decrease diffusion paths, shorten reaction times and temperatures

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

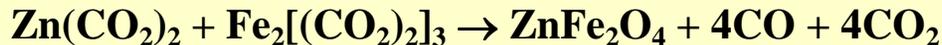
Disadvantage: difficult to prepare high purity, accurate stoichiometric phases if solubilities do not match

Coprecipitation Method

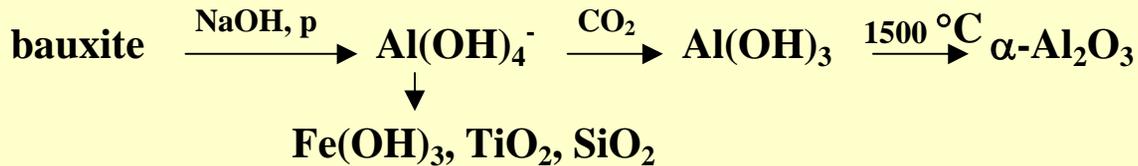
Spinels

oxalates: $\text{Zn}(\text{CO}_2)_2/\text{Fe}_2[(\text{CO}_2)_2]_3/\text{H}_2\text{O}$ 1 : 1 mixing, H_2O evaporation, salts coprecipitation

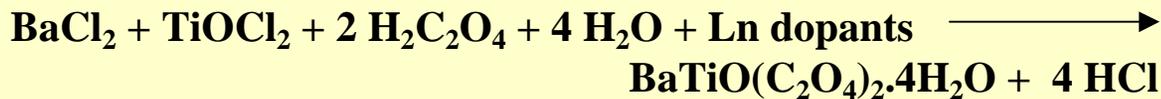
Solid-solution mixing on atomic scale, filter, calcine in air



Al_2O_3 Bayer Process



BaTiO_3

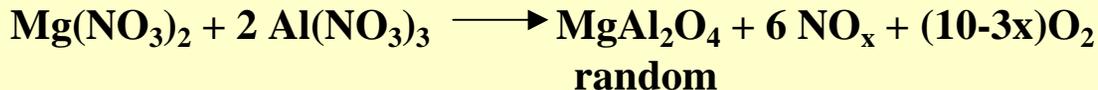


filtration, washing, drying, calcination @ 730°C

Coprecipitation Method

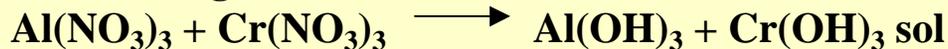
Spinel

$\text{Al}(\text{NO}_3)_3 + \text{Mg}(\text{NO}_3)_2 + \text{H}_2\text{O}$ freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T



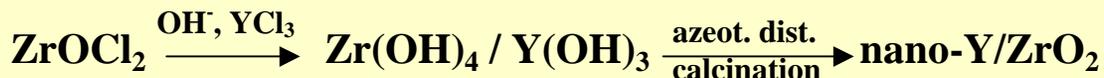
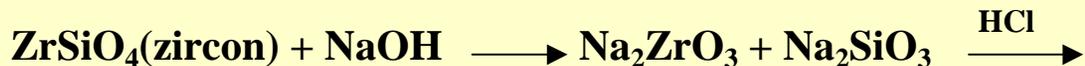
Ruby

Ion exchange



freeze drying gives solid $(\text{Al}/\text{Cr})(\text{OH})_3$ @ LN_2 temperature, 5 Pa
annealing @ 950 °C for 2.5 h gives solid solution $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$

Zirconia

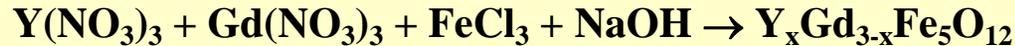


Coprecipitation Method

High- T_c Superconductors



Magnetic garnets, tunable magnetic materials



Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes REFeO₃ perovskite impurity

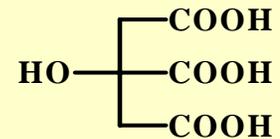
Isomorphous replacement of Y³⁺ for Gd³⁺ on dodecahedral sites, solid solution, similar rare earth ionic radii

complete family accessible, 0 < x < 3, 2Fe³⁺ O_h sites, 3Fe³⁺ T_d sites, 3RE³⁺ 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

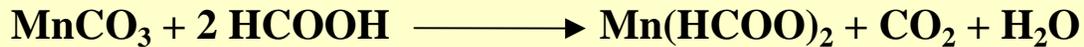
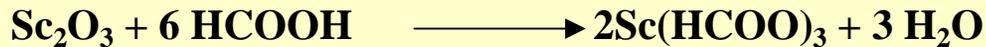
Low firing temperatures

Pechini and Citrate Gel Method

BaTiO₃

by conventional powder method at 1200 °C

Ba²⁺ + Ti(OⁱPr)₄ + citric acid at 650 °C



added to citric acid, water removal, calcination @ 690 °C gives

ScMnO₃

without citric acid only mixture of Sc₂O₃ and Mn₂O₃ is formed

Double Salt Precursors

Double salts of known and controlled stoichiometry such as:



Burn off organics 200-300 °C, then 1000 °C 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

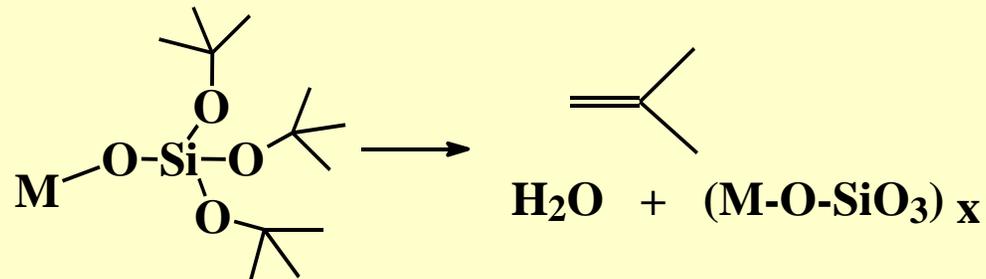
Juggling the electronic-magnetic properties of the O_h and T_d ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, °C
MgCr_2O_4	$(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100-1200
NiCr_2O_4	$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100
MnCr_2O_4	$\text{MnCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1100
CoCr_2O_4	$\text{CoCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1200
CuCr_2O_4	$(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	700-800
ZnCr_2O_4	$(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	1400
FeCr_2O_4	$(\text{NH}_4)_2\text{Fe}(\text{CrO}_4)_2$	1150

Single Source Precursor

Compounds containing desired elements in a proper stoichiometric ratio

Easy chemical pathway for ligand removal



Vegard's Law

Vegard law behavior:

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

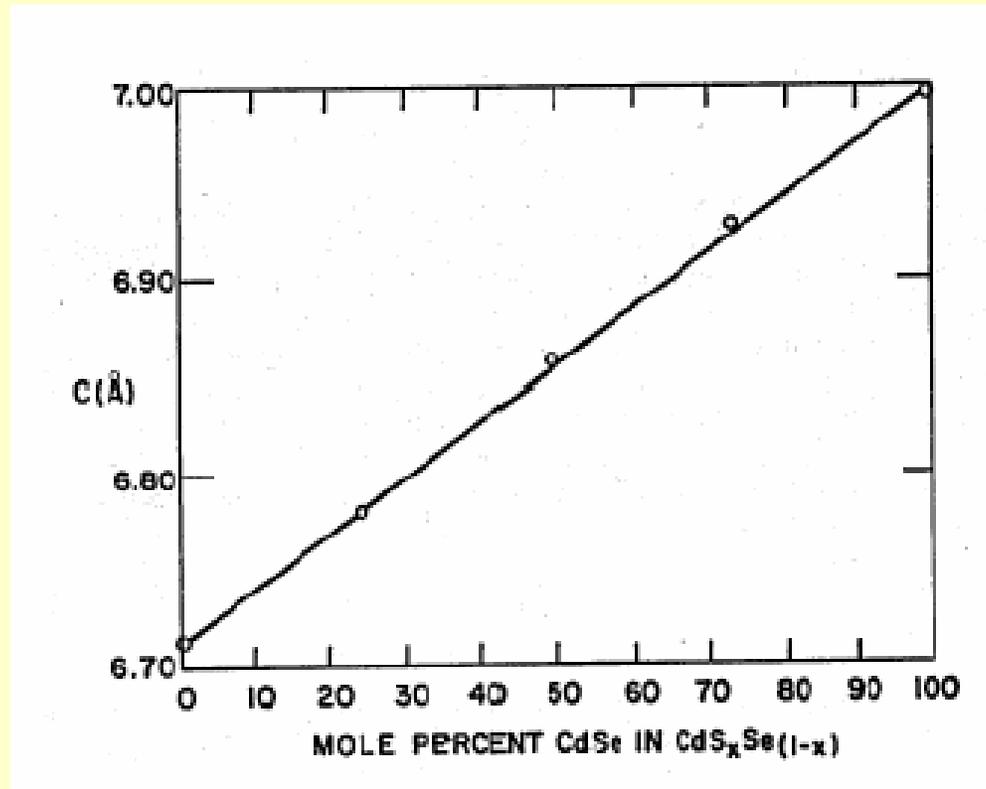
The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard's law

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

$$c(\text{CdSe}_{1-x}\text{S}_x) = x c(\text{CdS}) + (1-x) c(\text{CdSe})$$

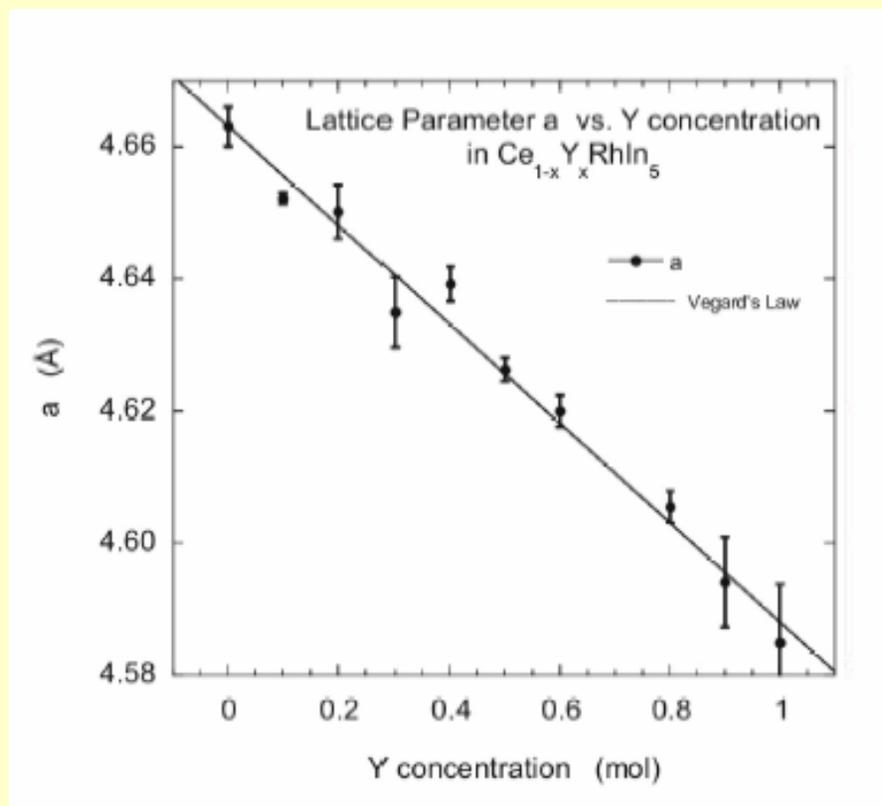


Vegard's Law

$$P(Y_x Ce_{1-x} RhIn_5) = x P(Y_x Ce_{1-x} RhIn_5) + (1-x) P(Y_x Ce_{1-x} RhIn_5)$$

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 $Ce_{1-x} Y_x RhIn_5$ system



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

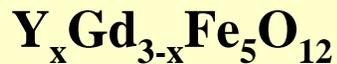
Vegard's Law

Vegard law behavior:

$$\mathbf{P (Y_x Gd_{3-x} Fe_5 O_{12}) = x/3 P (Y_3 Fe_5 O_{12}) + (3-x)/3 P (Gd_3 Fe_5 O_{12})}$$

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



3 T_d Fe^{3+} sites, 5 UPEs

2 O_h Fe^{3+} sites, 5 UPEs

Ferrimagnetically coupled material, oppositely aligned electron spins on the T_d and O_h Fe^{3+} magnetic sublattices

Counting spins $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ferrimagnetic at low T: $3 \times 5 - 2 \times 5 = 5$ UPEs

Counting spins $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ferrimagnetic at low T: $3 \times 7 - 3 \times 5 + 2 \times 5 = 16$ UPEs

$\text{Y}_x \text{Gd}_{3-x} \text{Fe}_5 \text{O}_{12}$ 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 , ($M = \text{alkali metal}$)

FLINAK: $LiF-NaF-KF$

M_2Q_x ($M = \text{alkali metal}$, $Q = S, Se, Te$)

molten salts ionic, low mp, eutectics, completely ionized

act as solvents or reactants, $T = 250-550\text{ }^\circ\text{C}$

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)

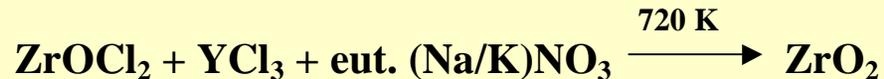
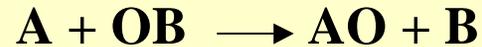
Flux Method

Lux-Flood formalism

oxide = strong base

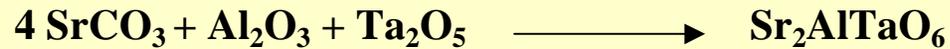
acid = oxide acceptor

base = oxide donor



Flux Method

fly ash (aluminosilicates)



900 °C in SrCl₂ flux

1400 °C required for a direct reaction



Flux Method

Electrolysis in molten salts

Reduction of TiO_2 pellets to Ti sponge in a CaCl_2 melt at $950\text{ }^\circ\text{C}$

O^{2-} dissolves in CaCl_2 , diffuses to the graphite anode

insulating TiO_2 \rightarrow TiO_{2-x} conductive

graphite anode

anodic oxidation



cathode TiO_2 pellet

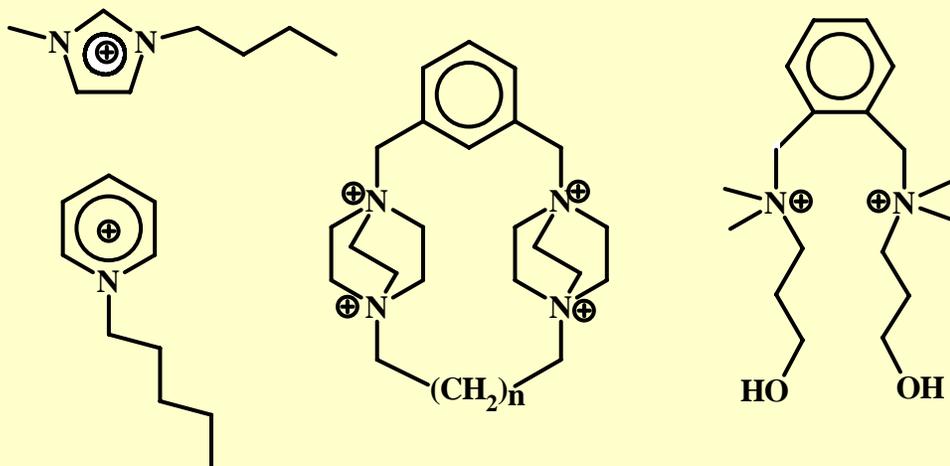
cathodic reduction



Ionic Liquids

Organic cations (containing N, P)

Inorganic anions: Cl^- , AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, PF_6^- , SnCl_3^- , BCl_3^- , BF_4^- , NO_3^- , $\text{OSO}_2\text{CF}_3^-$ (triflate), $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, PO_4^{3-}

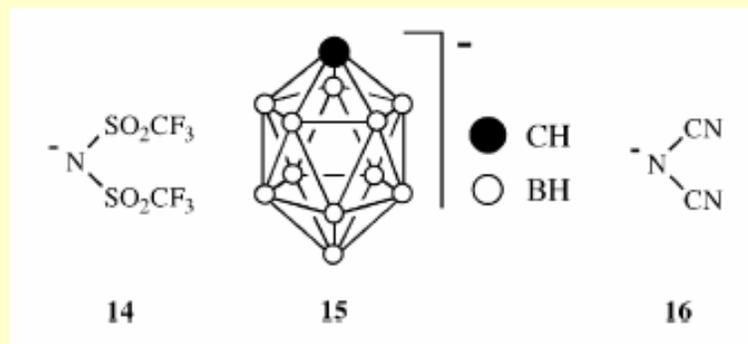
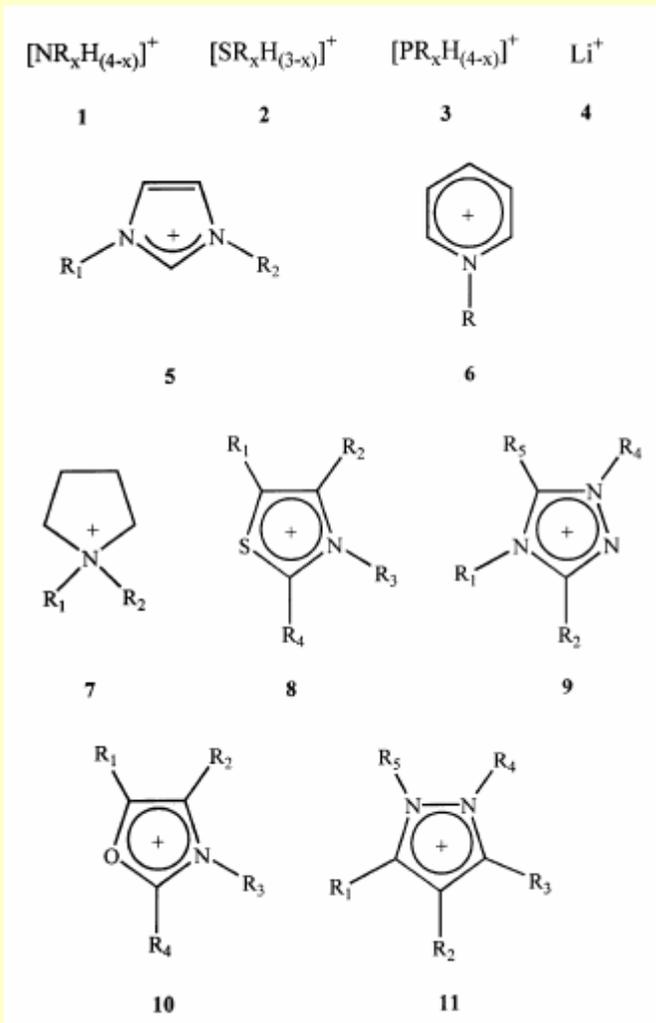


Ionic Liquids

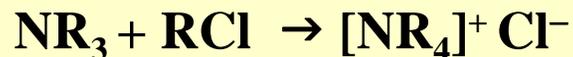
Oldest known (1914) : EtNH₃⁺NO₃⁻ mp 12 °C

- Liquids at room temperature or low mp**
- Thermal operating range from -40 °C to 400 °C**
- Highly polar, noncoordinating, completely ionized**
- Nonvolatile – no detectable vapor pressure**
- Nonflammable, nonexplosive, nonoxidizing, high thermal stability**
- Electrochemical window > 4V (not oxidized or reduced)**
- Immiscible with organic solvents**
- Hydrophobic IL immiscible with water**

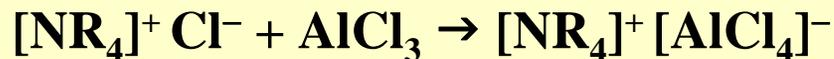
Ionic Liquids



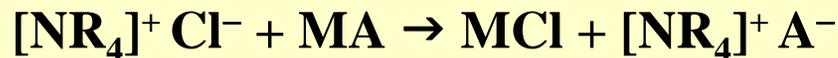
Synthesis of Ionic Liquids



Aluminates



Metal halide elimination



Reaction with an acid



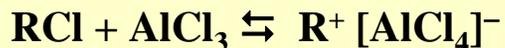
Ion exchange



Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

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



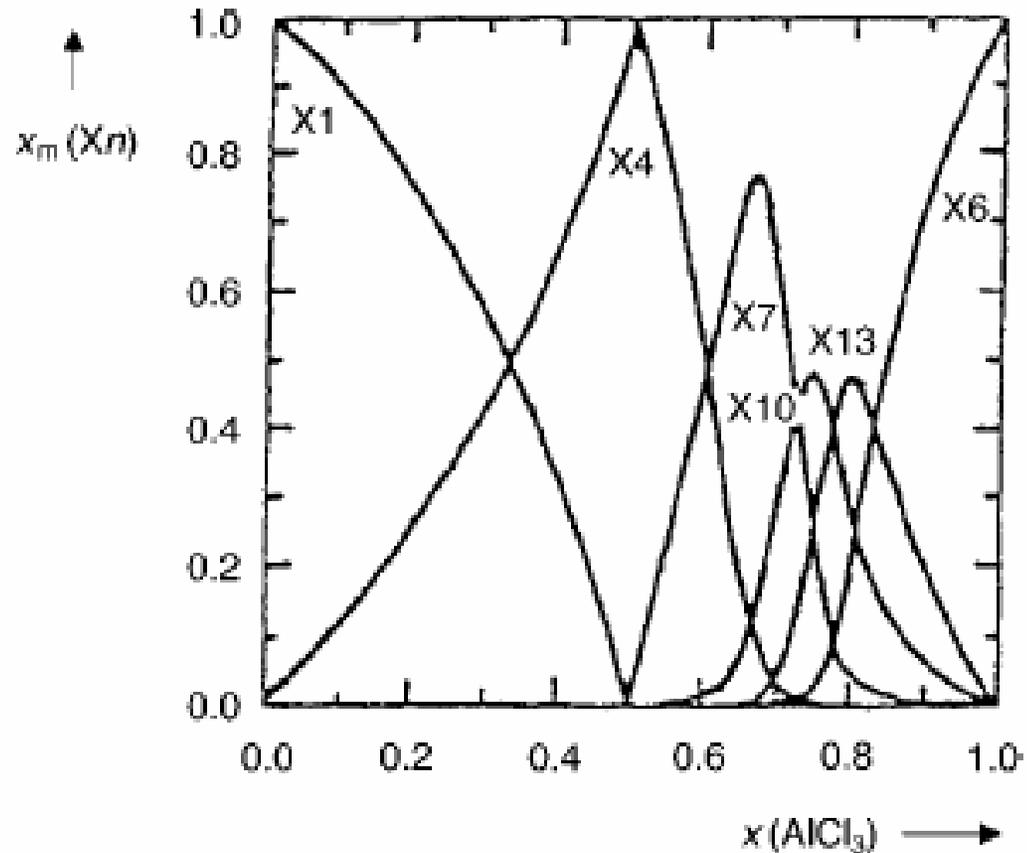
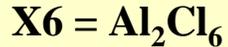
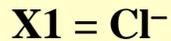
Acidic: excess of $AlCl_3$ as $[Al_2Cl_7]^-$ $x(AlCl_3) > 0.5$

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



Halogenoaluminate(III) Ionic Liquids



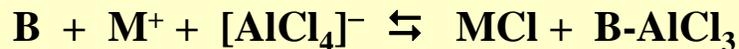
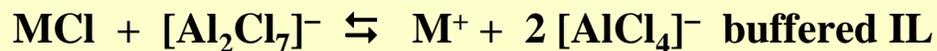
Acidic IL with an excess of AlCl_3



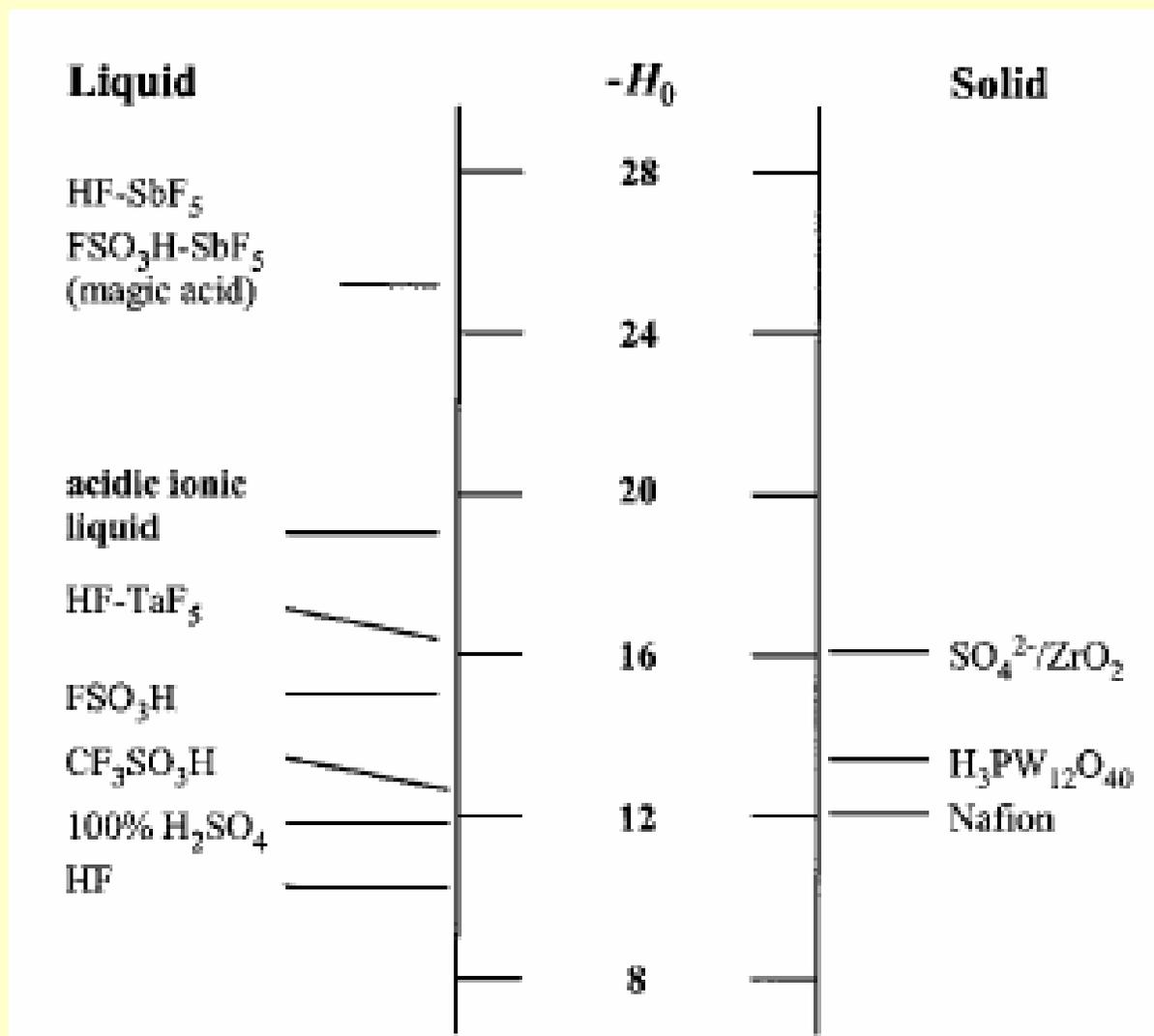
Proton extremely poorly solvated = high reactivity

Superacid $[\text{EMIM}]\text{Cl}/\text{AlCl}_3/\text{HCl}$ $H_0 = -19$ (HSO₃F: $H_0 = -15$)

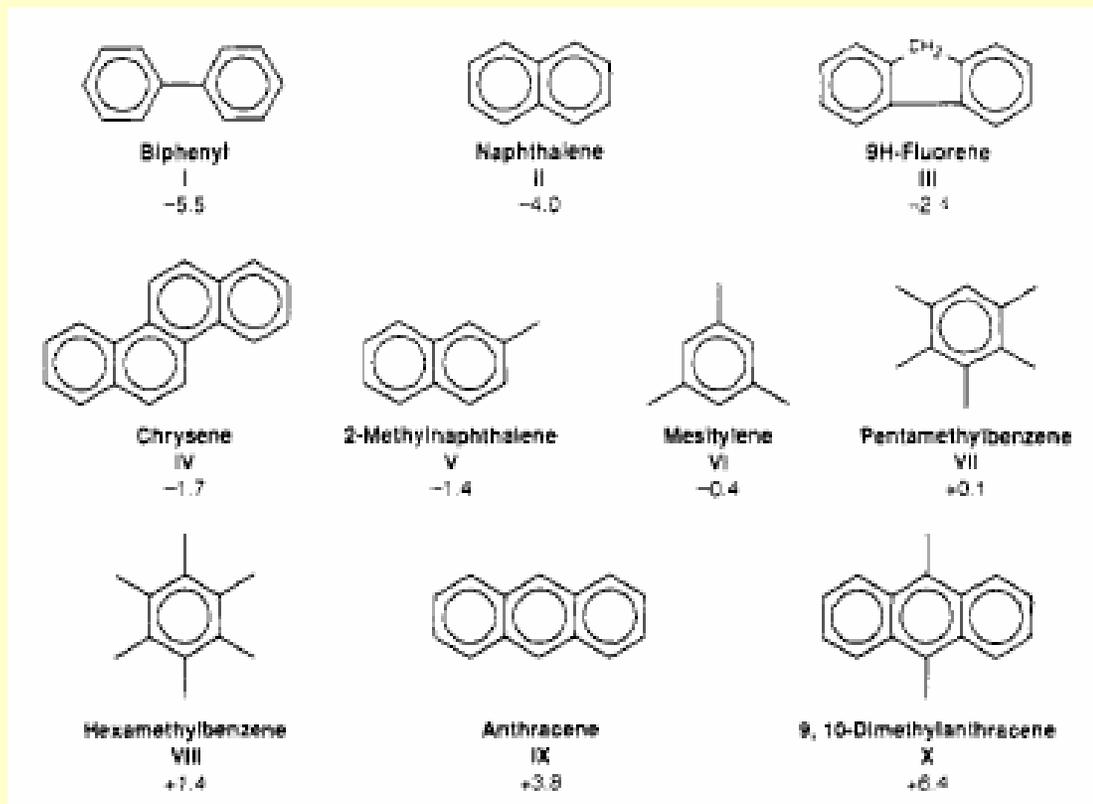
Latent acidity



Superacidity



Superacidic [EMIM]Cl/AlCl₃/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)
$\text{Na}_{13}[\text{La}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_{13}[\text{Tm}(\text{TiW}_{11}\text{O}_{39})_2]$	260.2
$\text{Na}_{13}[\text{Ce}(\text{TiW}_{11}\text{O}_{39})_2]$	263.0	$\text{Na}_{13}[\text{Yb}(\text{TiW}_{11}\text{O}_{39})_2]$	267.2
$\text{Na}_{13}[\text{Pr}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_5[\text{CrTiW}_{11}\text{O}_{39}]$	261.5
$\text{Na}_{13}[\text{Sm}(\text{TiW}_{11}\text{O}_{39})_2]$	256.0	$\text{Na}_5[\text{MnTiW}_{11}\text{O}_{39}]$	253.0
$\text{Na}_{13}[\text{Gd}(\text{TiW}_{11}\text{O}_{39})_2]$	265.1	$\text{Na}_5[\text{FeTiW}_{11}\text{O}_{39}]$	257.6
$\text{Na}_{13}[\text{Dy}(\text{TiW}_{11}\text{O}_{39})_2]$	265.2	$\text{Na}_6[\text{ZnTiW}_{11}\text{O}_{39}]$	257.4
$\text{Na}_{13}[\text{Er}(\text{TiW}_{11}\text{O}_{39})_2]$	261.0		

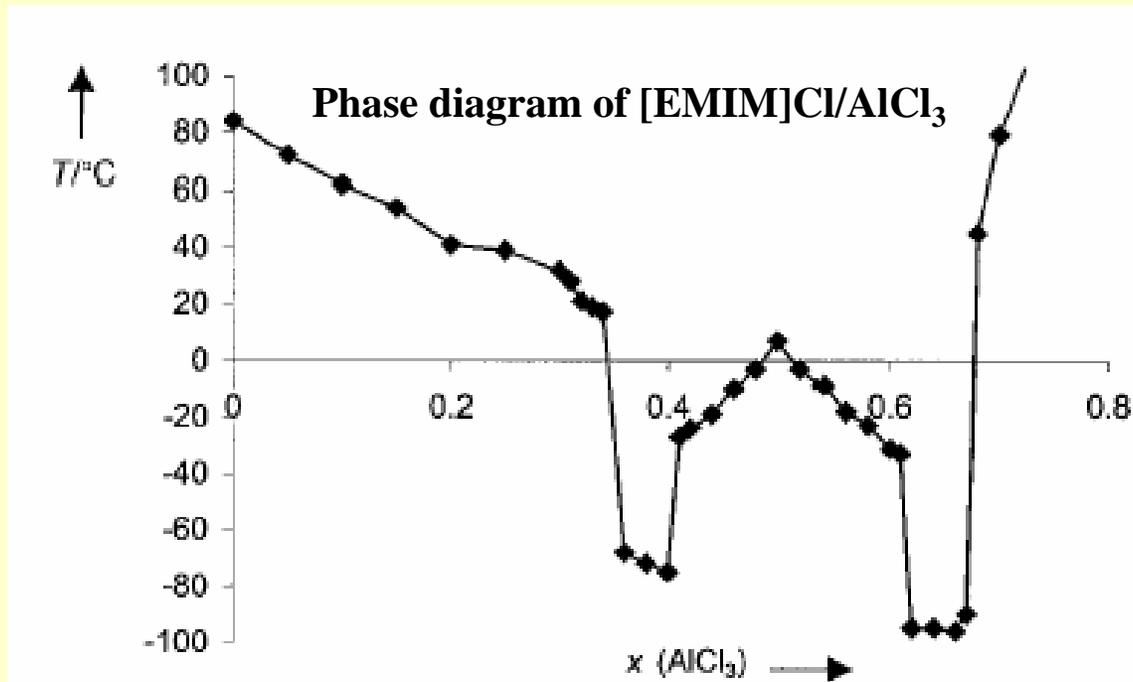
Melting Point of Ionic Liquids

Melting point is influenced by:

Cation – low symmetry, weak intermolecular interactions, good distribution of charge

Anion – increasing size leads to lower mp

Composition – Phase diagram



Melting Point of Ionic Liquids

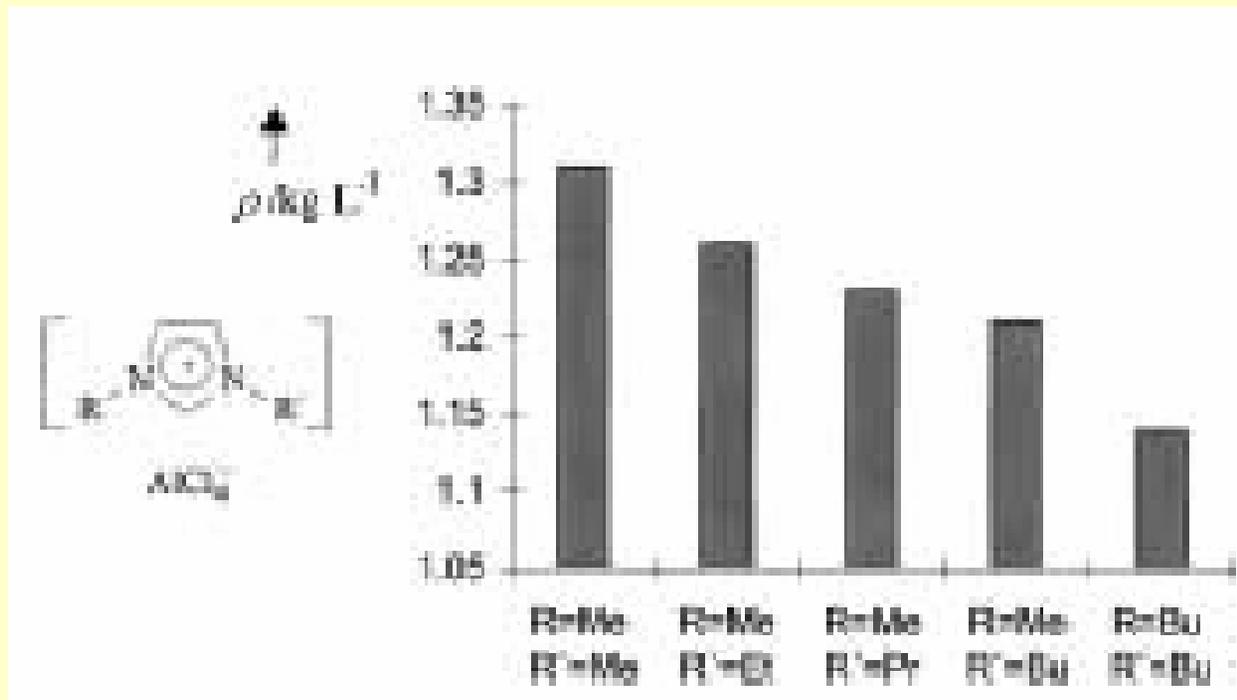


The chemical structure shows a five-membered imidazolium ring with a positive charge (+) in the center. One nitrogen atom is bonded to a methyl group (Me) and the other to an R group. To the right of the ring is a counterion X⁻.

R	X	mp/ ^o 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 ₃ SO ₃	-9
Et	(CF ₃ SO ₃) ₂ N	-3
Et	CF ₃ CO ₂	-14
n-Bu	CF ₃ SO 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]
 [A] ⁻	CF ₃ SO ₃ ⁻	90
	<i>n</i> -C ₄ F ₉ SO ₃ ⁻	373
	CF ₃ COO ⁻	73
	<i>n</i> -C ₃ F ₇ COO ⁻	182
	(CF ₃ SO ₂) ₂ N ⁻	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, CF₃COO, CF₃SO₃

Water-immiscible [BMIM] PF₆ (CF₃SO₂)₂N

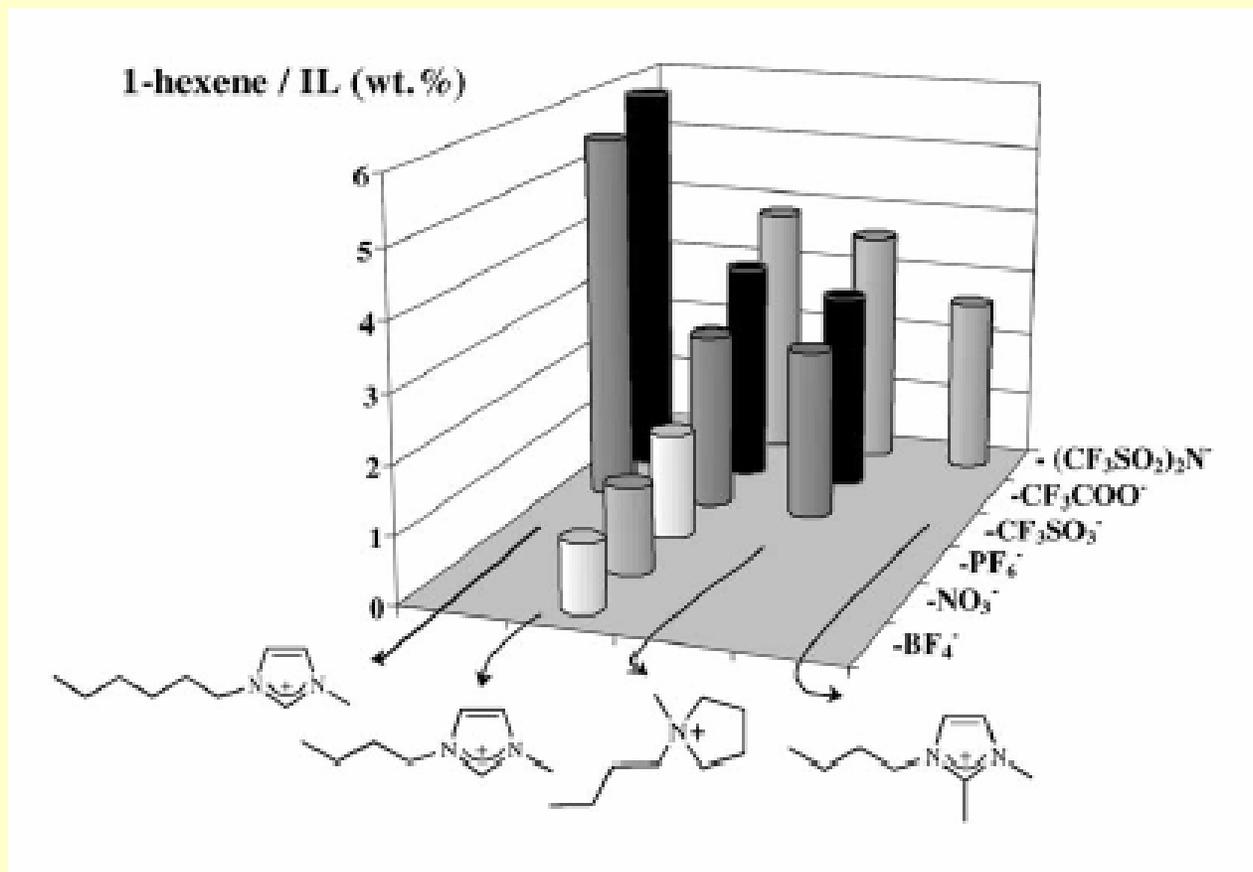
IL miscible with organic solvent IF their dielectric constant is above a certain limit given by the cation/anion combination

Polarity by E_(T)(30) scale

[EtNH₃][NO₃] 0.95 between CF₃CH₂OH and water

[BMIM] PF₆ 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

BiCl₃, SrCl₂, CaCl₂, CuCl₂ dissolve well

Constituent	BiCl₃	SrCl₂	CaCl₂	CuCl₂
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



Natural gas sweetening (H₂S, CO₂ removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U⁴⁺ oxidized to U⁶⁺)

Extraction

Enzyme activity

Applications of Ionic Liquids

Olefin polymerization

Ethene + TiCl_4 + AlEtCl_2 in acidic IL

Ethene + Cp_2TiCl_2 + $\text{Al}_2\text{Me}_3\text{Cl}_3$ in acidic IL



Olefin hydrogenation

Cyclohexene + H_2 + $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's catalyst)

Sound

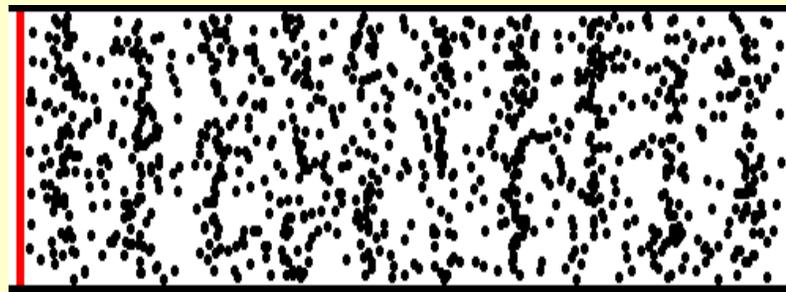
Sound = pressure wave, periodic compression/expansion cycles traveling through a medium possessing elastic properties (gas, liquid, solid)

**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

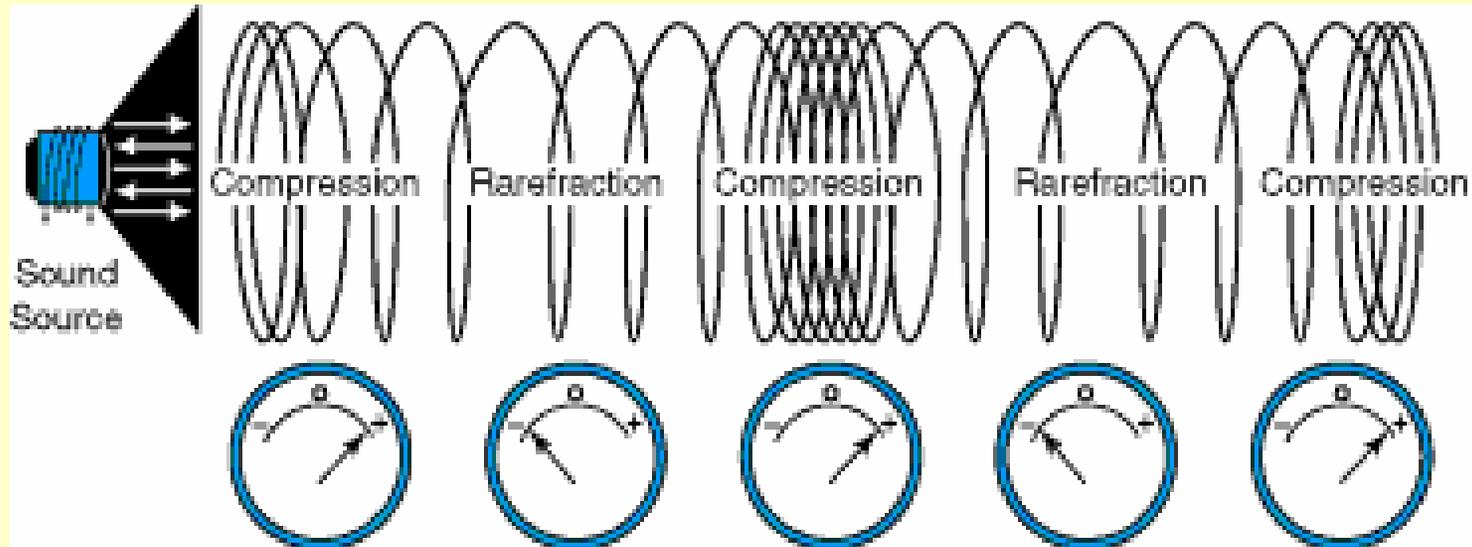


Sound

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

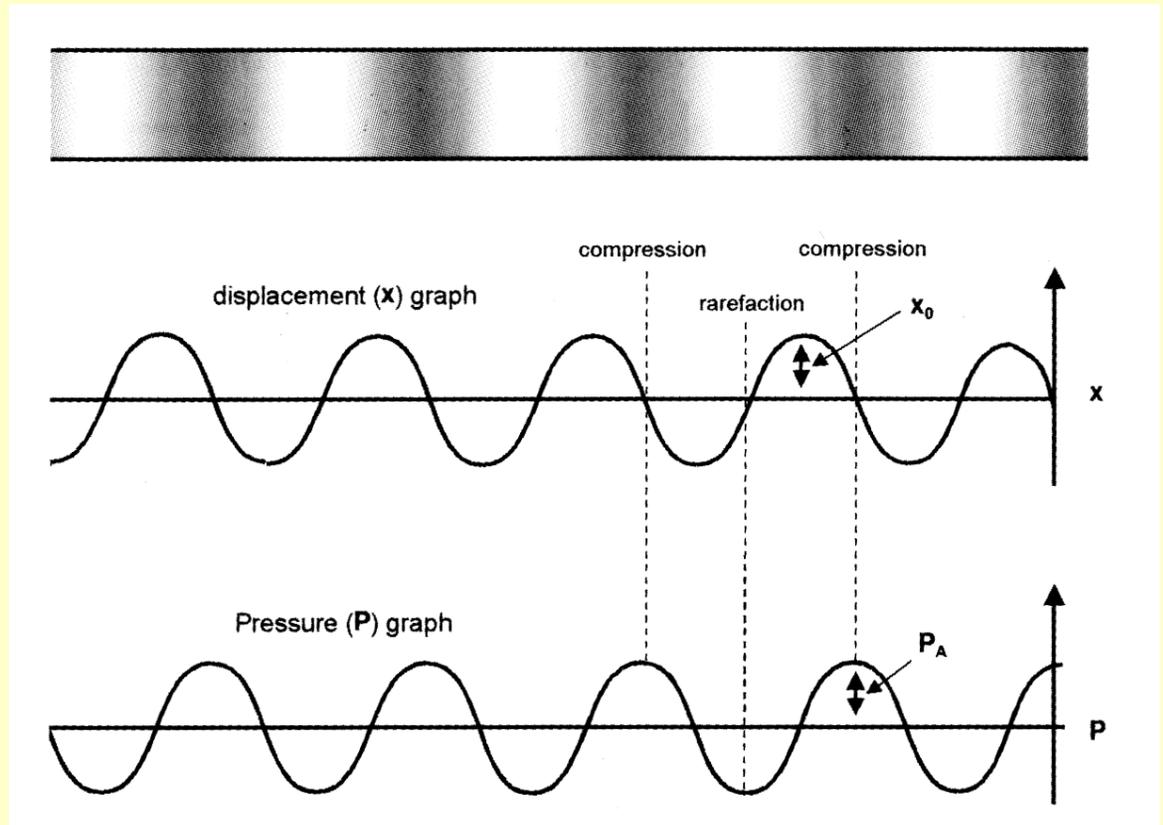
f sound frequency

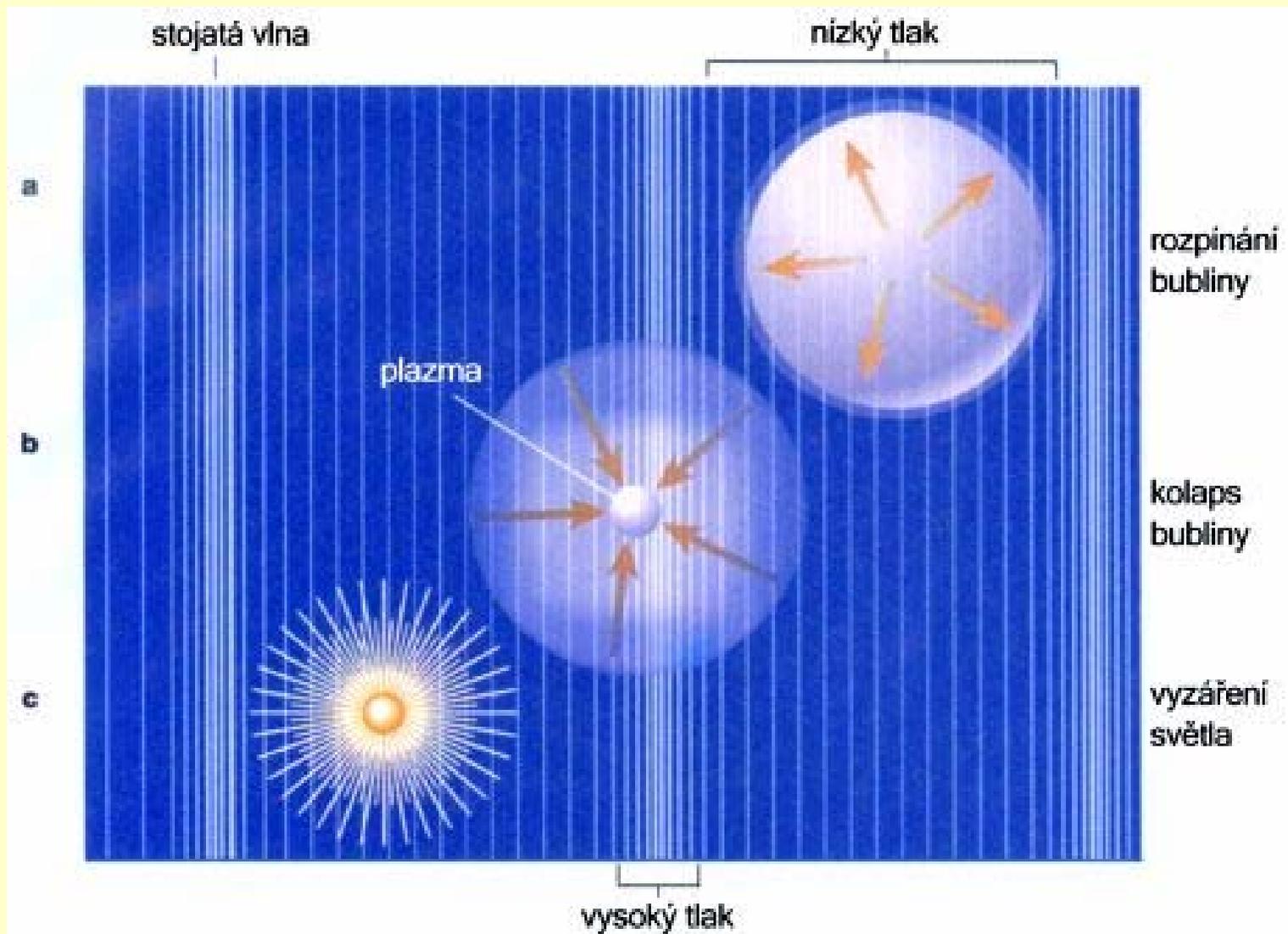
$$c = \lambda f$$

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

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

P_h hydrostatic pressure





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

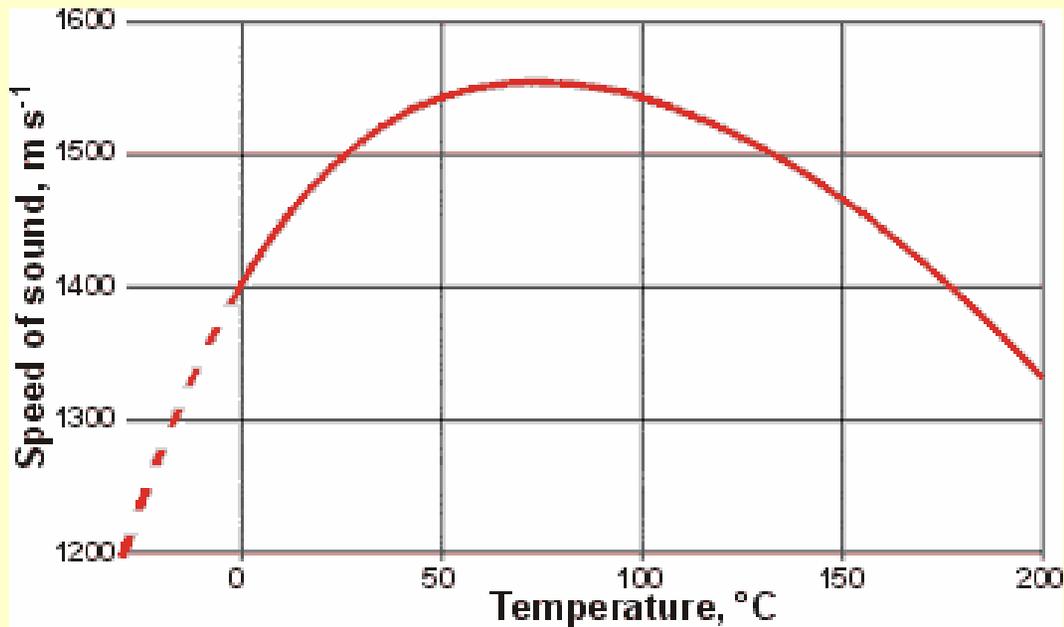
Substance	Speed of sound [m s⁻¹]
Air	343
Helium	965
Water	1482
Lead	1960
Steel	5960
Granite	6000

The speed of sound

The speed of sound (u)

$$u^2 = 1/\kappa_S \rho = [\partial P/\partial \rho]_S \sim 1/(\langle (\nabla V)^2 \rangle)$$

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



Sound Intensity

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

<i>Source of Sound</i>	<i>Intensity (W/m²)</i>	<i>Sound level (dB)</i>
Jet Airplane 30 m away	10²	140
Air-raid Siren, nearby	1	120
Threshold of Pain	10⁻¹	120
Concert	~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/m²)

10 dB = 10 as intense

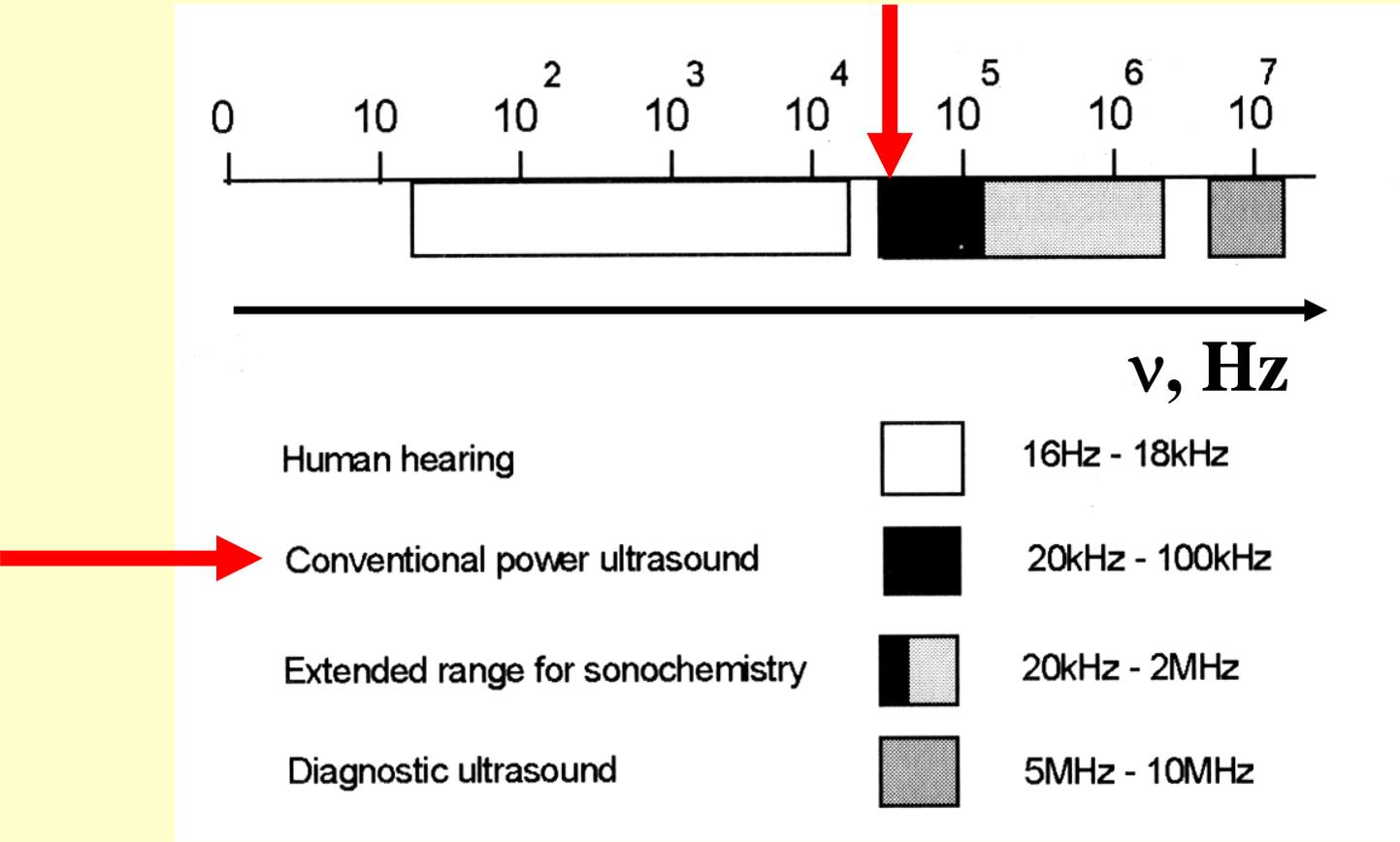
20 dB = 10² as intense

30 dB = 10³ as intense

120 dB = 10¹² 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

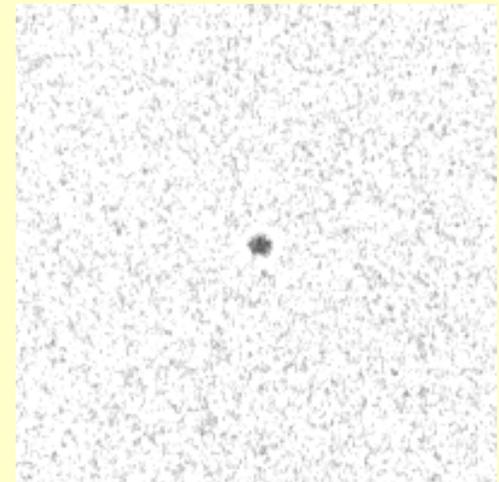
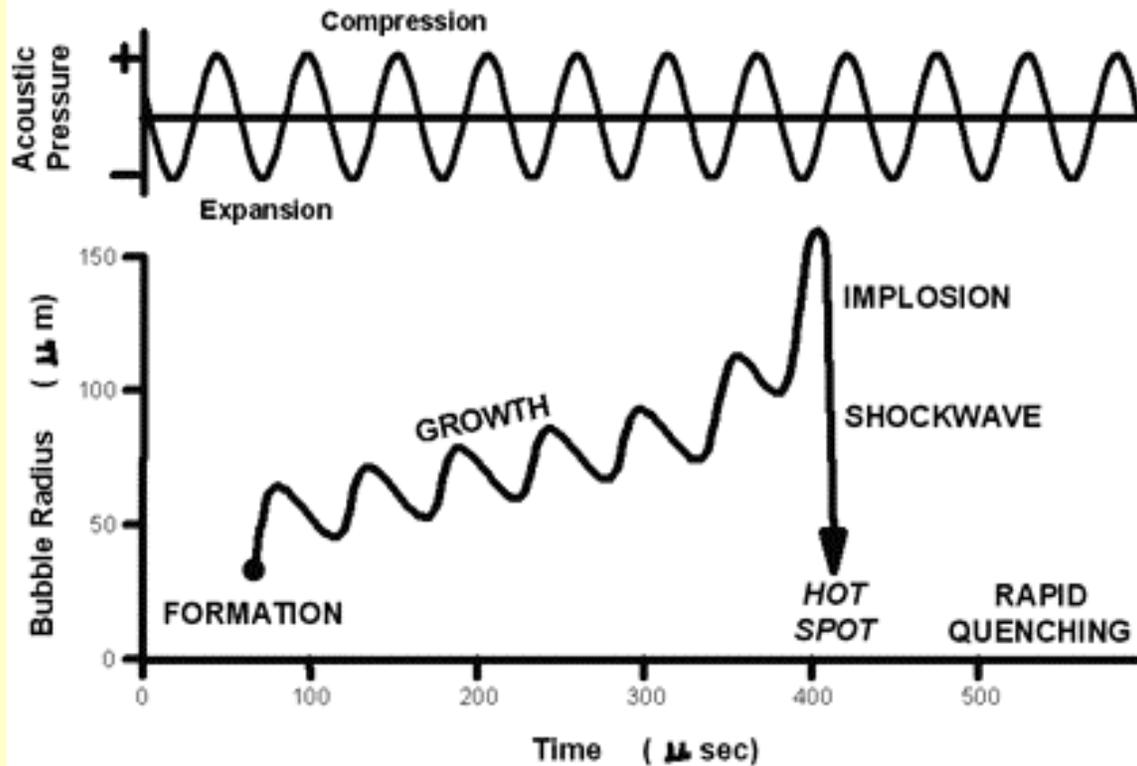
the liquid jet expands, the pressure recovers

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

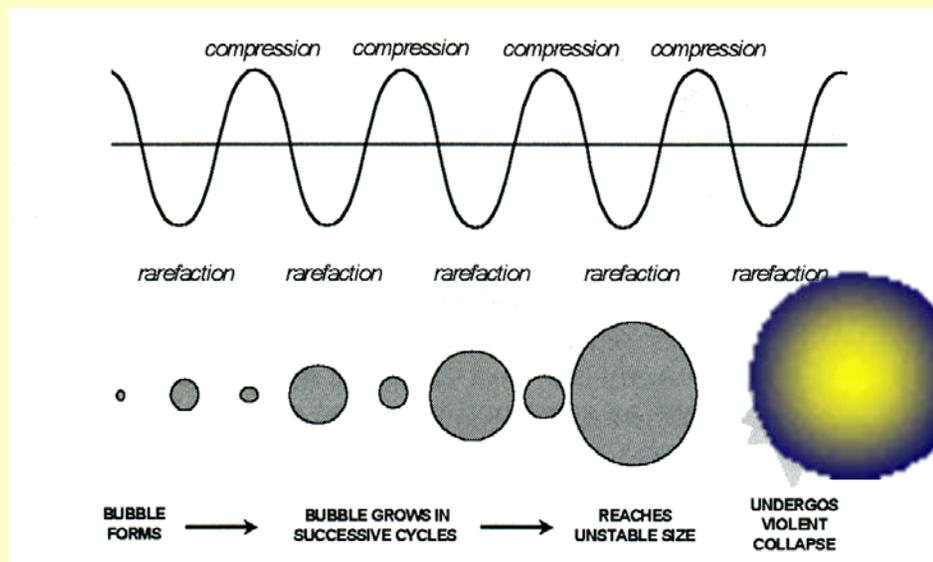
transient cavitation - transient cavities expand rapidly collapse violently

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**



Cavitation

Bubble collapse = implosion (1 ns)

- **HOMOGENEOUS**

liquid: spherically symmetrical implosion, shear forces

Hot spots = adiabatic compression, life time 2 μ s

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,

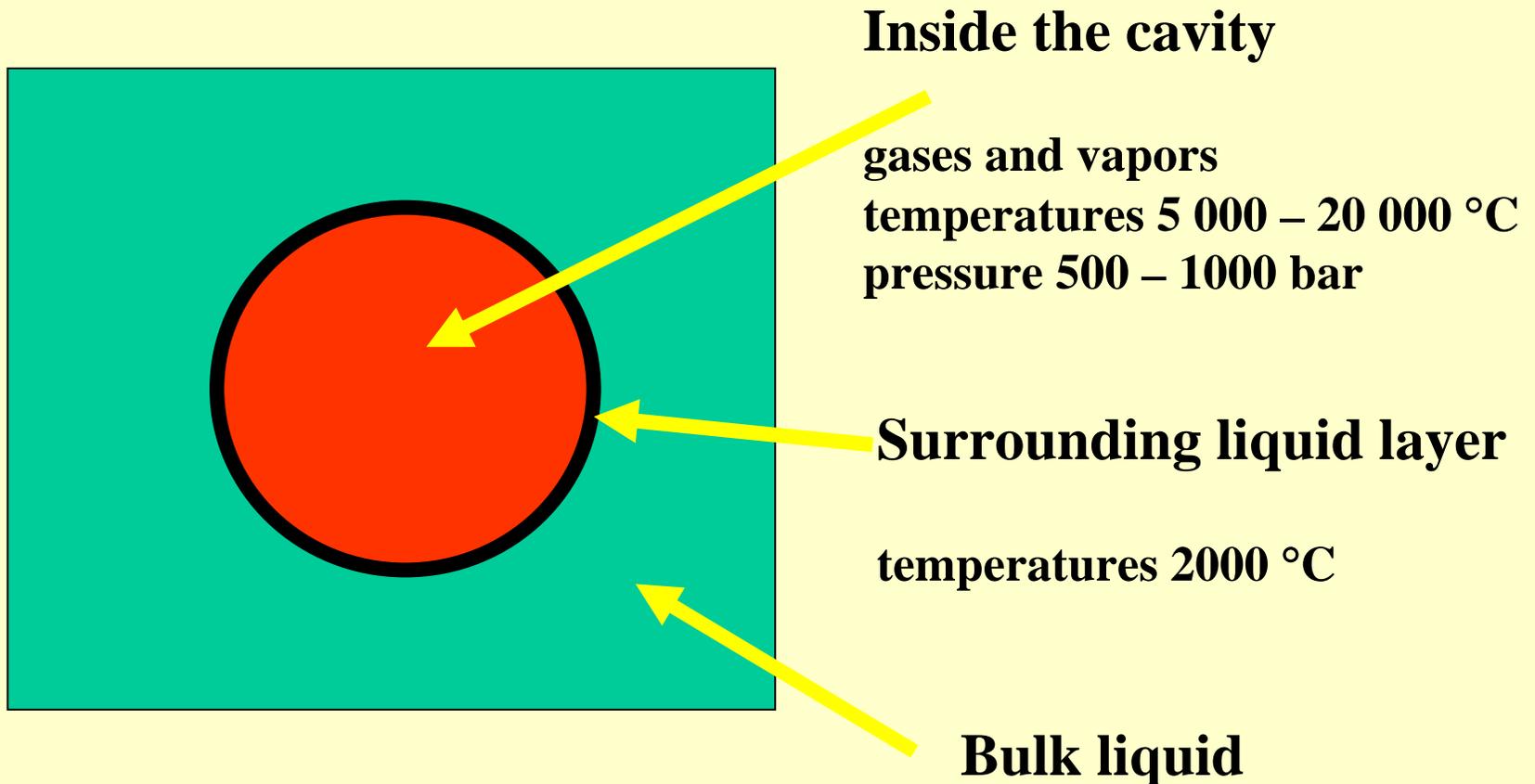
high speed microjets of liquid (400 km h⁻¹)



Microjet - bubble implosion

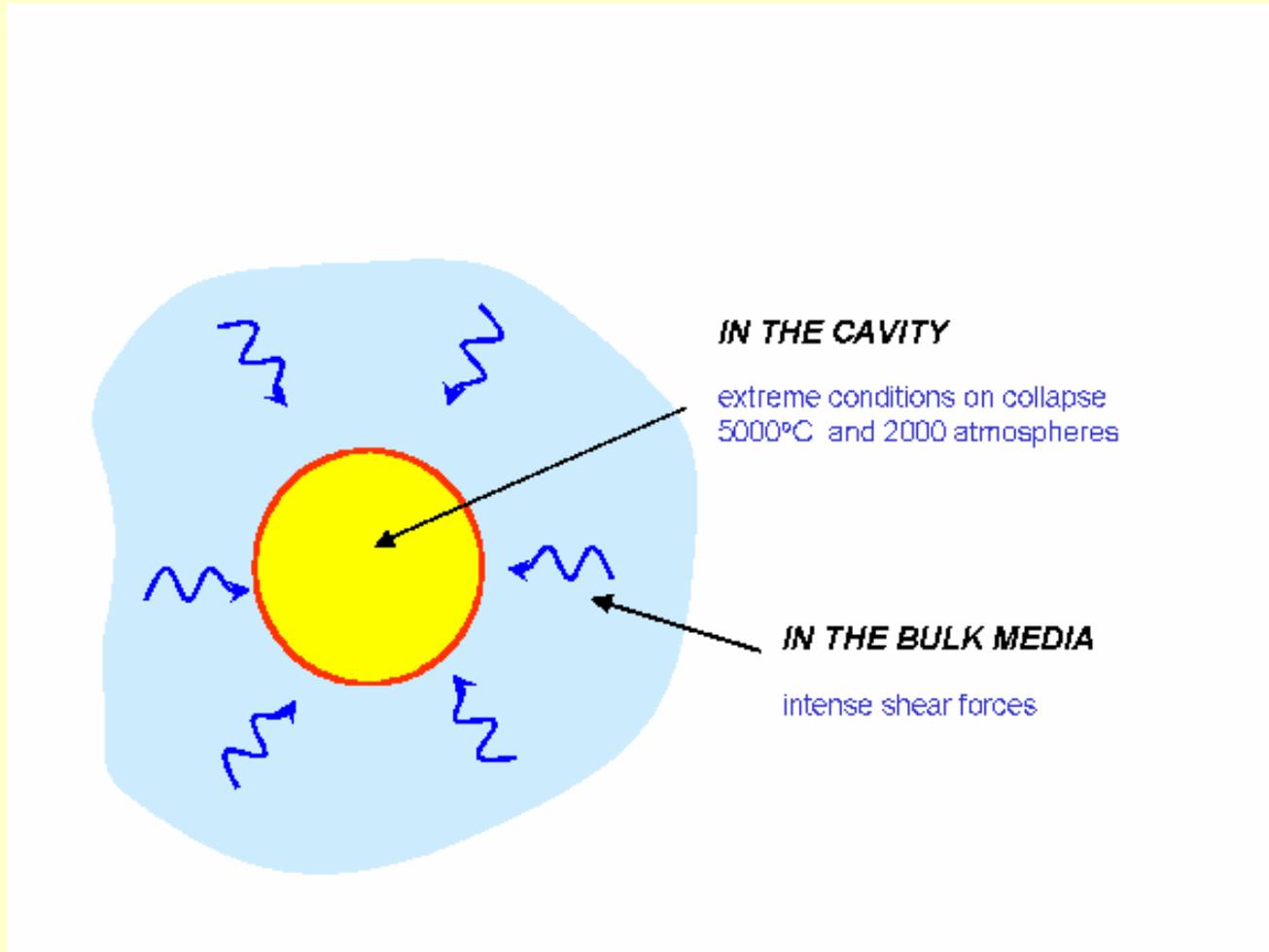
Homogeneous Sonochemistry

Two-Site Mechanism



shear forces

Two-site Mechanism



Heterogeneous Sonochemistry

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

surface erosion

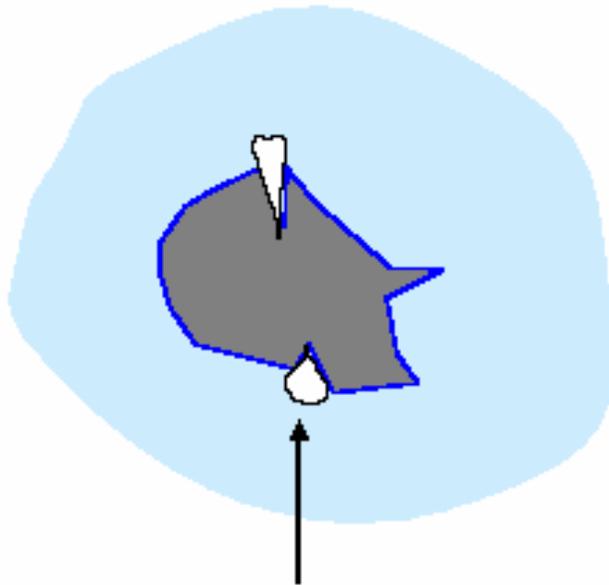
removal of unreactive coatings (oxides, nitrides, carbonaceous)

fragmentation of brittle materials, increased surface area



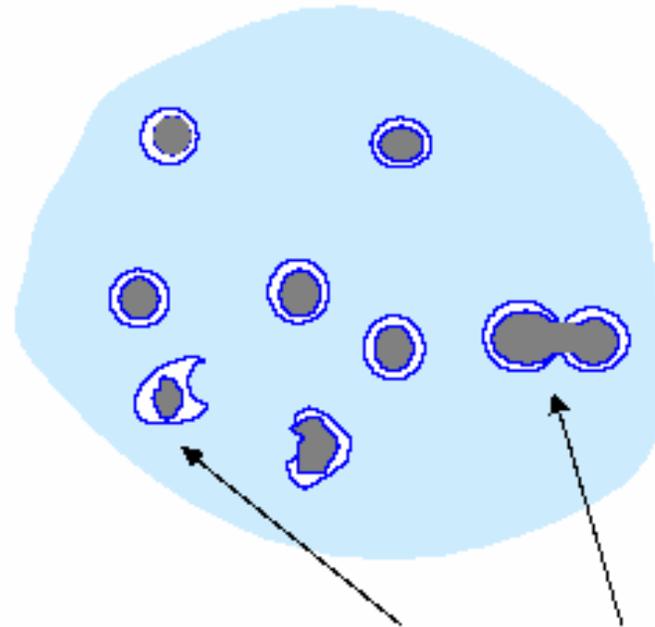
Heterogeneous Sonochemistry

LARGE PARTICLES



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

SMALL PARTICLES



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

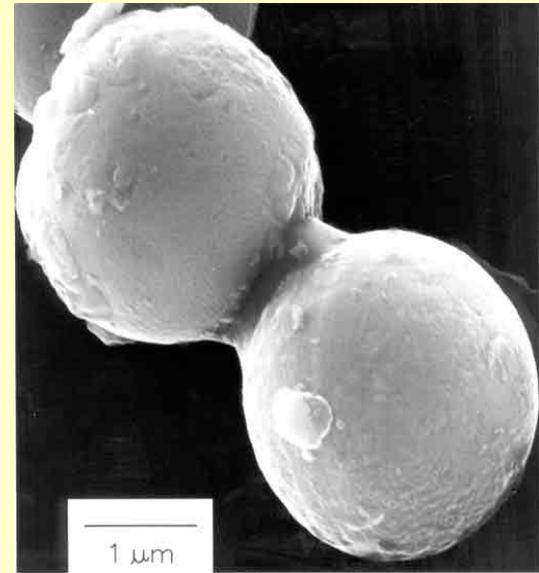
Heterogeneous Sonochemistry

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**



SONOCHEMICAL METHOD

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

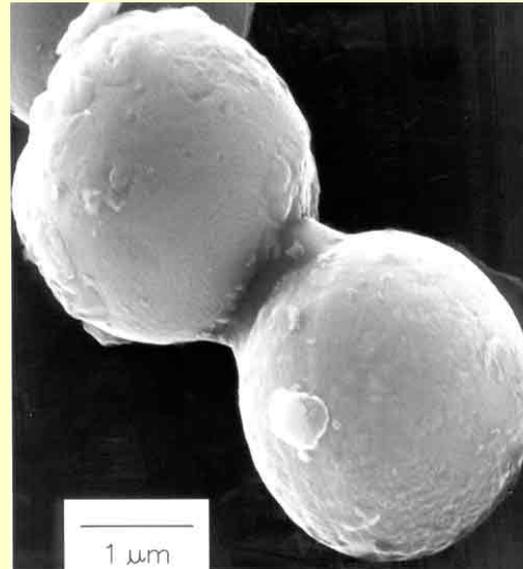
surface smoothing, surface coating removal

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)



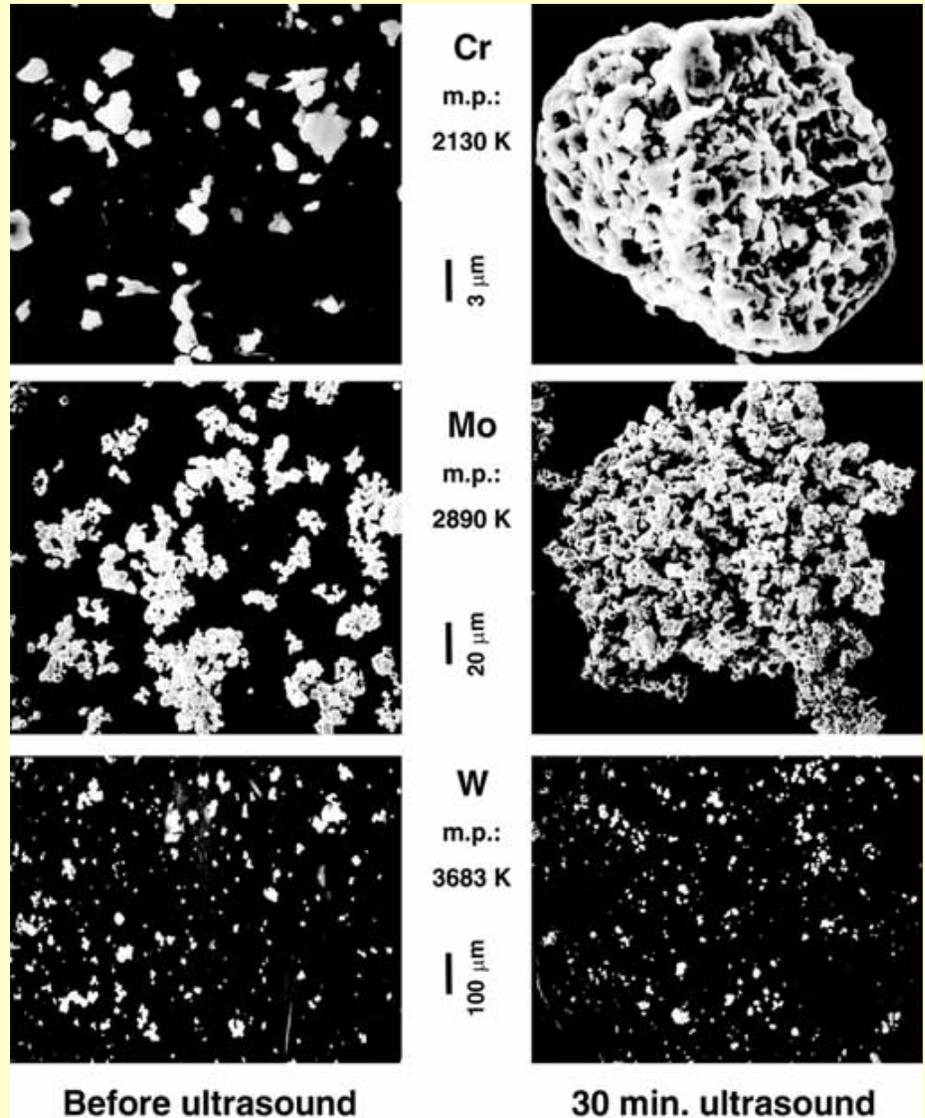
Heterogeneous Sonochemistry

Metal powders

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

W (mp 3683 K) does not

temperatures at the point of impact ~ 3000 °C



Before ultrasound

30 min. ultrasound

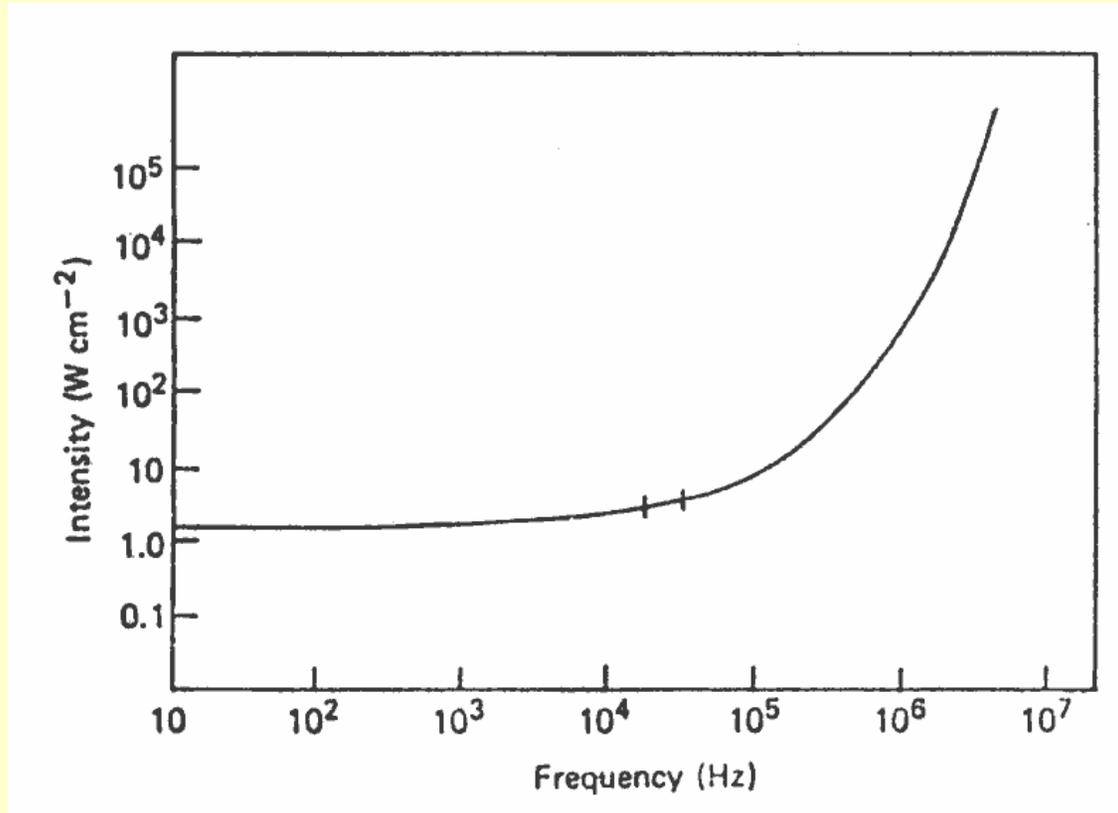
Cavitation Corrosion of the Tip



Control of sonochemical reactions

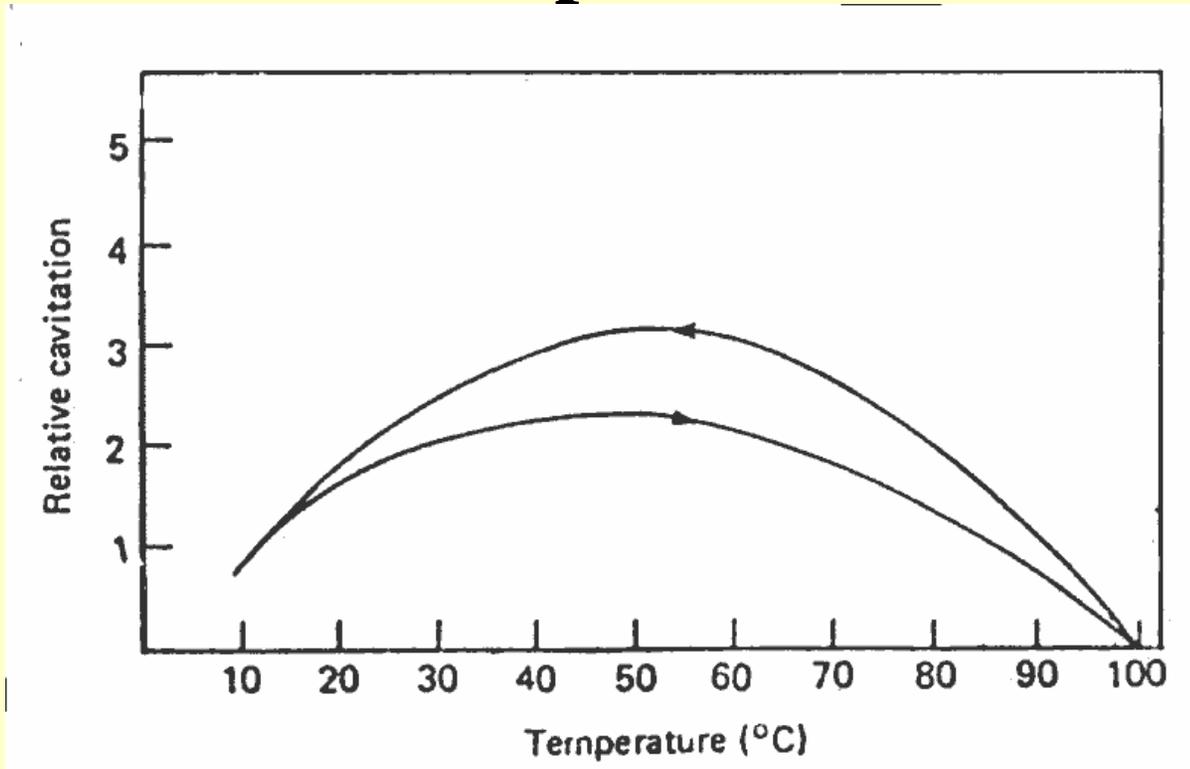
- frequency 20-40 kHz, the higher the frequency, the higher power needed to actuate cavitation, rarefaction phase shortens at high freq.
- volatile reactants, primary reaction site inside the bubbles, diameter 200 μm , 5000 $^{\circ}\text{C}$, easier bubble formation, more vapors inside bubbles, but the cavitation is cushioned
- nonvolatile reactants, reaction in the thin layer (200 nm) surrounding the bubble, 2000 $^{\circ}\text{C}$, 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.

Control of sonochemical reactions

■ ambient gas important

energy developed on bubble collapse:

monoatomic (Ar) > diatomic (N₂) > triatomic (CO₂)

Xe: low thermal conductivity, heat of the collapsing cavity retained

He: high thermal conductivity, heat of the collapsing cavity dissipated, 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

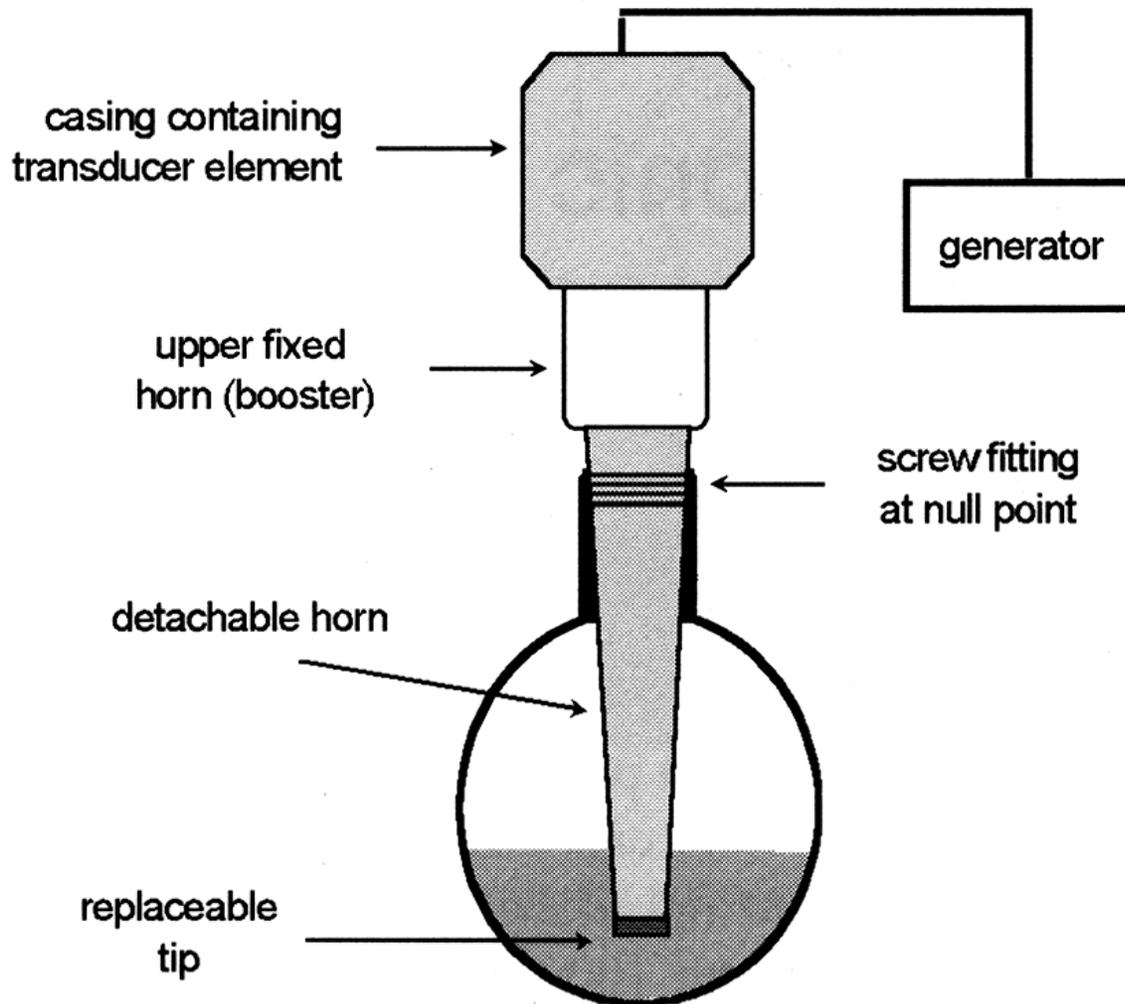
liquid whistle homogeniser, a jet of liquid passed through an orifice on a thin metal blade, vibrations, cavitation, mixing of immiscible liquids, ketchup, mayonnaise

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, opposite charges applied on crystal sides, contraction/expansion, quartz, $\text{Pb}(\text{Zr}/\text{Ti})\text{O}_3$ ceramics (PZT), up to MHz

Generation of Ultrasound



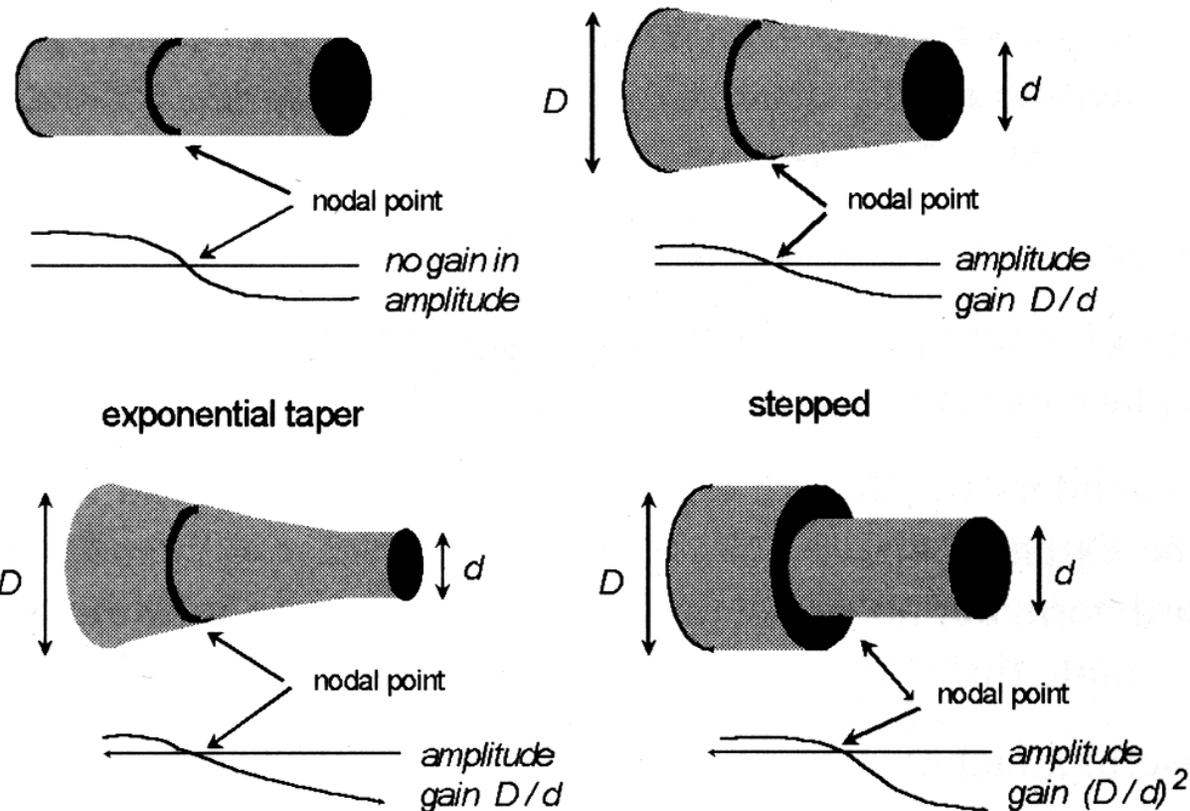
Sonochemical Reactor



SONOCHEMICAL METHOD

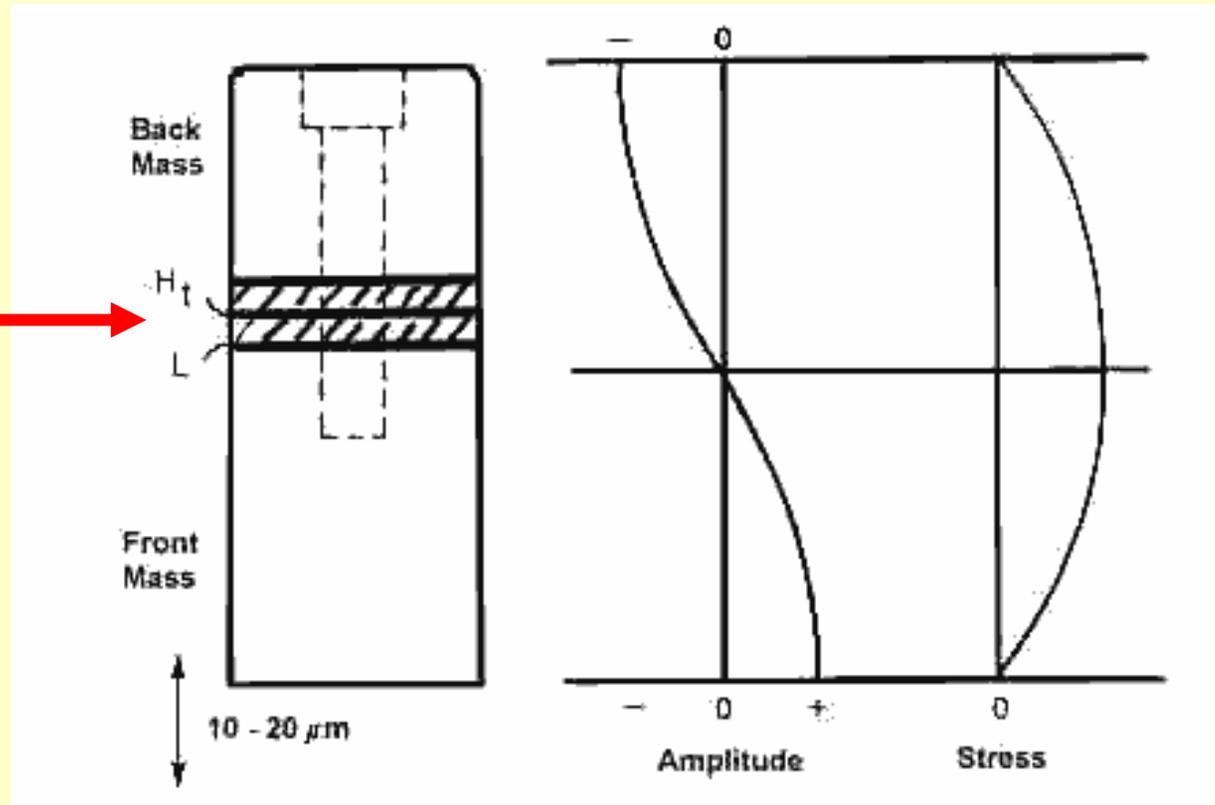
Ti alloy horn, minimum length is a half-wavelength of sound in a material, 26 cm for 20 kHz in Ti, multiples of 13 cm

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 cm³ 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



precursor decomposition:

metals



oxides



nitrides, carbides, sulfides

alkane cracking

polymer degradation, lower MW, surface modification

emulsification of immiscible liquids (oil-water, Hg-organics,

polymer-inorganics)

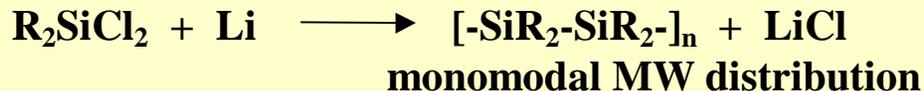
SONOCHEMICAL METHOD

♦ 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



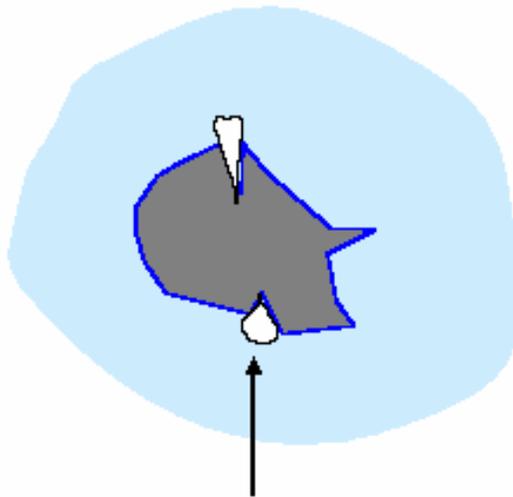
Protein microspheres

diameter 2 μm , hollow

emulsification, crosslinking cysteine -S-S- by superoxide

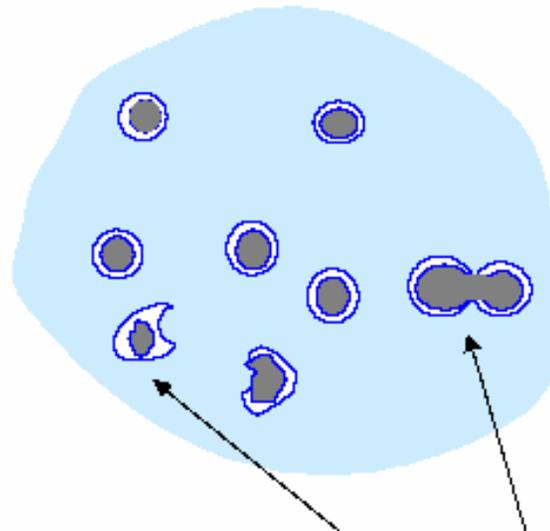
SONOCHEMICAL METHOD

LARGE PARTICLES



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

SMALL PARTICLES



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