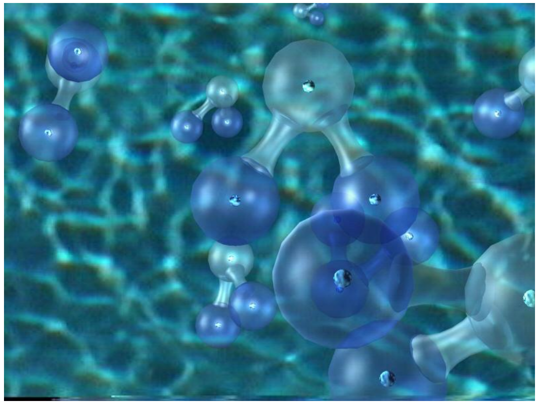
Labortechnik

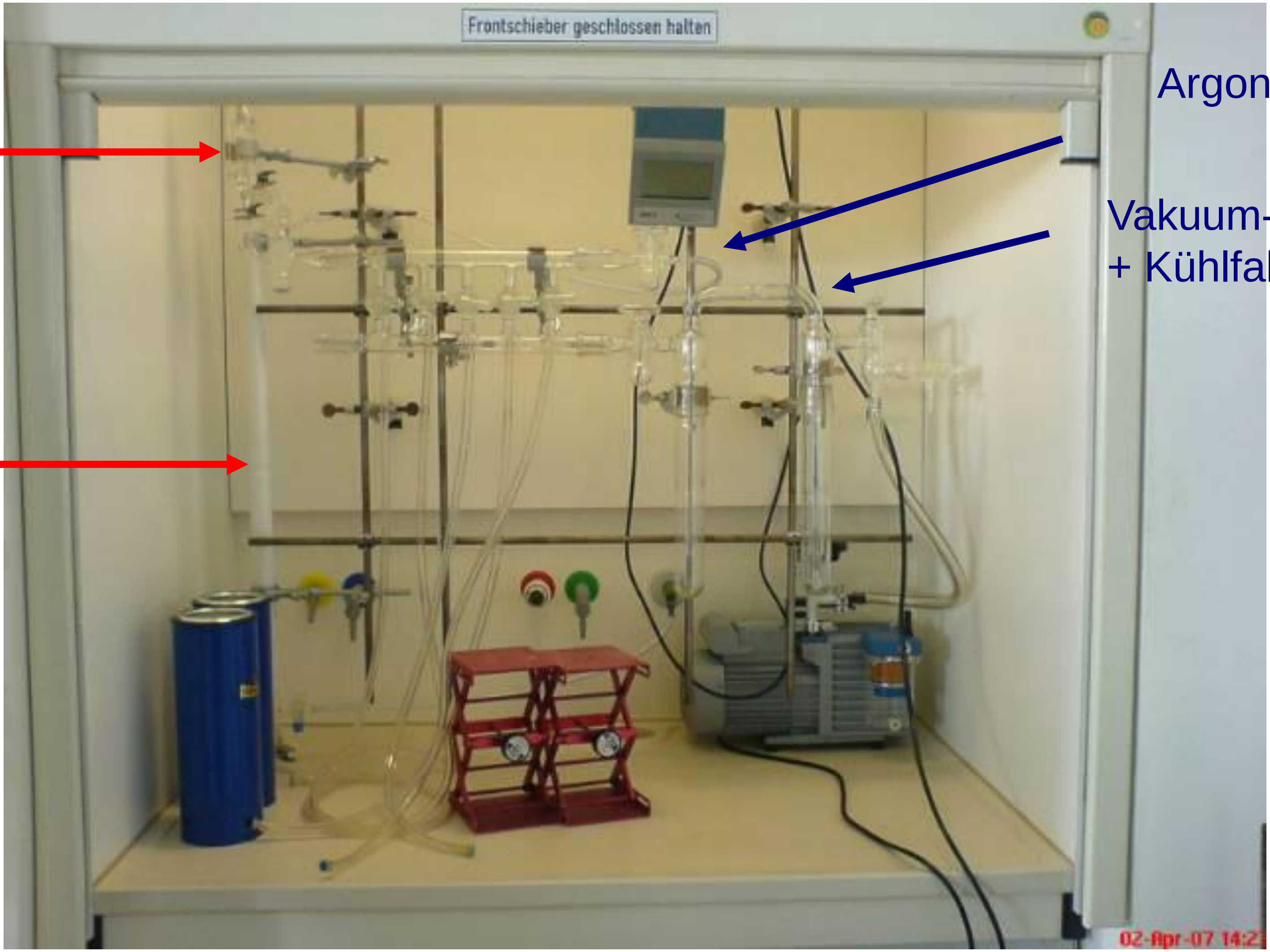
Axel Schulz
Institut für Chemie
der Universität Rostock
2019

Inhalt

- Vakuumtechnik
- Chemische Werkstoffe
- Kühlmittel
- Reaktionsmedien



Schlenck-HV-Anlagen (AK Schulz)



Überdruck-ventil

Trocken-säule

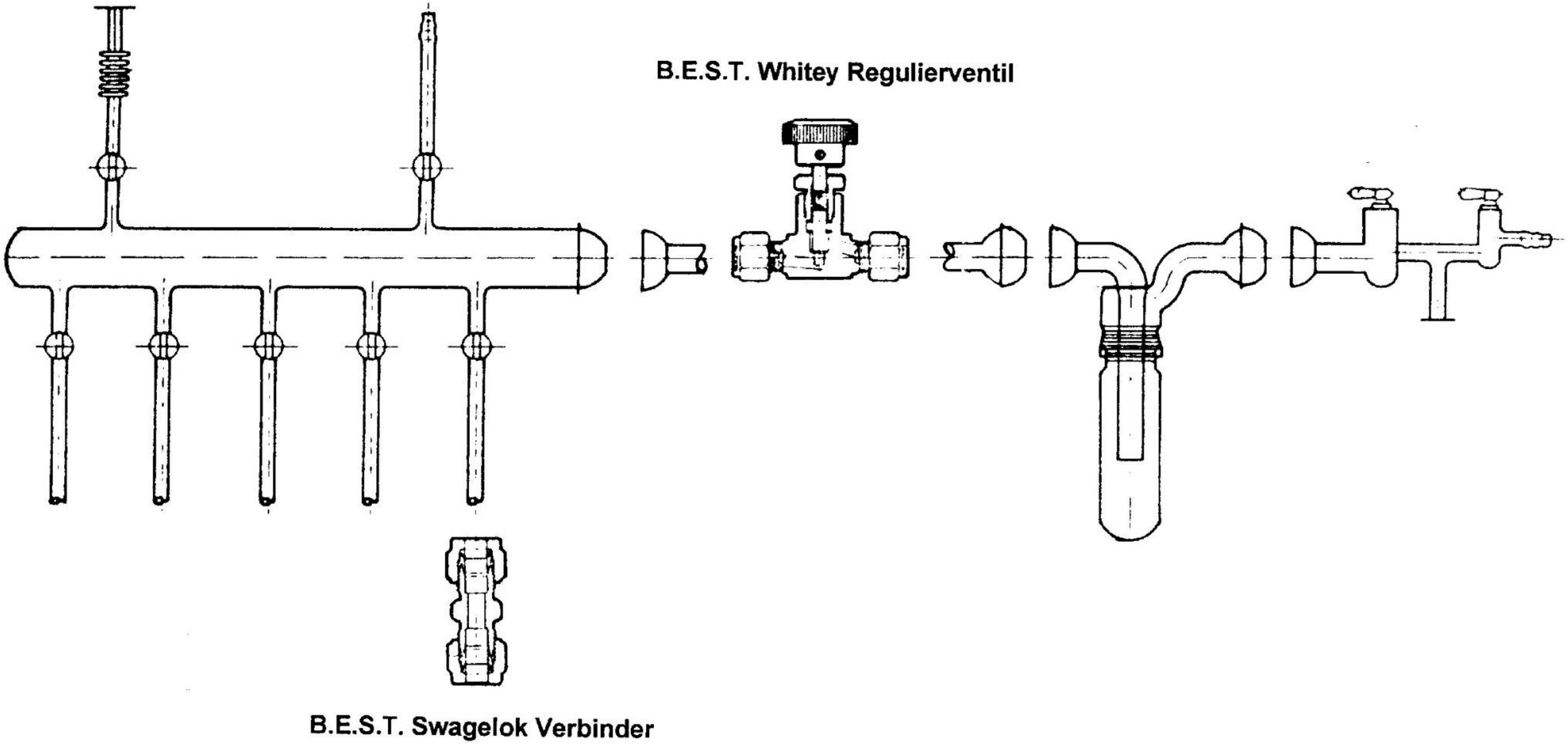
Argon-Line

Vakuum-Line + Kühlfallen

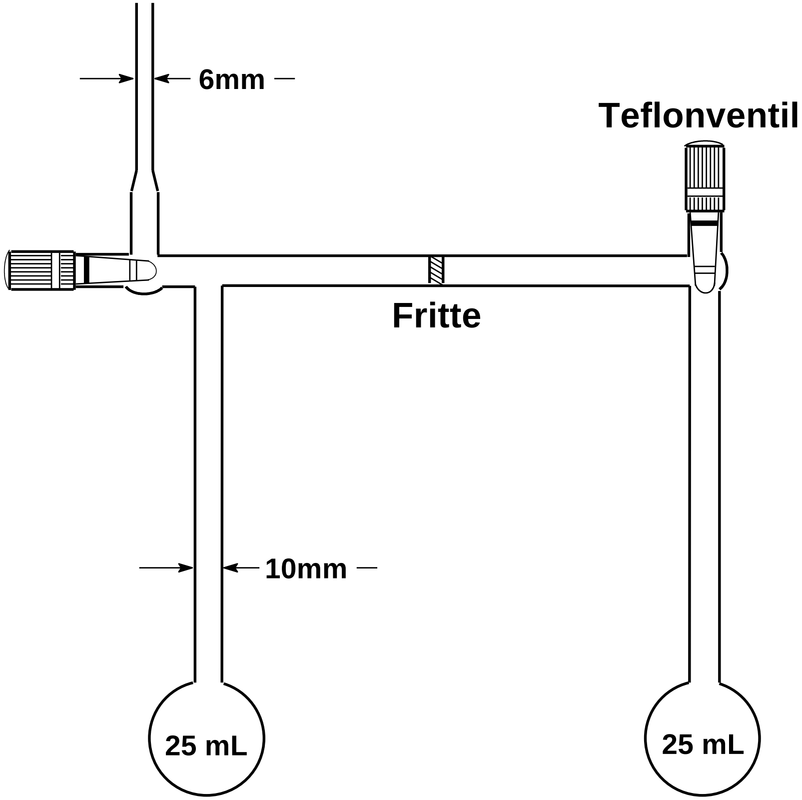
Schlenk-HV-Analgen (AK Schulz)

Drehschieberpumpen garantieren ein Vakuum bis 10^{-3} mbar

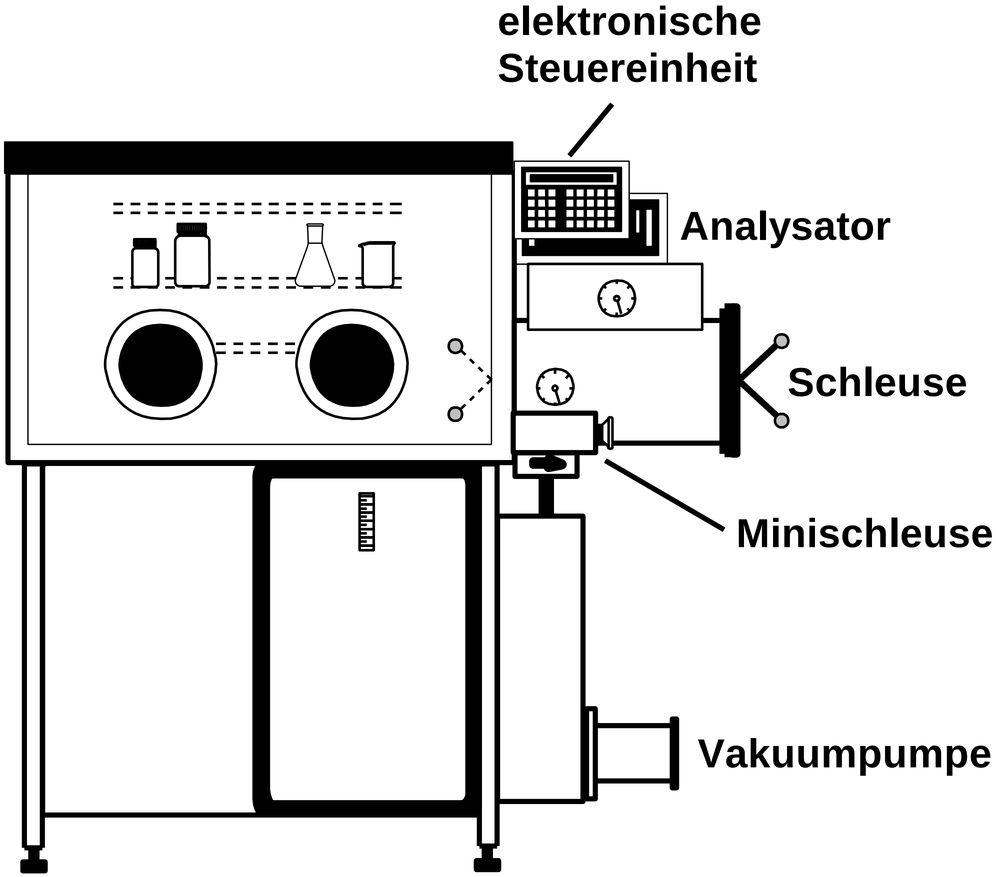
Vakuumanlage aus Edelstahl



Zweikugelkolben



Glovebox-Technik



elektronische Steuereinheit

Analysator

Schleuse

Minischleuse

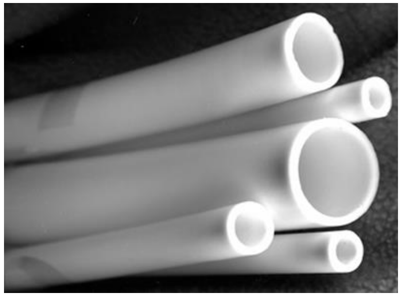
Vakuumpumpe

Arbeiten unter HV-Bedingungen mit Inertgas

- Dreimaliges Ausheizen der Apparatur unter Vakuum, jeder Durchgang mindestens 5 Minuten
- Nicht zu wenig, aber auch nicht zu viel Fett (2/3 der Oberfläche)
- Beim Arbeiten mit Schlenk-Apparatur, Füllstand des flüssigen Stickstoffs in Dewar-Gefäßen regelmäßig überprüfen
- Schliffe beim Verbinden oder beim Verschließen sorgfältig eindrehen → Dichtigkeit checken
- Verbinden zweier Apparaturen unter Schutzbedingungen nur im Gegenstrom, d.h. unter anliegendem Überdruck des Inertgases

Chemische Werkstoffe

- Fluorkunststoffe (-200°C - +200°C):



PTFE (1938 Dupont: Teflon; Hoechst AG: Hostaflon)

$$CHCl_3 + 2HF \xrightarrow{SbFCl_4\,(SbCl_5 + HF)} CHF_2Cl + 2HCl$$

$$2\,CHF_2Cl \xrightarrow{\Delta T,\,-2HCl} C_2F_4 \longrightarrow 1/n(C_2F_4)_n$$

Polychlortrifluorethylen (PCTFE, auch Kel-F) (härter, durchscheinend)

Perfluoralkoxy-Copolymer (PFA)

Zersetzung T > 260° - 400°C : Teflonfieber!

Metallische Werkstoffe

- Edelstahl (Fe 65, Ni 12, Cr 17, Mo 2.5, Mn 2.0, Si 1 %)

  Bis 600 °C, HNO_3, H_2SO_4, H_3PO_4, HF, F_2, …

- Monel (Ni 66.0, Cu 31.5, Fe 1.2)

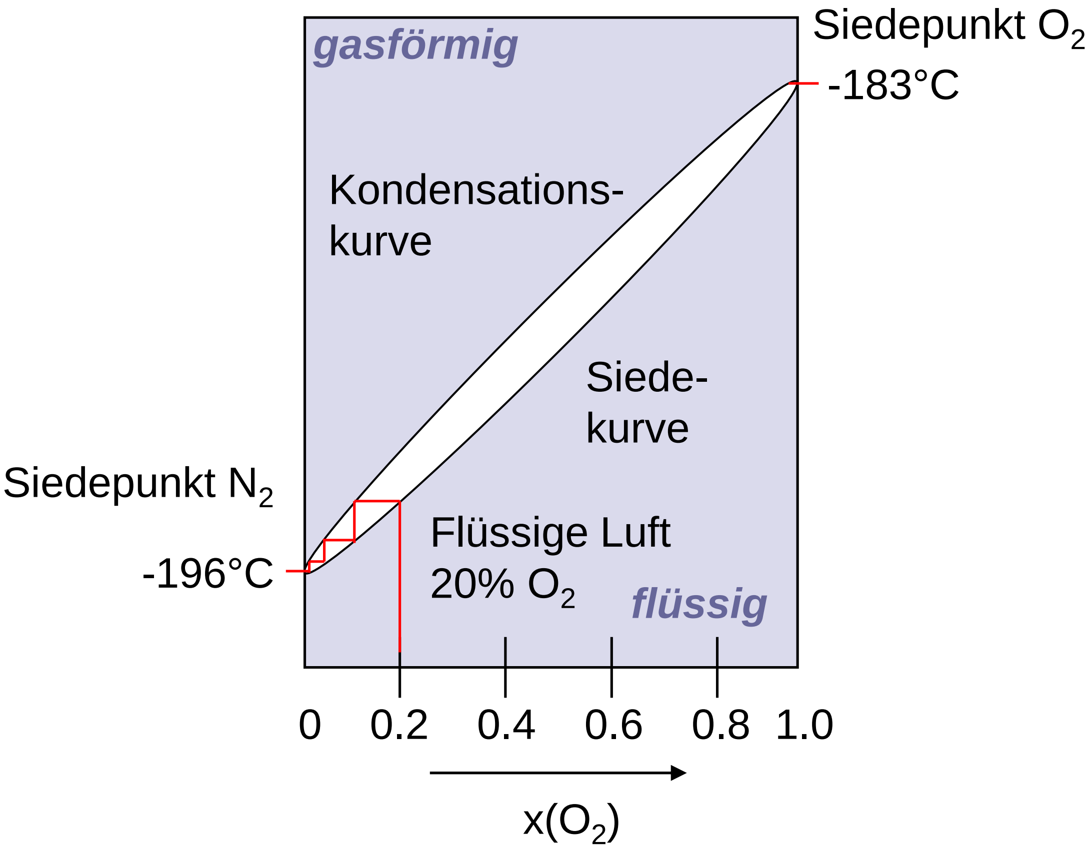
  Bis 400 °C, HNO_3, H_2SO_4, H_3PO_4, HF, F_2, …

  KEIN Ammoniak!

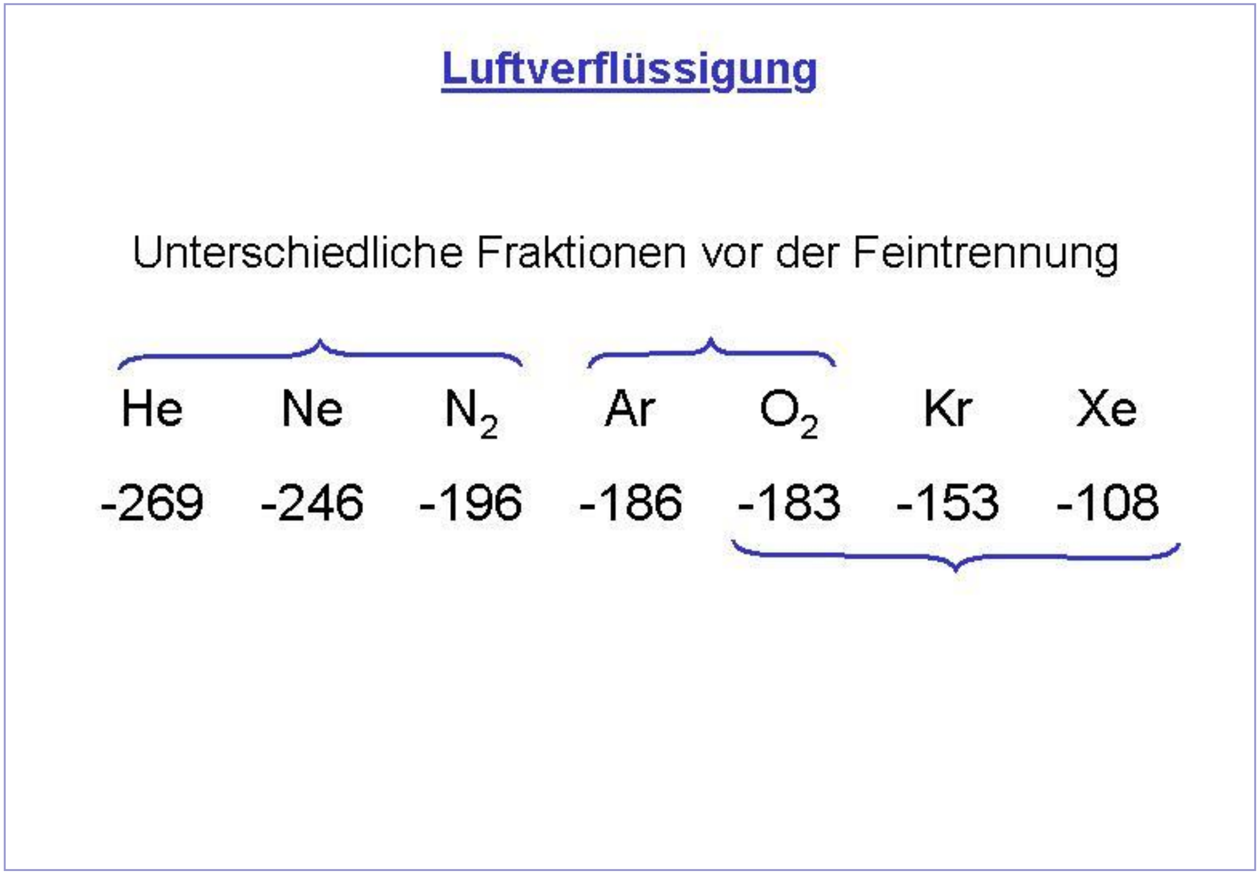
- Nickel (> 99%)

  Bis 300 °C, HNO_3, H_2SO_4, H_3PO_4, HF, F_2, …

Luftverflüssigung – Stickstoff als Kühlmittel



Siedepunkte von Gasen



Luftverflüssigung

Unterschiedliche Fraktionen vor der Feintrennung

He	Ne	N_2	Ar	O_2	Kr	Xe
-269	-246	-196	-186	-183	-153	-108

Vorsicht Sauerstoff / Argon kann bei Kühlung mit N_2 einkondensiert werden!

Kühlbäder – Einstellen der Temperatur

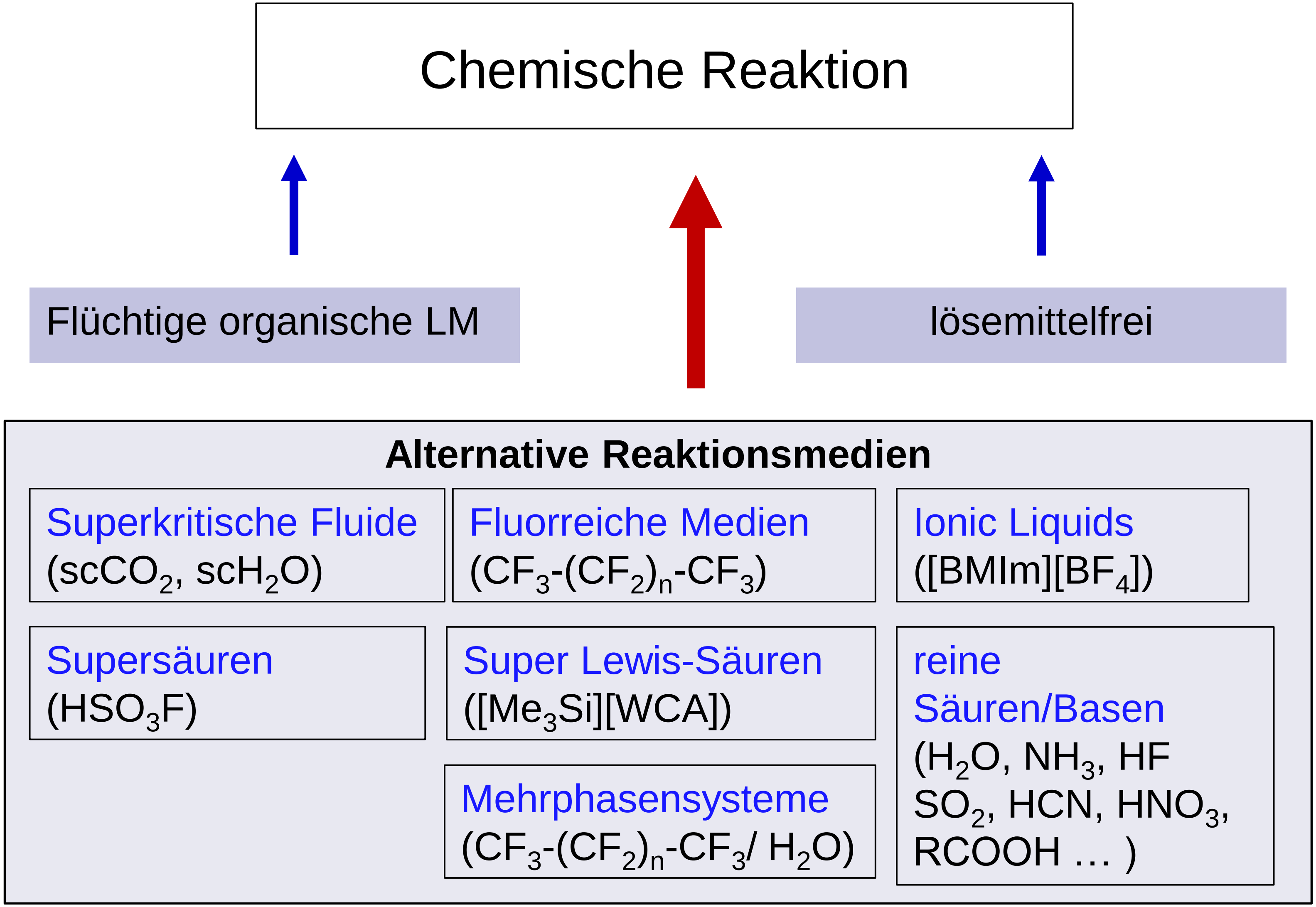
- Mit Stickstoff

Badinhalt	**Temperatur (K)**
N_2 (l) + Cyclohexan	279
N_2 (l) + Acetonitril	232
N_2 (l) + Oktan	217
N_2 (l) + Heptan	182
N_2 (l) + Hexa-1,5-dien	132
N_2 (l) + Isopropanol	Bis 195 (AK Schulz)
CO_2 (s) + Aceton	195

Beim Anmischen des Kältebades das Lösemittel in einem Dewar-Gefäß vorlegen und unter ständigem Rühren vorsichtig flüssigen Stickstoff zugeben

- Mit CO_2 + Alkohol (-78 °C)

Reaktionsmedien



Chemische Reaktion

Flüchtige organische LM

lösemittelfrei

Alternative Reaktionsmedien

Superkritische Fluide
($scCO_2$, scH_2O)

Fluorreiche Medien
(CF_3-$(CF_2)_n$-CF_3)

Ionic Liquids
($[BMIm][BF_4]$)

Supersäuren
(HSO_3F)

Super Lewis-Säuren
($[Me_3Si][WCA]$)

Mehrphasensysteme
(CF_3-$(CF_2)_n$-CF_3/ H_2O)

reine Säuren/Basen
(H_2O, NH_3, HF
SO_2, HCN, HNO_3,
RCOOH …)

Einfluss des Mediums

- Beeinflusst:

1. Produktverteilung, Mechanismus, Reaktionsgeschwindigkeit oder Gleichgewichte
2. Stabilität von Edukten, Produkten, Übergangszuständen (Intermediaten) im jeweiligen Solvens

- Physikalische Eigenschaften:

1. Geeignete Temperaturspanne (Flüssigphase)
2. Ausreichende Flüchtigkeit, Entfernen des LM vom Produkt
3. Stabilität (elektrochemisches Fenster, Licht, Säure/Base etc.)

- Kosten (scale-up)
- Erlaubnis

Eigenschaften von Lösemitteln

Eigenschaften	**Maßeinheit**
Molekular physikalisch	Dipolmoment
Stofflich physikalisch	Dichte Viskosität Kohesiver Druck Dielektrizitätskonstante Brechungsindex Schmelz- und Siedepunkt
Chemische	Donornummer Akzeptornummer
Solvatochromisch	E^N_T, a, b and p*

Trocknen von Lösemittel

- Mit Molekularsieben (vers. Silikate/Schichtsilikate)

1. **Statisch**: Lagern über Molekularsieben, abfiltrieren vor Benutzung
2. **Dynamisch**: LM wird mit geringer Geschwindigkeit über eine Molsiebsäule gepresst – Grubbs-Type SPS

Trocknen von Lösemittel

- **Trocknen mit Natrium**

  - Einpressen von Natriumdraht in das entsprechende Lösemittel

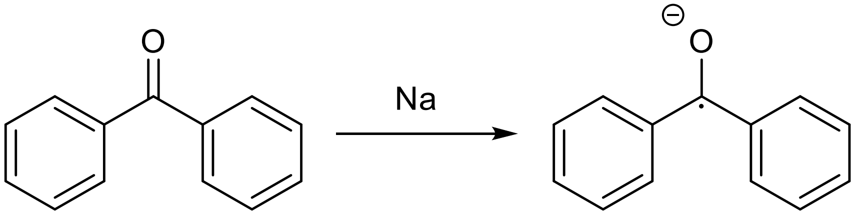
  - Wasser reagiert mit Metall unter H_2-Bildung

- **Ketyl-Trocknung**

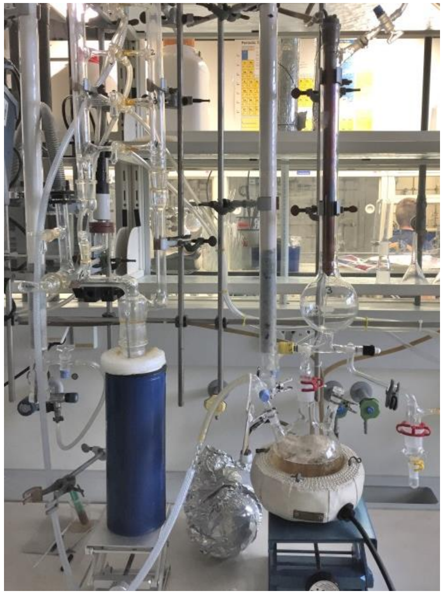
  - vorgetrocknetes LM wird im Argon-Gegenstrom über Natrium unter Rückfluss erhitzt

  - Zugabe geringer Mengen an Benzophenon

  - blau/violette Färbung zeigt erfolgreiche Trocknung an



Ketyl-Radikal



Verschiedene Trocknungsmittel

Trocknungsmittel	Verwendung	Nicht verwenden für	Anmerkungen
Molekularsiebe	organische Lösungsmittel; Gase (< 100 °C)	ungesättigte Kohlenwasserstoffe; polare Gase	gut geeignet, da regenerierbar bei Erhitzen bis zu 300 °C
Na_2SO_4, $MgSO_4$ (wasserfrei)	Lösungen, Ester		
Silica-Gel	häufig im Vakuum-Exsikkator	$(HF)_n$	geeignet, um Reste aus Lösungsmitteln zu entfernen
$CaCl_2$ (wasserfrei)	Kohlenwasserstoffe, Aceton, Ether, Neutrale Gase; HCl-Gas	Alkohole, Ammoniak, Amine	preisgünstig
K_2CO_3 (wasserfrei)	Aceton, Amine	saure Stoffe	hygroskopisch
NaOH, KOH (wasser-frei)	Ammoniak, Amine, Kohlenwasserstoffe	Aldehyde, Ketone, saure Stoffe	hygroskopisch
CaO, BaO	neutrale und alkalische Gase, Amine, Alkohole, Ether	Aldehyde, Ketone, saure Stoffe	gut geeignet für die Trocknung von Gasen
CaH_2	Kohlenwasserstoffe, Ketone, Ether, CCl_4, dmso, Ester, Acetonitril	saure Stoffe, Alkohole, Ammoniak, Nitro-verbindungen	Wasserstoffentwicklung, deshalb ist dessen Ableitung zu beachten
P_4O_{10}	neutrale und saure Gase, Acetylen, CS_2, Kohlenwasserstoffe	basische Substanzen, Alkohole, Ether, HCl, $(HF)_n$	hygroskopisch
H_2SO_4 conc	neutrale und saure Gase	ungesättigte Verbindungen, Alkohole, Ketone, H_2S, HI, basische Stoffe	Vorsicht beim Umgang mit conc. H_2SO_4
Natrium	Ether, Kohlenwasserstoffe, tertiäre Amine	chlorierte Kohlenwasserstoffe, Alkohole	Vorsicht bei der Vernichtung von Na-Resten

[1] L. Beyer, J. A. Cornejo, Koordinationschemie, Studienbücher Chemie, ˝ Vieweg+Teubner Verlag | Springer Fachmedien Wiesbaden 2012

Lösemittel - Klassifizierung

- unpolare Kohlenwasserstoffe:
  Hexan, Pentan (n-Alkane), Cyclohexan, Toluol, Xylole
  Benzol darf nicht mehr verwendet werden.
- wenig polare Lösungsmittel:
  Dichlormethan, Chloroform, Diethylether, MTBE, Essigsäureethylester, Fluorbenzol
  Trichlorethylen („Tri“) und Tetrachlormethan („Tetra“) sollten nicht mehr verwendet werden.
- polare Lösungsmittel:
  Tetrahydrofuran, Dimethylformamid, Acetonitril, Aceton,
  Hexamethylphosphorsäuretriamid („HMPT“) darf nicht mehr verwendet werden.
- protische polare Lösungsmittel:
  Methanol, Ethanol, Ethandiol, Ethandiolmonomethylether, Essigsäure, Wasser

Apolar, polar and nonpolar solvents

Assignment	Liquids
apolar	xenon, neon, argon
nonpolar/polarizable	CCl_4, C_6H_6, cyclohexane
dipolar aprotic	$HCCl_3$, dimethyl formamide, dimethyl sulfoxide
dipolar protic	ethanol, methanol, water, ammonia

Apolar should only be referred to solvents with spherical charge distribution, all other should be considered polar!

(forbidden: benzene, hexamethylphosphoracidtriamide HMPT;
should not be used: $HCCl_3$, CCl_4, freon gases)

Wechselwirkungen in Lösemitteln

Solvent	**M (g/mol)**	**m.p. (°C)**	**b.p. (°C)**	**Intermolecular forces**
Propane	44	-188	-42	dispersive
Acetonitrile	41	-44	82	permanent dipole
Ethanol	46	-114	78	permanent dipole, H-bonding
LiCl	42.4	605	>1300	electrostatic/ionic

Cohesive pressure (in MPa): $c = \Delta U_{vap} / V_{molar}$
H_2O 2302, MeOH 997, CH_2Cl_2 362, C_6H_6 357, Et_2O 251, C_7F_8 136

$$\varepsilon_i = \varepsilon_0 \frac{F_0}{F_i}$$

Dielectric constants $\varepsilon_r = \varepsilon_{solvent}/\varepsilon_0$
H_2O 78, CH_2Cl_2 4.8, Et_2O 4.2, C_6H_6 2.3

$$E = \frac{q_+ q_-}{4\pi\varepsilon_i d}$$

Acceptor number AN (rel. ^{31}P NMR shift of $Et_3P{=}O$)
[redacted]
H_2O 54.8, CH_2Cl_2 20.4, Et_2O 3.9, C_6H_6 8.2

Donor number DN^N (between 0-1, normalized enthalpy on adduct formation with $SbCl_5$)
Et_2O 0.49, H_20 0.46, CH_2Cl_2 0.10, C_6H_6 <0.01
[redacted]

Physikalische Daten einiger Lösemittel

Solvens	Fp. / °C	Kp. / °C (10^5 Pa)	$\varepsilon/\varepsilon_o$ (bei °C)	$p_D/10^5$ Pa (20 °C)
H_2O	0.0	100.0	81.7 (18)	0.03
HF	–83.55	19.51	83.6 (0); 175(–73)	1.03
NH_3	–77.76	–33.3	26.7 (–60)	8.57
HCN	–14.0	25.7	158.1 (0)	0.82
H_2SO_4	10.37	300 (Zers.)	100 (20)	–
SO_2	–72.7	–10.0	17.6 (–20)	3.30
BrF_5	–60.51	40.8	7.8 (20)	0.43
AsF_3	–8.5	63.0	5.7 (s)	0.10
ClCN	–6.0	13.0		1.34
NC–CN	–27.9	–21.2	1.00 (g)	4.88
SO_2ClF	–125	7		1.64
$CFCl_3$*	–111	23.6	2.28 (29)	0.89
CF_2Cl_2*	–158	–29.8	2.13 (29)	5.68
$(F_2ClC)_2$*	–94	3.65	2.26 (25)	1.82

* Handelsnamen: $CFCl_3$, R-11; CF_2Cl_2, R-12; $(F_2ClC)_2$, R-114; Nomenklatur: R-*abcd*, *a*: Zahl der Doppelbindungen, *b*: Zahl der Kohlenstoffatome –1, *c*: Zahl der Wasserstoffatome + 1, *d*: Zahl der Fluoratome, Rest = Chloratome, (engl.: Freon-*abcd*).

Unerwartete Reaktionen mit dem Lösemittel

- Reinigungsmethoden (z.B. Me_3SiN_3)
- Halogenierte Lösungsmittel (Reaktion mit Alkalimetallen, Licht)
- Halogen / Pseudohalogen Austauschreaktionen (z.B. $CH_2Cl + N_3^-$)
- Unerwartete Reaktionen (z.B. Azide in CS_2)
- Kinetische Probleme (z.B. Fe^{3+} katalysiert NH_3 Zersetzung und $NaNH_2$ Bildung)
- Rolle von Verunreinigungen (e.g. Hydrolyse, Katalyse, Reaktion mit Reaktionsgefäß, Rührfische, Silikonfett …)
- Was war vorher im Reaktionsgefäß? (z.B. Pd Nanopratikel)

Hydrothermal – supercritical water

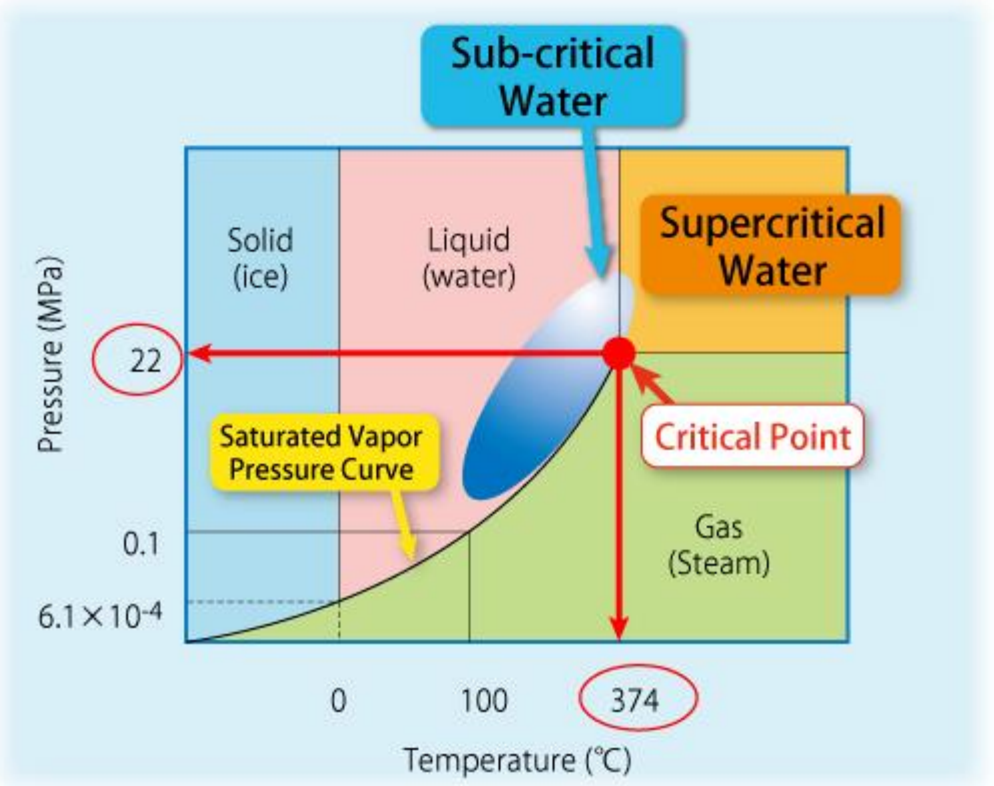
ε_{H2O} = 81.7 ε_0 : In H_2O 1% of attraction between ions compared to vacuum

Hydrothermal: 30°C – 374°C (high pressure): formation of many natural and synthetic minerals

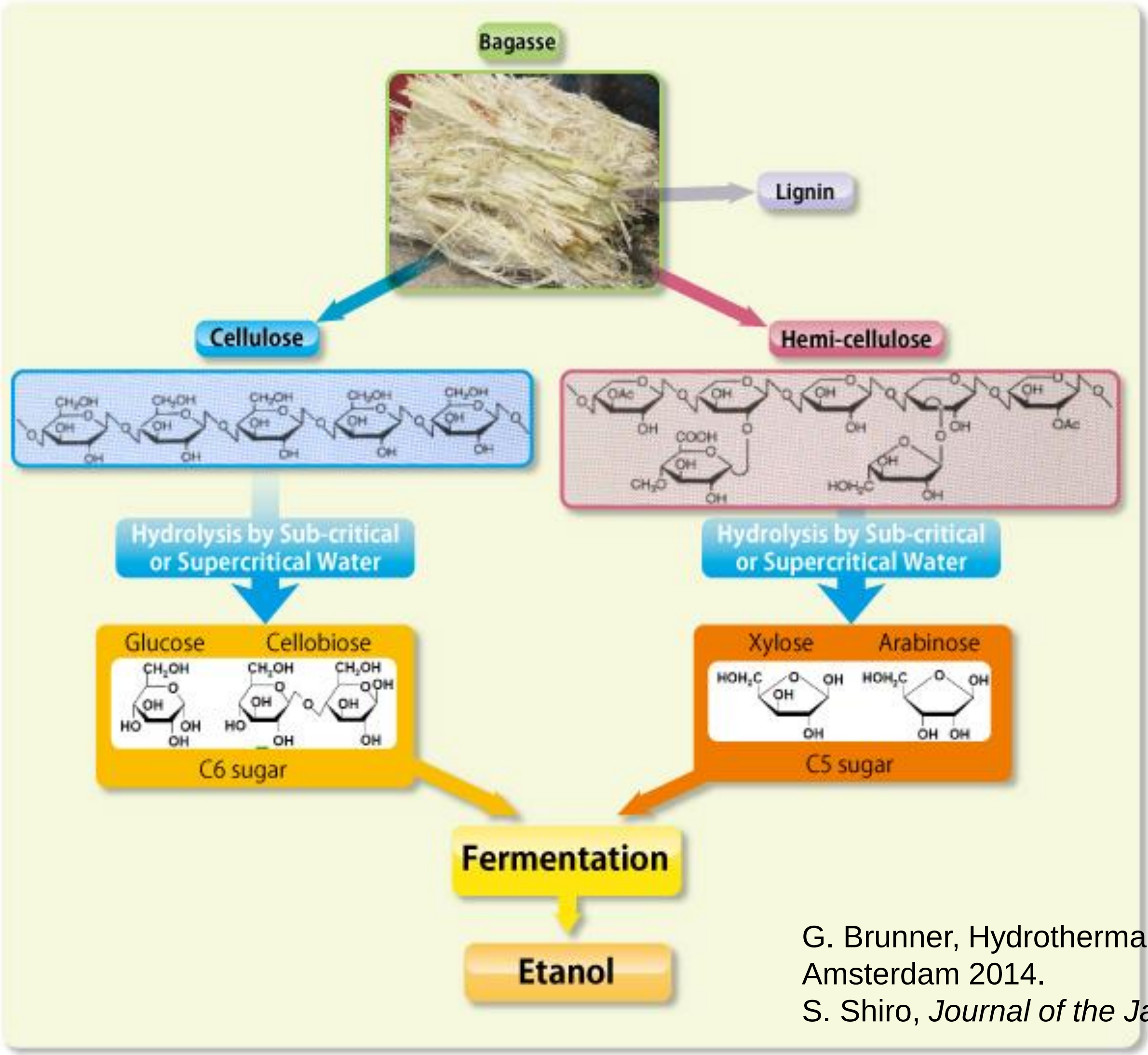
scH_2O (beyond 374°C, 220 bar)

Special properties
density of normal water
but
viscosity of H_2O gas

If T and p is increased, H_2O transforms from a solvent for ionic compounds (salts) into a solvent for polar and nonpolar (organic) compounds e.g. benzene



Application of scH_2O



Solvent / decomposition
waste materials,
radiactive waste,
organic compounds

for generation of
nanoparticles
single crystals

for heat transfer
Powerstations

for mass transfer
Heterogenous catalysis
extraction

G. Brunner, Hydrothermal and Supercritical Water Processes, Amsterdam 2014.
S. Shiro, *Journal of the Japan Institute of Energy*, **2009**, *7* , 363.

Polywater ("Anomalous" Water)

1962 USSR
1969 USA

- almost no vapor pressure
- density ~1.4 g/cm^3,
- mixable with water (dependent on chain length of the polymer)
- stabil up to ~500°C.
- polywater is the reason why no water on other planets found
- danger: earth water could polymerize

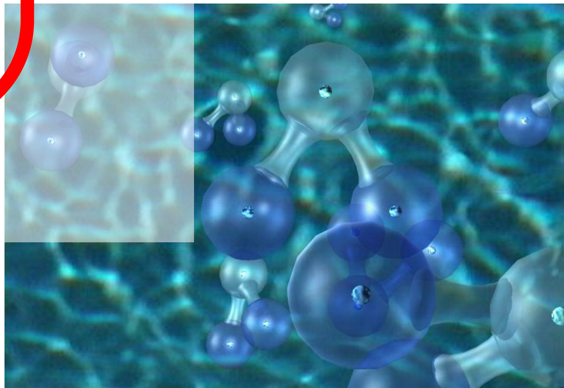
N. Nikolai Fedyakin *Kolloid Zhournal.* **1962**, *24*, 497.
E. Willis, G. K. Rennie, C. Smart, B. A. Pethica, *Nature* **1969**, *222*, 159.

FLOP

Polywater: 5 % water + 95 % Salts (Silikate, Borate, Chloride, Sulfate, …

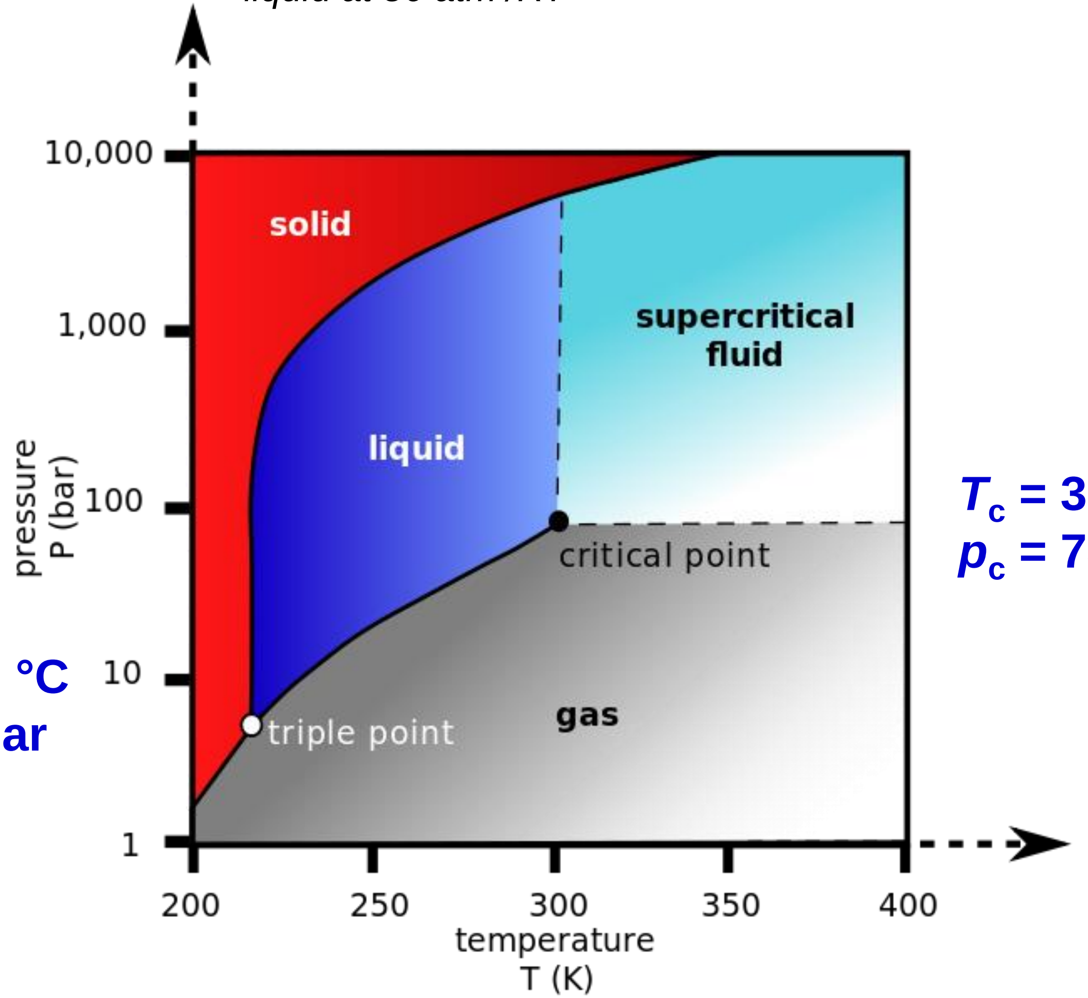
„I regard the polymer as the most dangerous material on earth….Scientists everywhere must be alerted to the need for extreme caution in the disposal of polywater. Treat it as the most deadly virus ...“

F. J. Donahue *Nature* **1969**, *224*, 198.



CO_2: phase diagram

sublimation of CO_2 (dry ice) @ 1atm/RT (above -78°C)
liquid at 56 atm /RT



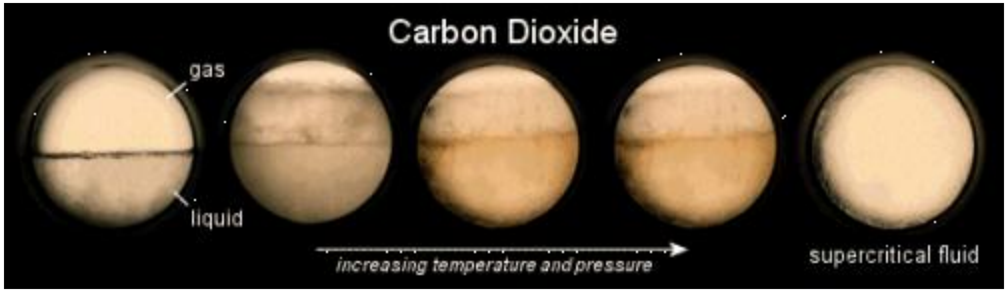
T_c = 31.0 °C
p_c = 73.75 bar

T_{triple} = -57.0 °C
p_{triple} = 5.2 bar

Supercritical CO_2

Green chemistry?

$T_c = 31.0\ °C$
$p_c = 73.75$ bar

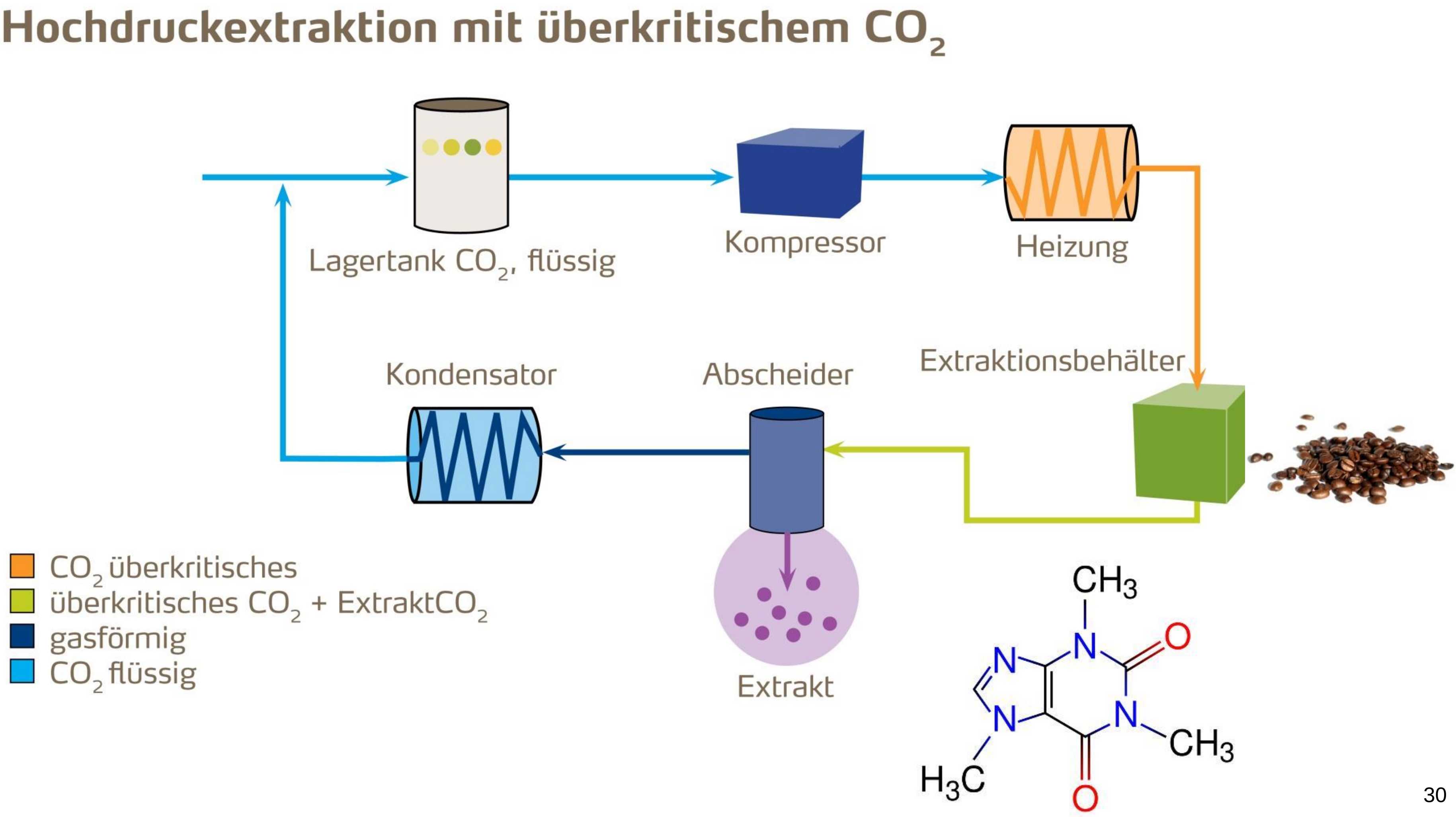


- Application: bio-, multiphasic, metallorganic, heterogeneous catalysis, food chemistry
- Advantage: smaller pressure and temperature (cf. H_2O), easy to remove, non-toxic
- Disadvantage: autoclave for high pressure

W. Leitner, *Acc. Chem. Res*. **2002**, 35, 746-756.
H.-Q. Fan, Y.-M. Li, A. S. C. Chan, *Chem. Rev.* **2002**, *102*, 3385.
R. H. Fish, *Chem. Eur. J.* **1999**, *5*, 1677.
W. Leitner, *Chem. i. u. Zeit* **2003**, *37*, 32.
G. Musie, M. Wei, B. Subramaniam, D. H. Busch, Coord. *Chem. Rev.* **2001**, 219-222, 789.
P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, *99*, 475.
A. Baiker, *Chem. Rev.* **1999**, *99*, 453.

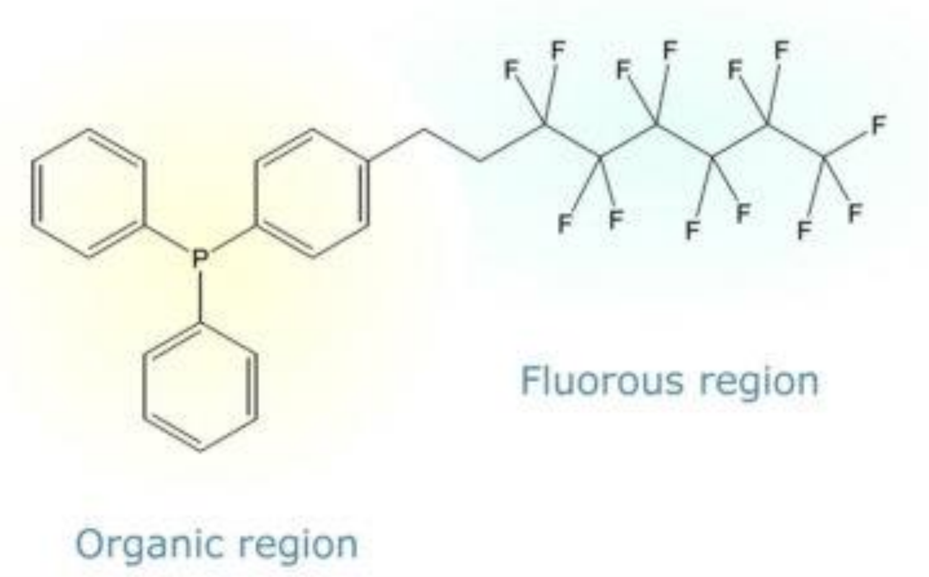
Application in food chemistry

decaffeination, aroma extraction



Fluorous chemistry

Fluorous molecules comprise an organic domain and a highly fluorinated domain. Ideally, the organic domain controls reactivity and the fluorinated domain controls separation. The aim is to facilitate separation.

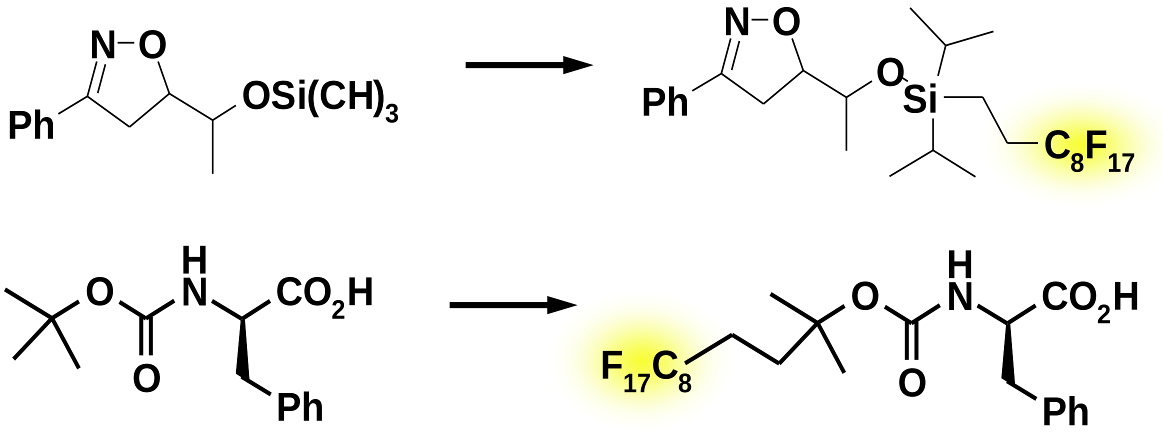


Two basic approaches

Fluorous compounds with integral (permanent) fluorinated domains:

$$Bu_3SnH \longrightarrow (C_6F_{13}CH_2CH_2)_3SnH$$

Fluorous compounds with removable (temporary) fluorinated domains (tags):

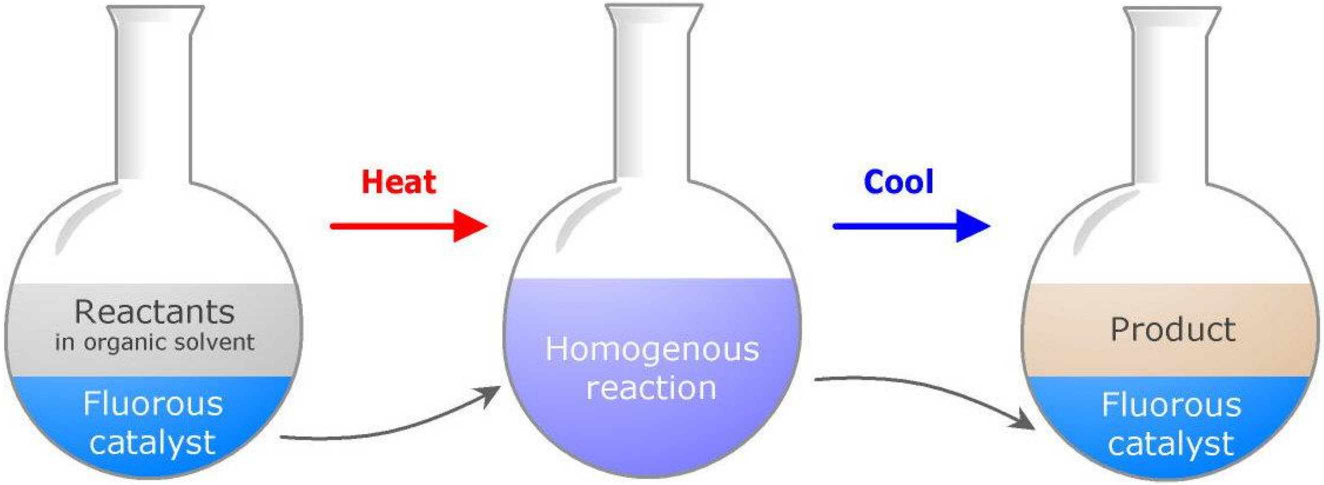


"Heavy" versus "light"

Generally, > 60% fluorine by weight is called a **"heavy fluorous"** compound. These materials have limited solubility in non-fluorous media, typically require perfluorinated solvents, and are expensive - all of which limits practical adoption.

"Light fluorous" compounds (< 40% by weight) are miscible in organic solvents and cost less. Since they typically will not form a separate fluorous liquid phase, light fluorous compounds are separated using a companion fluorous stationary phase.

Fluorous biphasic catalysis



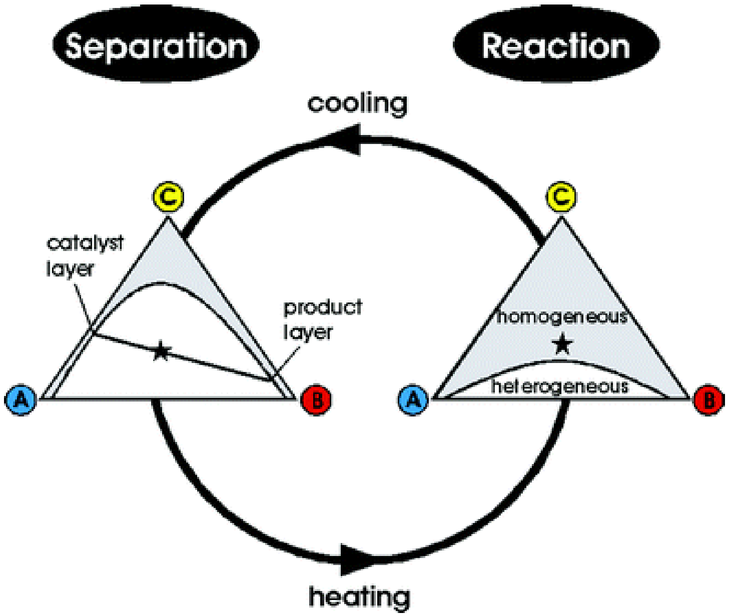
Fluorous-tagged ligands enable reliable L-L separation of catalyst – important for toxic and/or expensive catalysts. Variation shown here is ***thermomorphic*** fluorous biphasic catalysis. Solubility of the fluorous species in organic phase is promoted with heat, improving kinetics.

T. Horvath, J. Rabai, *Science* **1994**, *266*, 72-75.

K. Olofsson, S. Y. Kim, M. Larhed, D. P. Curran, A. Hallberg, *J. Org. Chem.* **1999**, *64*, 4539-4541.

Fluorous Chemistry

biphasic media - thermomorphic phase separation



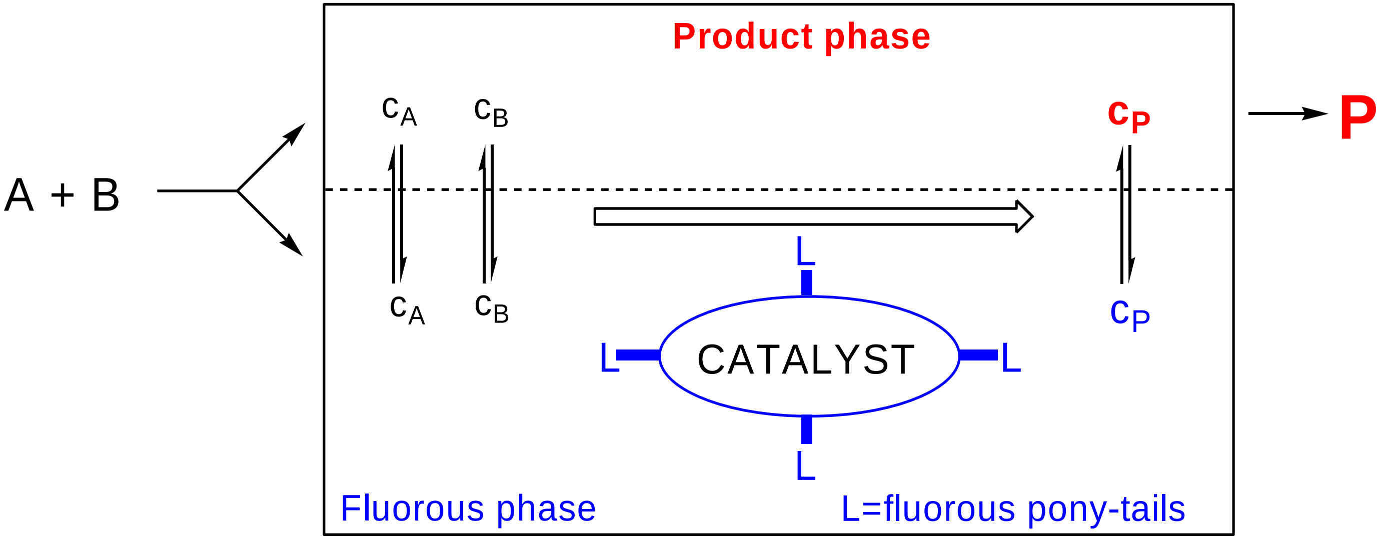
★ = operating point

Combination	Upper	Lower
3 mL c-$C_6F_{11}CF_3$ 3 mL *n*-Hexane	one phase	
3 mL c-$C_6F_{11}CF_3$	12.5%	58.7%
3 mL *n*-Hexane	51.3%	27.2%
1 mL Toluene	36.2%	14.1%
3 mL c-$C_6F_{11}CF_3$	1.3%	85.3%
3 mL Toluene	98.7%	14.7%

"The large molar volumes of the fluorocarbons compared with the corresponding hydrocarbons leads to unusually low "internal pressure" or "cohesive energy densities", while their molecular weights aid in maintaining them in the liquid state; the net result of which is to make many of their solutions with ordinary liquid hydrocarbons deviate from Raoult's law to such an extent as to from two liquid phase, a state of affairs comparatively rare among non-polar liquids."

J. H. Hildebrand, D. R. F. Cochran, *J. Am. Chem. Soc.* **1949**, *71*, 22.

Fluorous biphase catalysis



The fluorous phase could be any partially or fully fluorinated saturated hydrocarbon with or without functional groups provided there are minimal attractive interactions between those groups.

I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72.
I. T. Horváth, J. Rábai, *US 5,463,082* **1995**.
I. T. Horváth, *Acc. Chem. Res*. **1998**, *31*, 641.

Ionic Liquids

$$\Delta G = \Delta H - T_{melt} \cdot \Delta S = 0$$
$$T_{melt} = \Delta H / \Delta S$$

Why 100 °C?

(No idea – better salt melt)

- low symmetry
- charge delocalization within cation (wcc) and anion (wca)
- bulky substituents (size + large conformation space)
- „small“ mol. mass

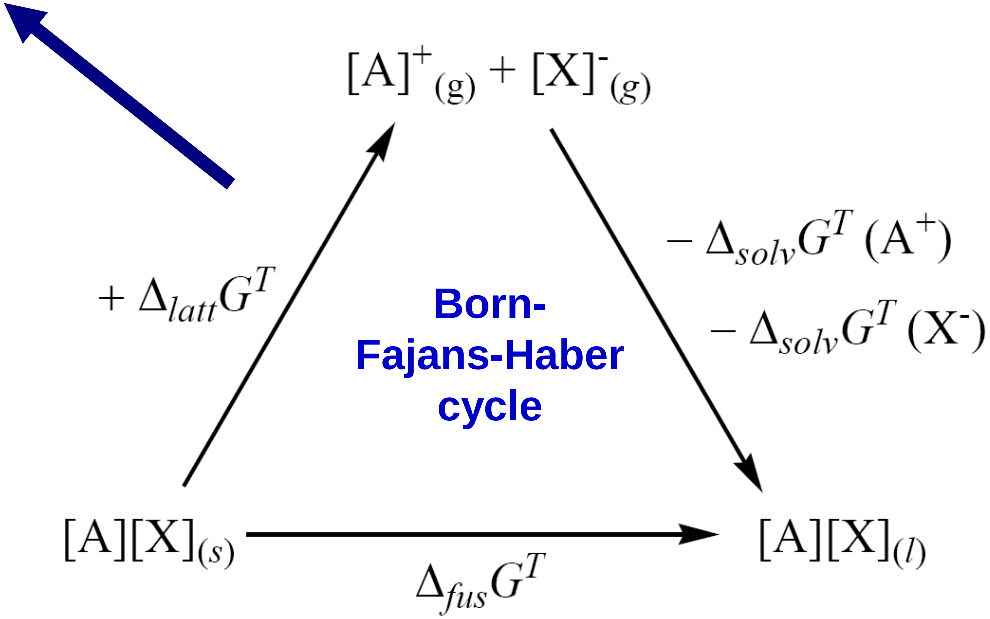
↓

leads to

small lattice energie and large entropy

↓

10^{18} ILs



$$\begin{tikzcd}
 & {[A]^+_{(g)} + [X]^-_{(g)}} \arrow[dr, "- \Delta_{solv} G^T (A^+) \; - \Delta_{solv} G^T (X^-)"] & \\
{[A][X]_{(s)}} \arrow[ur, "+ \Delta_{latt} G^T"] \arrow[rr, "\Delta_{fus} G^T"'] & & {[A][X]_{(l)}}
\end{tikzcd}$$

Born-Fajans-Haber cycle

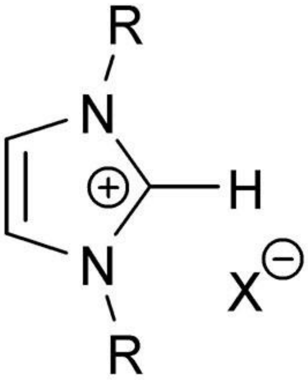
Ionic liquids

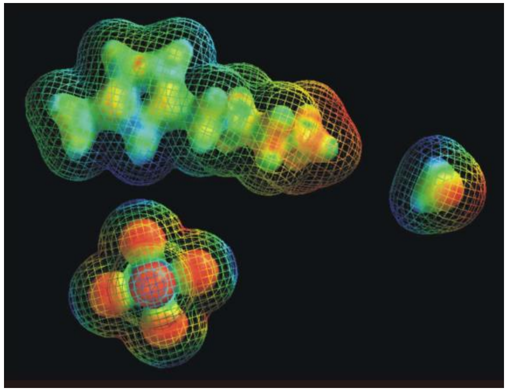
Alternative to organic solvents

Pros: very low vapor pressure, tuneable, wide electrochemical window, often chemically and thermal robust, highly polar, interesting mixing behavior

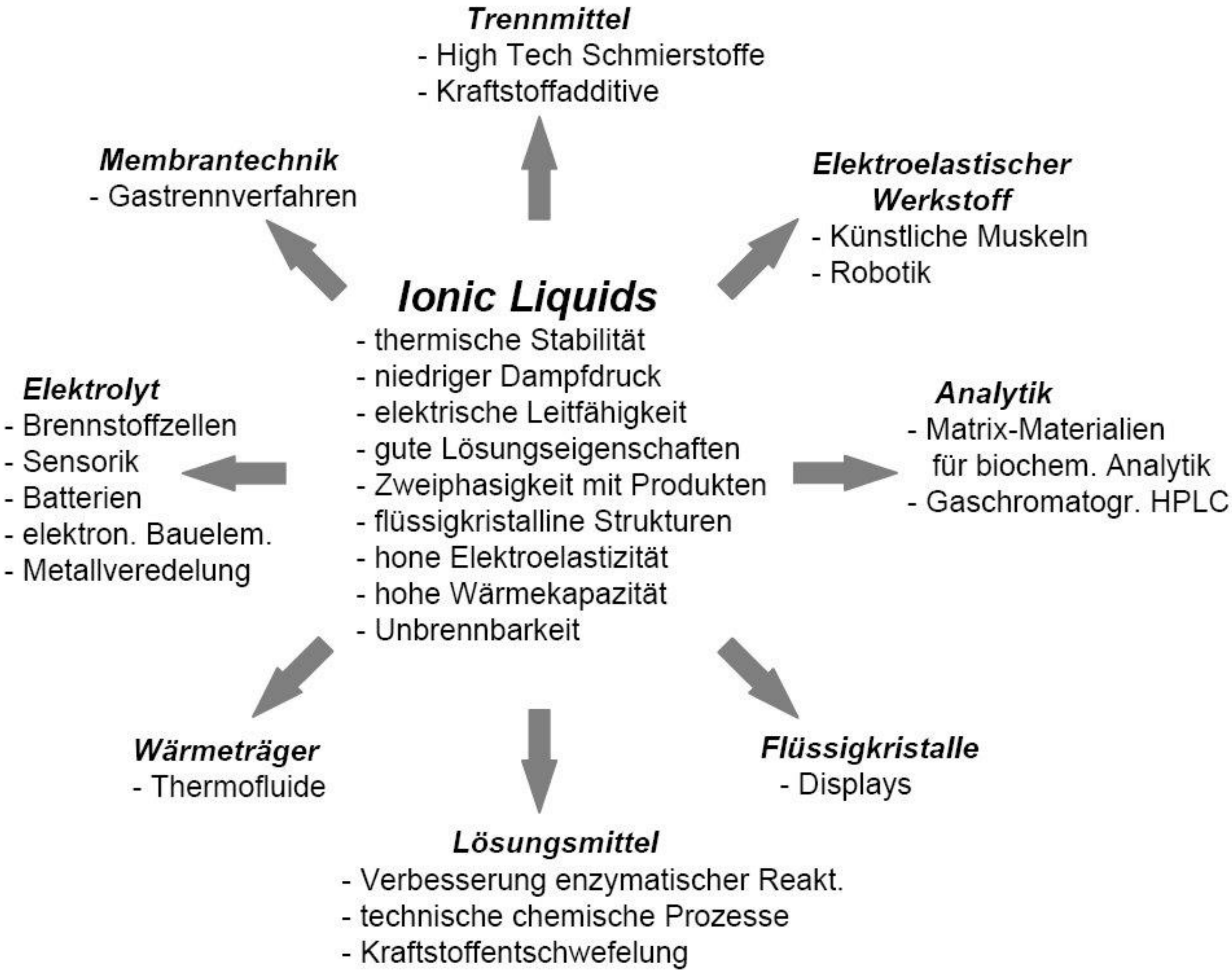
Cons: expensive, separation problems, highly toxic (**green solvent ☺**)

Application: catalysis, separation, synthesis media





P. Wasserscheid, *Chem. i. u. Zeit* **2003**, *37*, 52.
P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926.



Ionic Liquids

- thermische Stabilität
- niedriger Dampfdruck
- elektrische Leitfähigkeit
- gute Lösungseigenschaften
- Zweiphasigkeit mit Produkten
- flüssigkristalline Strukturen
- hone Elektroelastizität
- hohe Wärmekapazität
- Unbrennbarkeit

Trennmittel
- High Tech Schmierstoffe
- Kraftstoffadditive

Elektroelastischer Werkstoff
- Künstliche Muskeln
- Robotik

Analytik
- Matrix-Materialien für biochem. Analytik
- Gaschromatogr. HPLC

Flüssigkristalle
- Displays

Lösungsmittel
- Verbesserung enzymatischer Reakt.
- technische chemische Prozesse
- Kraftstoffentschwefelung

Wärmeträger
- Thermofluide

Elektrolyt
- Brennstoffzellen
- Sensorik
- Batterien
- elektron. Bauelem.
- Metallveredelung

Membrantechnik
- Gastrennverfahren

Synthesis in Ionic Liquids

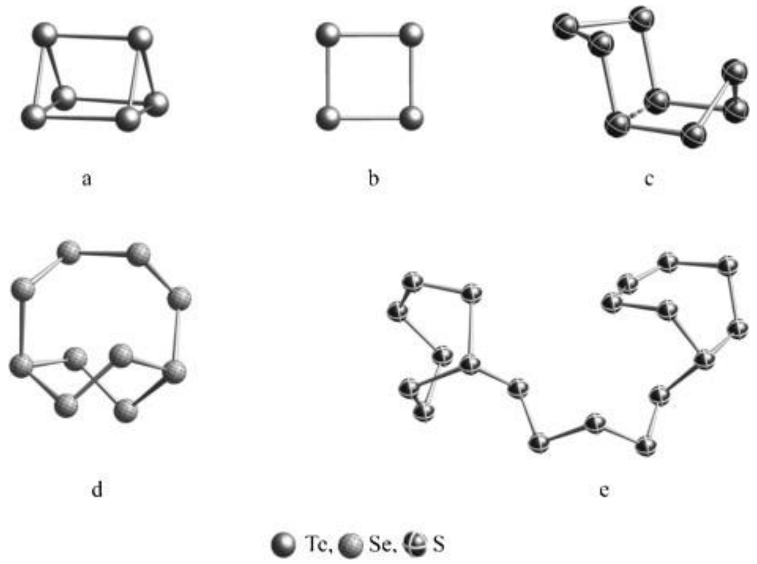
examples: Te_4^{2+} or Te_6^{4+}

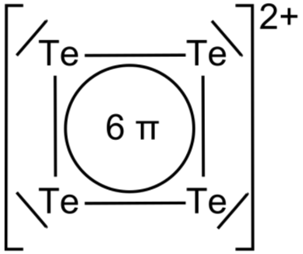
$E + [BMIm]Cl + x\ AlCl_3$

$E^1 + E^2X_n$

$$\xrightarrow{\textit{Intermediate formation of IL}}$$

E_n^{m+} cations as chloridoaluminates
(also binary and ternary cations etc.)





DFG Priority program: Material synthesis near room temperature

E. Ahmeda, M. Ruck *Coordination Chemistry Reviews* **2011**, *255*, 2892–2903.

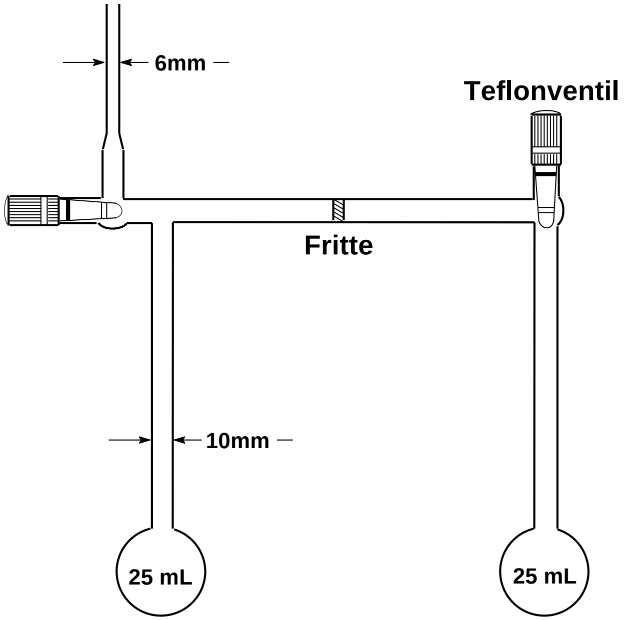
Highly polar, highly acidic solvents:

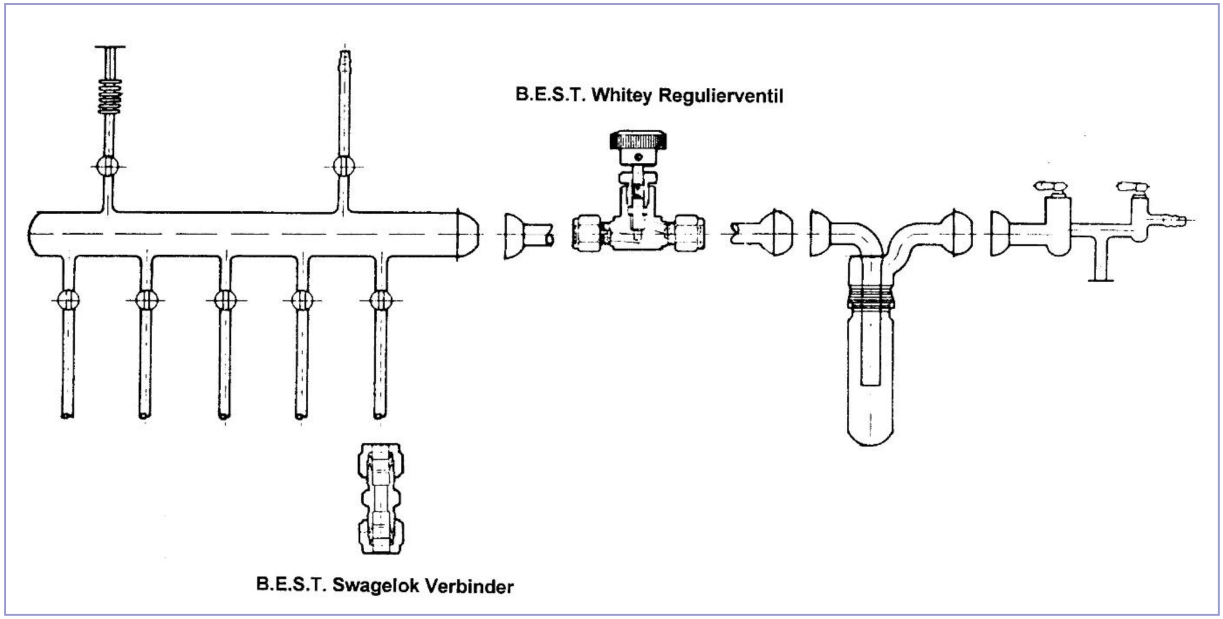
Liquid SO_2 &Oleum

$Te_x + AsF_5$ in liquid SO_2 $\longrightarrow$ Te_4^{2+} or Te_6^{4+}

aprotic

pro‘s: easy to remove, large dipole
con‘s: vapor pressure 0.33 Mpa, special equipment





protic

Te_x + oleum (H_2SO_4/SO_3) $\longrightarrow$ Te_4^{2+} or Te_6^{4+}

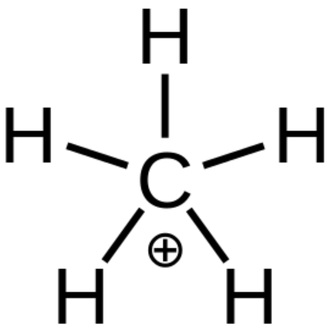
Superacids

SbF_5: strongest molecular Lewis acid (oily liquid)

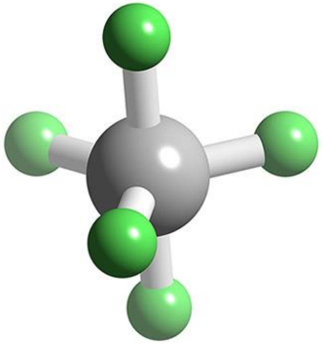
Superacid is an acid with an acidity greater than 100% pure H_2SO_4 (historical definition).

Krossing et al. "*A Unified pH Scale for All Phases*" *Angew. Chem. Int. Ed.* **2010**, *49*, 6885.

Superacid *is a medium in which the chemical potential of the proton is higher than in pure sulfuric acid.*



protonated methane



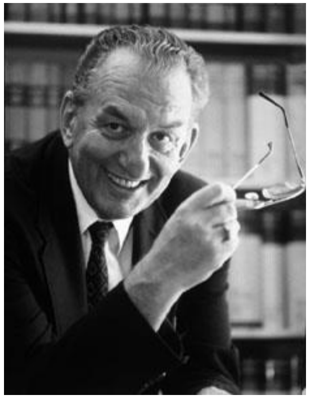
Examples

Fluorosulfuric acid, HSO_3F

Trifluoromethane sulfuric acid, CF_3SO_3H

Generation of carbocations

George A. Olah, Nobel laureate 1994



$$SbF_5 + 2\ FSO_3H \longrightarrow H_2SO_3F^+ + SbF_5(SO_3F^-)$$

Superacids – Hammett acidity values

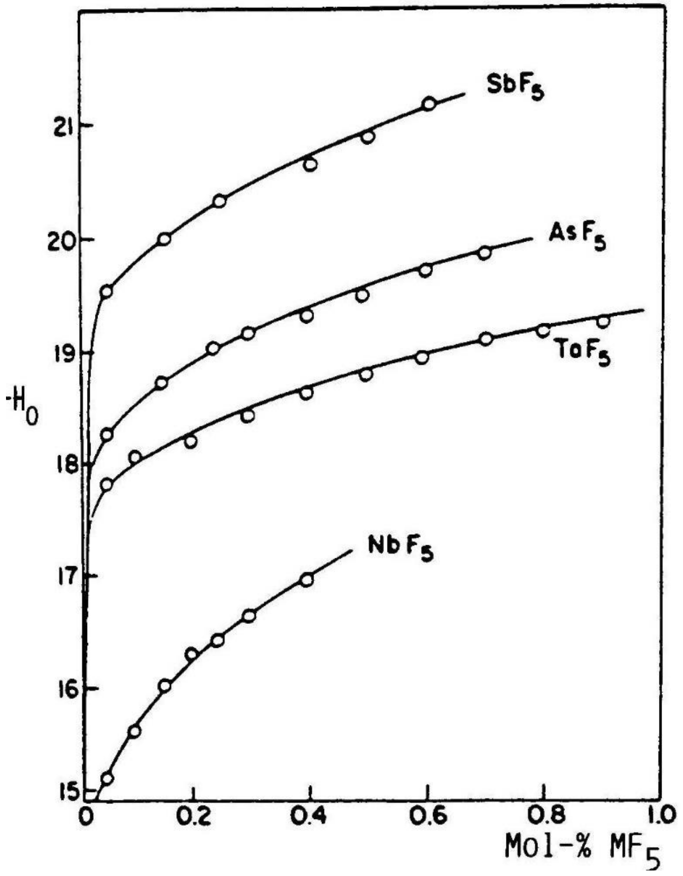
Acid	**$-H_0$**
H_2SO_4	11.9
CF_3SO_3H	13.8
HSO_3F	15.1
HF	15.1
HSO_3F / +20% SbF_5	20
HF / +0.5% SbF_5	21

Magic acid protonates methane!

$$BH^+ \longrightarrow B + H^+ \qquad (\text{B} = p\text{-nitroaniline})$$

$$H_0 = -\lg[H^+] = pK(BH^+) - \lg\frac{[BH^+]}{[B]}$$

Hammett acidity function



H_0-values for solutions of MF_5 in AHF

Superacids

AHF/SbF$_5$ strongest superacid, 2•10^{19} stronger than 100% H_2SO_4

$$\boxed{2HF + SbF_5 \longrightarrow H_2F^+ + SbF_6^-}$$

anion = wca

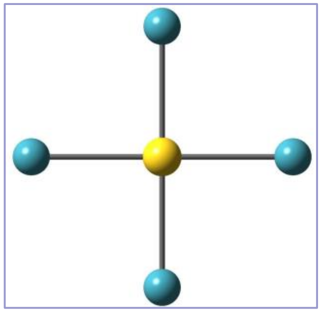
Application

carbocations · inorganic polycations · transition metalls in low oxidation states · non-classical metal carbonyls · protonated fullerenes

---

$$\overset{+III}{Au}F_3 + 6\ \overset{0}{Xe} + 3\ H^+ \xrightarrow{HF\ /\ SbF_5} \overset{+II}{Au}\overset{0}{Xe}{}_4^{2+} + \overset{+1/2}{Xe}{}_2^{+} + 3\ HF$$

$T_{Zersetzung}$ = -40°C



d(AuXe) = 2.74 Å

S. Seidel, K. Seppelt, *Science* **2000**, *290*, 117-118.

Super Lewis Acids

Superacids (stronger than 100%-H_2SO_4)

1988: $[H–F–H]^+[Sb_2F_{11}]^-$ (= 2 $HF·SbF_5$)

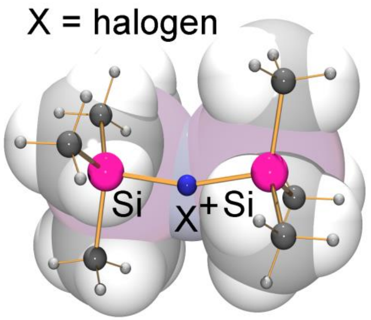
D. Mootz, K. Bartmann
Angew. Chem. **1988**, *100*, 424

$$HF + H^+ \xrightarrow{HF/SbF_5} [H–F–H]^+$$

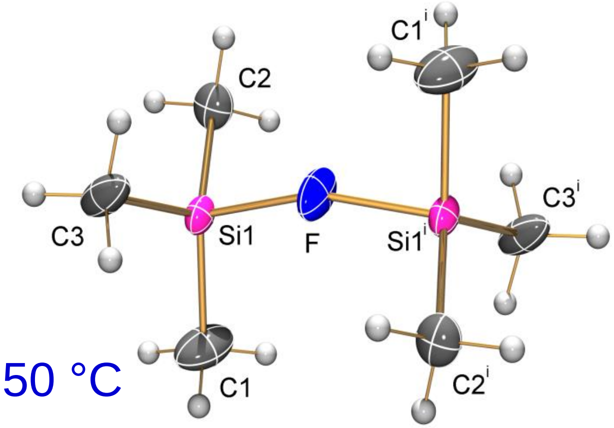
Me_3Si^+ is the „big brother“ of the proton!

Super-Lewis-acidic media?

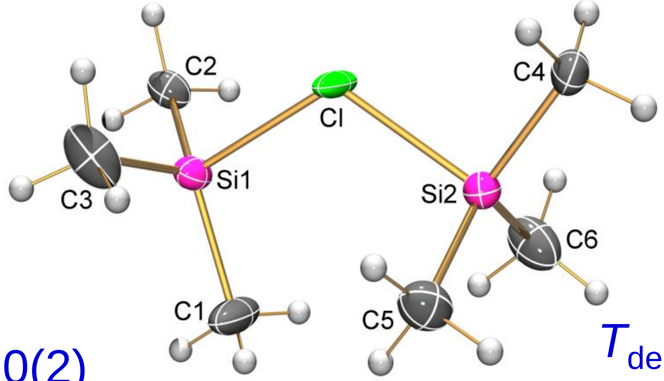
Haloniumions: „X^+“



$$Me_3SiX + [Me_3Si\cdot solvate]^+[wca]^- \xrightarrow[-solvate]{solvent\,=\,Me_3SiX} [Me_3Si-\overset{\oplus}{X}-SiMe_3]^+[wca]^-$$



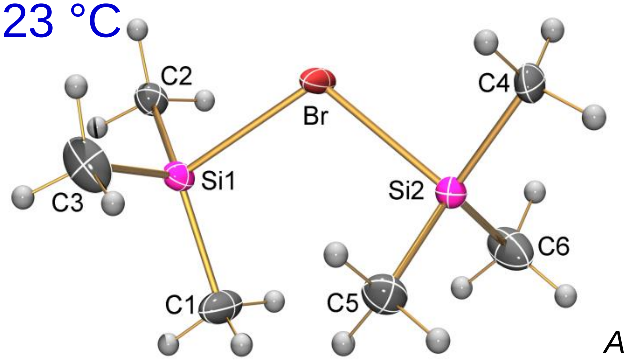
T_{dec}: 150 °C



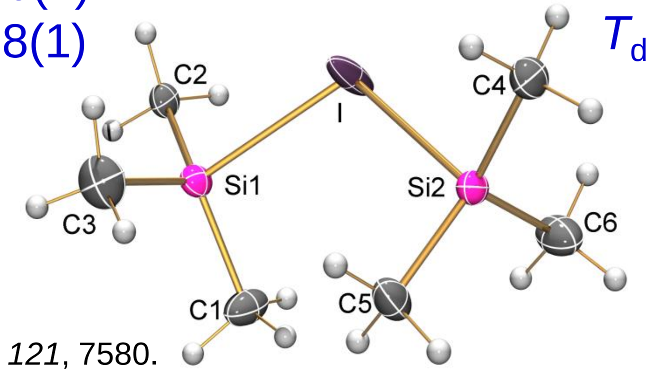
T_{dec}: 116 °C

Si-X-Si / °

163.0(3) 119.0(2)
114.2(1) 111.8(1)



T_{dec}: 123 °C



T_{dec}: 120 °C

Angew. Chem. **2009**, *121*, 7580.

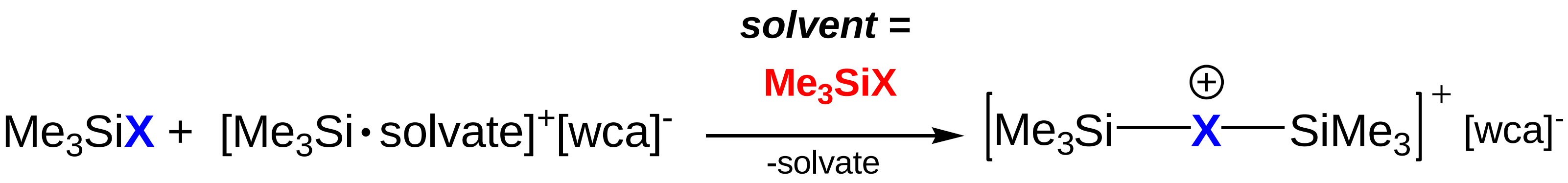
Pseudohalonium „X⁺"

Superacids

Olah	*J. Am. Chem. Soc.* **1983**, *105*. 5657.
Christie	*J. Am. Chem. Soc.* **1993**, *115*, 1836.

$$HN_3 + H^+ \xrightarrow{\textbf{HF/SbF}_5} [H_2N_3]^+$$

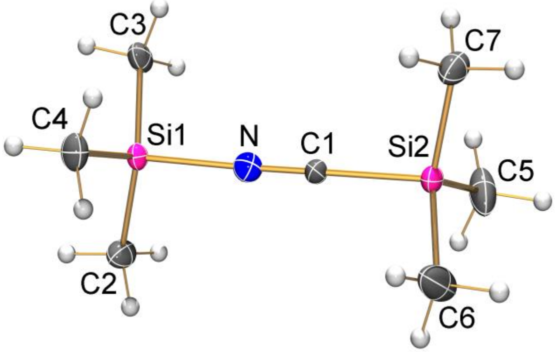
Me_3SiX / Me_3Si^+ = super Lewis acids ($X = N_3$, OCN, SCN, CN)

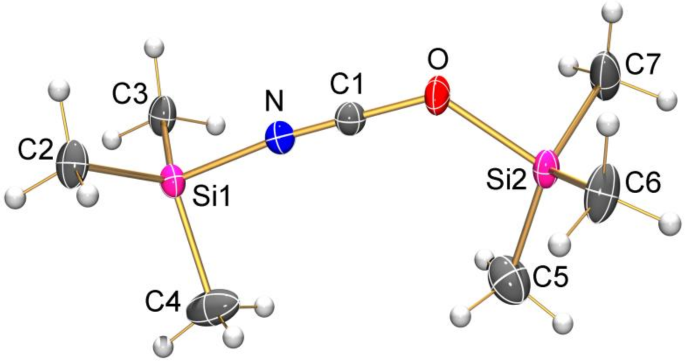


$$Me_3Si\mathbf{X} + [Me_3Si\cdot\text{solvate}]^+[\text{wca}]^- \xrightarrow[\text{-solvate}]{\textit{solvent} = \; Me_3SiX} \left[Me_3Si - \overset{\oplus}{\mathbf{X}} - SiMe_3\right]^+ [\text{wca}]^-$$

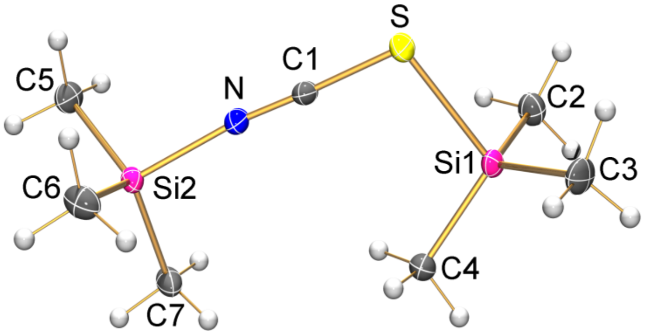
Chem. Eur. J. **2010**, *16*, 7276 – 7281

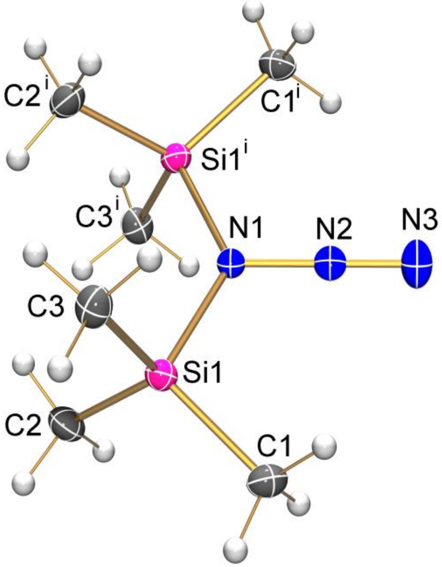
Pseudohaloniumions





wca = $B(C_6F_5)_4^-$





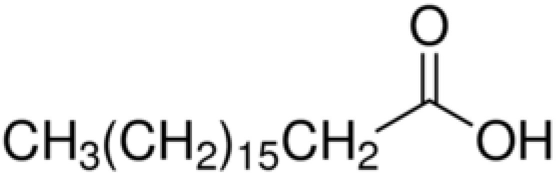
Carboxylsäuren – Elegante Synthesen

(lösemittelfrei)

$$C_{17}H_{35}CO_2H + NaX \xrightarrow{140°C} C_{17}H_{35}CO_2Na + HX\uparrow$$

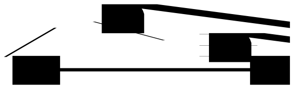
Stearinsäure

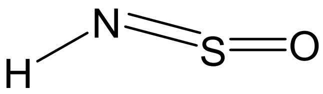
X = Halogen, Pseudohalogen

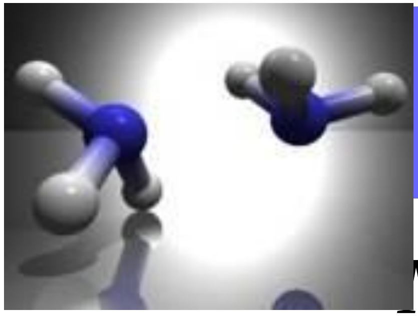


m.p. 69°C

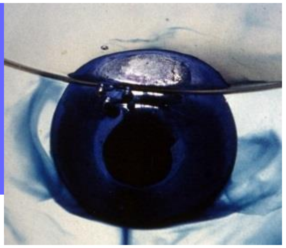
Anwendung
Synthese von hoch labiler HN_3 oder HNSO







„Superbase“



$$M \xrightarrow{NH_3(l)} M(NH_3)_n^+ + e(NH_3)_m^-$$

$$2NH_3 \overset{\longrightarrow}{\longleftarrow} NH_4^+ + NH_2^-$$

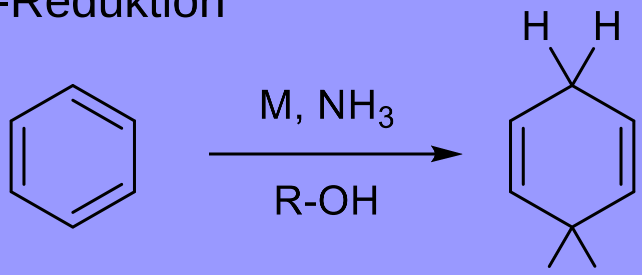
$c_{NH_4^+} \bullet c_{NH_2^-} = 10^{-29}$ (-33°C)

$$NH_3 + e_{am}^- \overset{\longrightarrow}{\longleftarrow} NH_2^- + 1/2H_2;$$

$$K_c = \frac{c(NH_2^-) * p_{H_2}^{1/2}}{c(e_{am}^-)}$$

m.p.	−77,7 °C
b.p.	−33 °C
vapor pressure	8.573 bar (20 °C)

Birch-Reduktion



M, NH_3

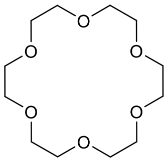
R-OH

M = Li, Na, K

Reaction of non-metals with alkali metals in liquid ammonia

nonmetal	metal	product
P	Li-Cs	M_3P, M_3P, M_3P_{11}
O_2	Li, Na, K, Rb	Li_2O, Li_2O_2, LiO_2, Na_2O, Na_2O_2, KO_2, K_2O_2, Rb_2O_2, RbO_2
S_8	K	K_2S, K_2S_2, K_2S_4, K_2S_x

Elektride: $Cs^+(18C6)_2 \cdot e^-$



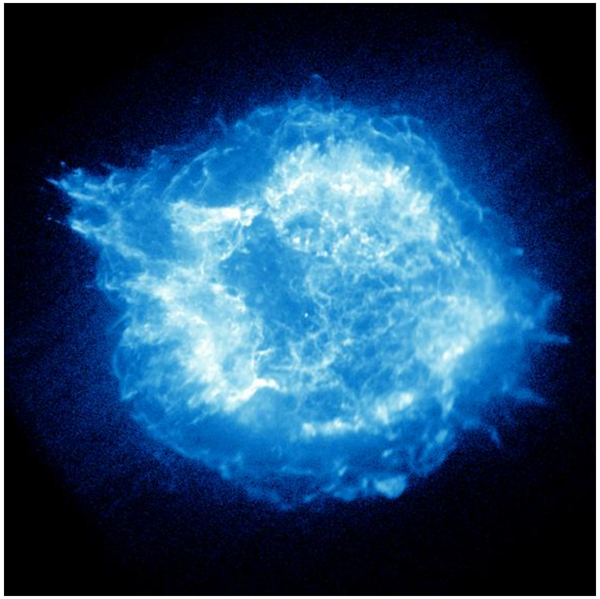
18C6: Kryptand

A very unusual reaction medium: a super nova

Chandra's Cas A in the Light of Glowing Silicon Ions

X-ray of He-like

Si^{12+}



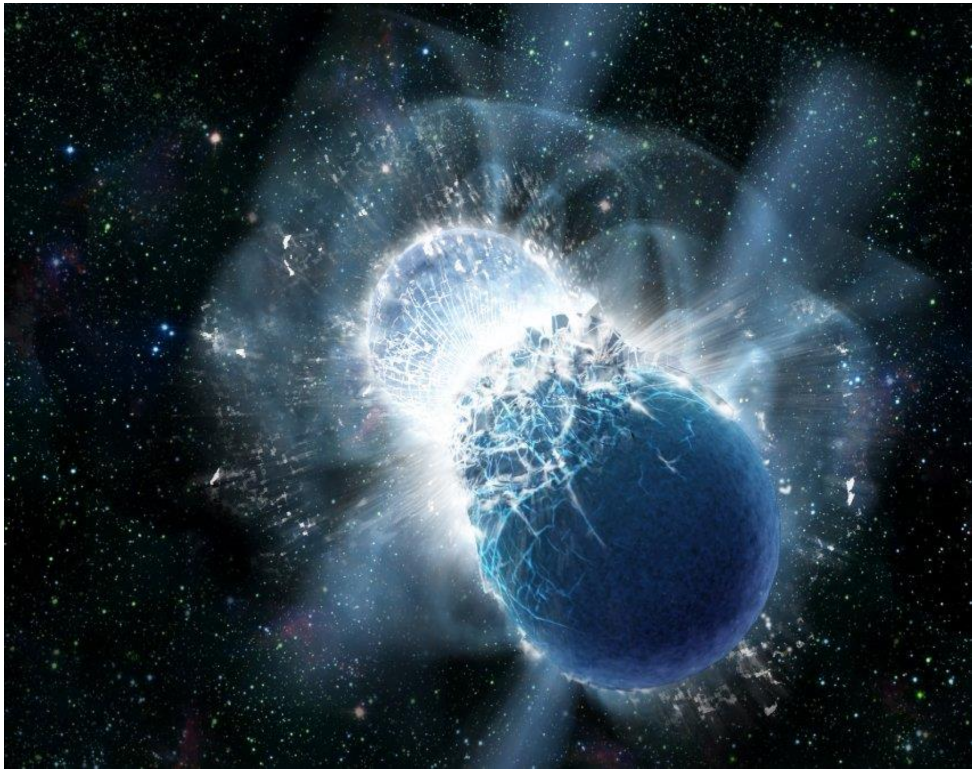
silicon ions heated to about fifteen million degrees Celsius, so the ions retain only two orbital of fourteen orbital electrons

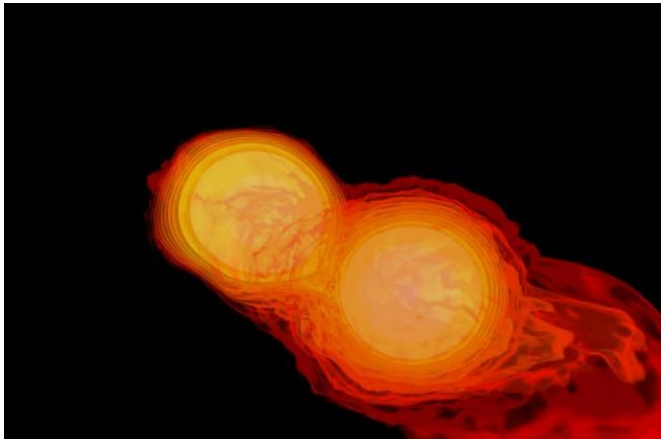
http://chandra.harvard.edu/photo/2004/casa/

What happens when neutron stars collide?

Collision of two neutron stars with the side product:

7.35 10^{23} kilogram of gold





http://www.wired.co.uk/news/archive/2013-08/05/kilonova

http://www.spiegel.de/wissenschaft/weltall/neutronenstern-kollision-schleudert-gold-ins-all-a-911787.html#js-article-comments-box-pager

End