Dry High-Pressure Methods

Chemistry at the Earth's surface at 100 kPa
Chemistry in the Universe at hight pressures and temperatures deep within the planets and stars

Laboratory:
Pressures up to 250 GPa, high temperatures ~7000 °C
1 bar = 100 kPa   1 Mbar = 100 GPa
p-V work during compression to 1 Mbar equivalent to approx. 1 eV chemical bond energy

In-situ observations by diffraction, spectroscopy to probe chemical reactions, structural transformations, crystallization, amorphization, phase transitions

Methods of obtaining high pressures

- **Anvils, diamond, tetrahedral and octahedral**
- **Shock waves (km s^{-1})**
- **Explosions, projectiles**
- **Go to another planet: Jupiter**

(hydrogen is metallic at 100 Gbar)

PRESSURE SCALE

Pressure, bar	System
	1 Mbar = 100 GPa
10^{-12}	high vacuum chamber
1	atmospheric pressure
1.5	kitchen pressure cooker
2.0	car tire
50	a lady in stilleto heels
60	breakdown of human nervous system - divers
73.8	critical pressure of CO_2
150	autoclave (safety burst disc)
221.2	critical pressure of H_2O
10^3	pressure at the bottom of the ocean (11 km)
2.10^3	LDPE
10^4	Earth crust (30 km)
10^5	synthetic diamond production
$3.4.10^6$	pressure at the center of the Earth (6378 km)
10^7	Saturn, Jupiter, metallic hydrogen
10^8	neutron stars

Dry High-Pressure Methods

Pressure techniques useful for synthesis of unusual structures, TD metastable yet kinetically stable when pressure released = pressure and temperature quenching, reconstructive transformation hindered at low temperature, insufficient thermal energy for bond-breaking

High pressure phases
- **higher density**
- **higher coodination number**
- **higher symmetry**
- **transition to from nonmetal to metal**
- **band mixing**

Pressure/Coordination Number Rule: increasing pressure – higher CN

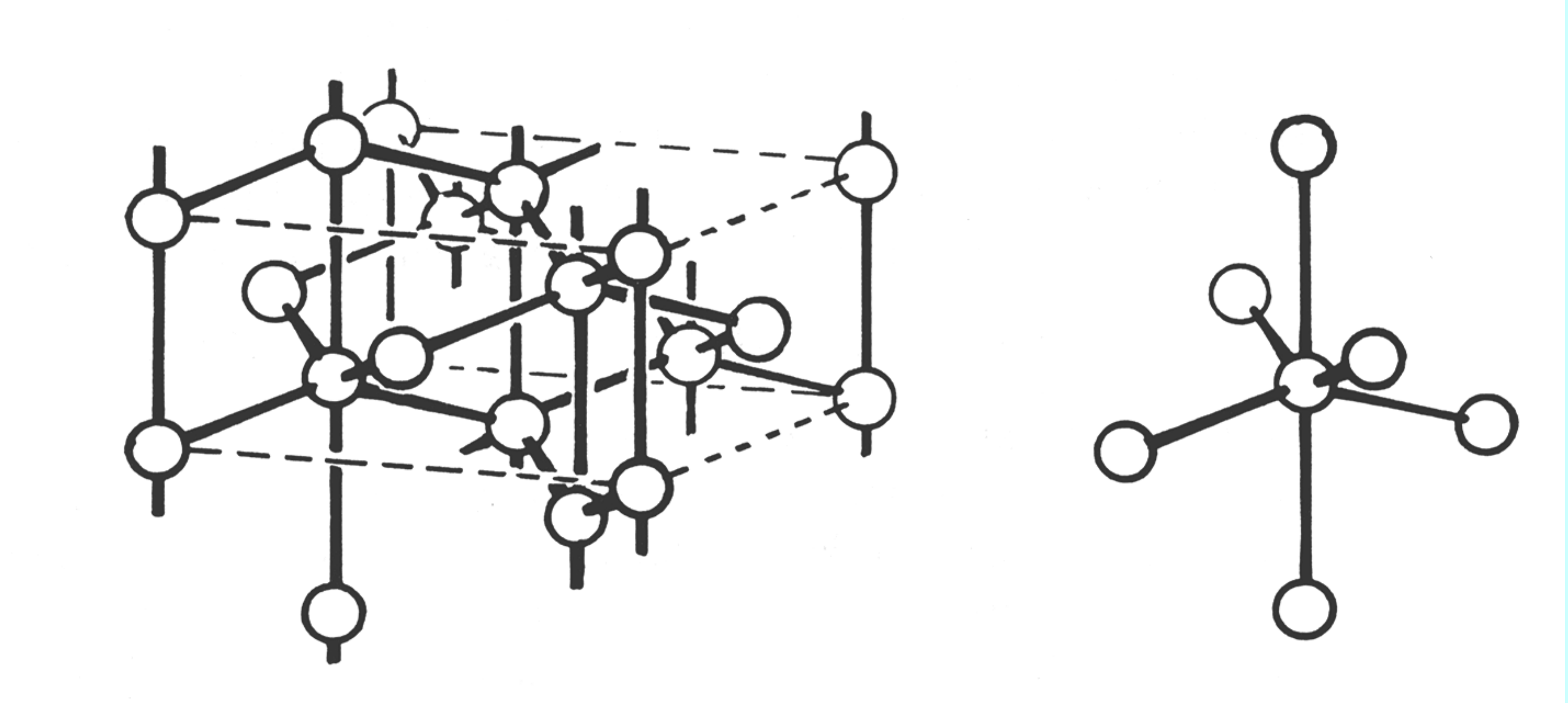
Pressure/Distance Paradox: increasing pressure – longer bonds

Gray Sn (diamond type) stable below 13 °C
Coordination number 4, Sn-Sn bond length 281 pm

White Sn
Coordination number 6, Sn-Sn bond lengths 302 and 318 pm

Dry High-Pressure Methods

White Sn CN = 6

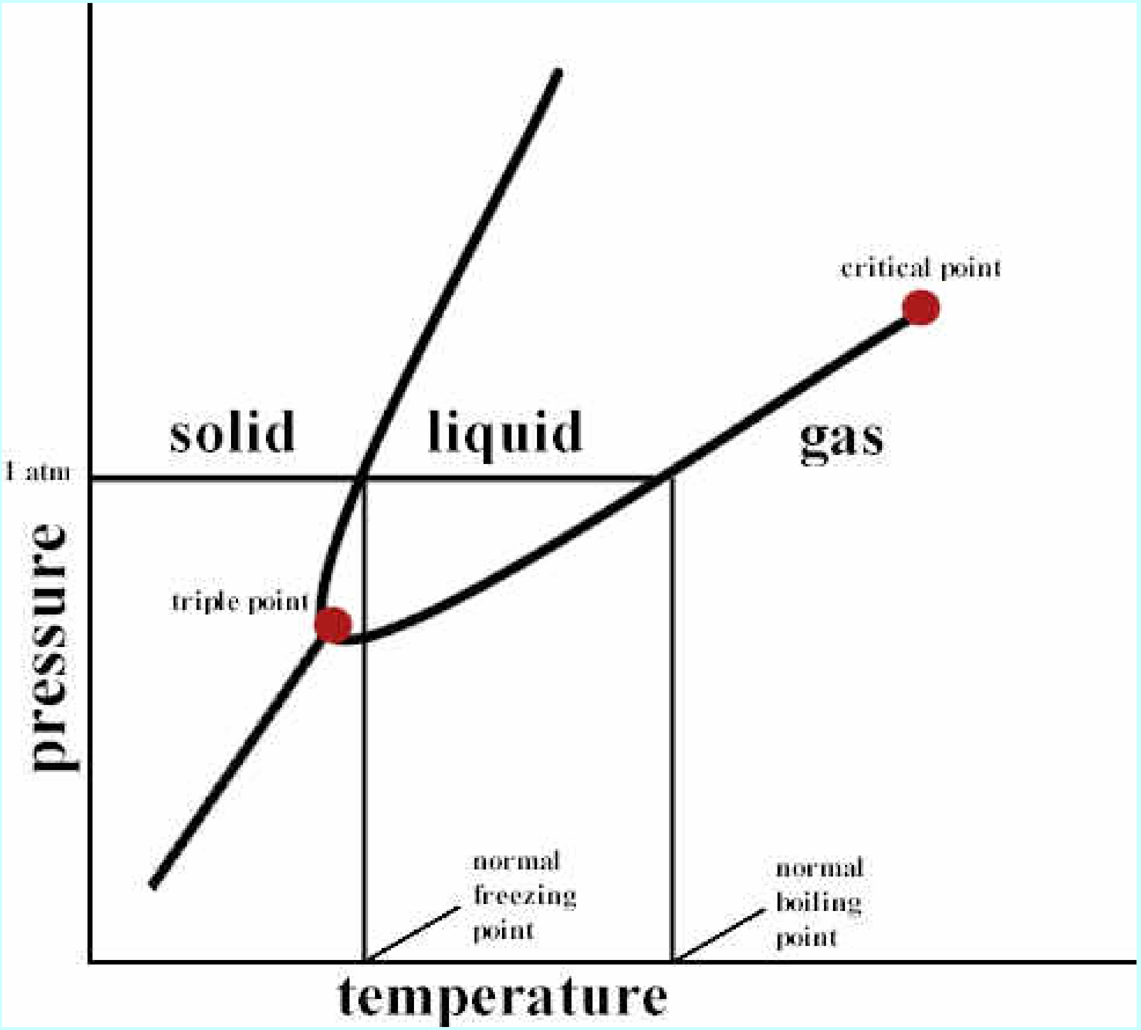


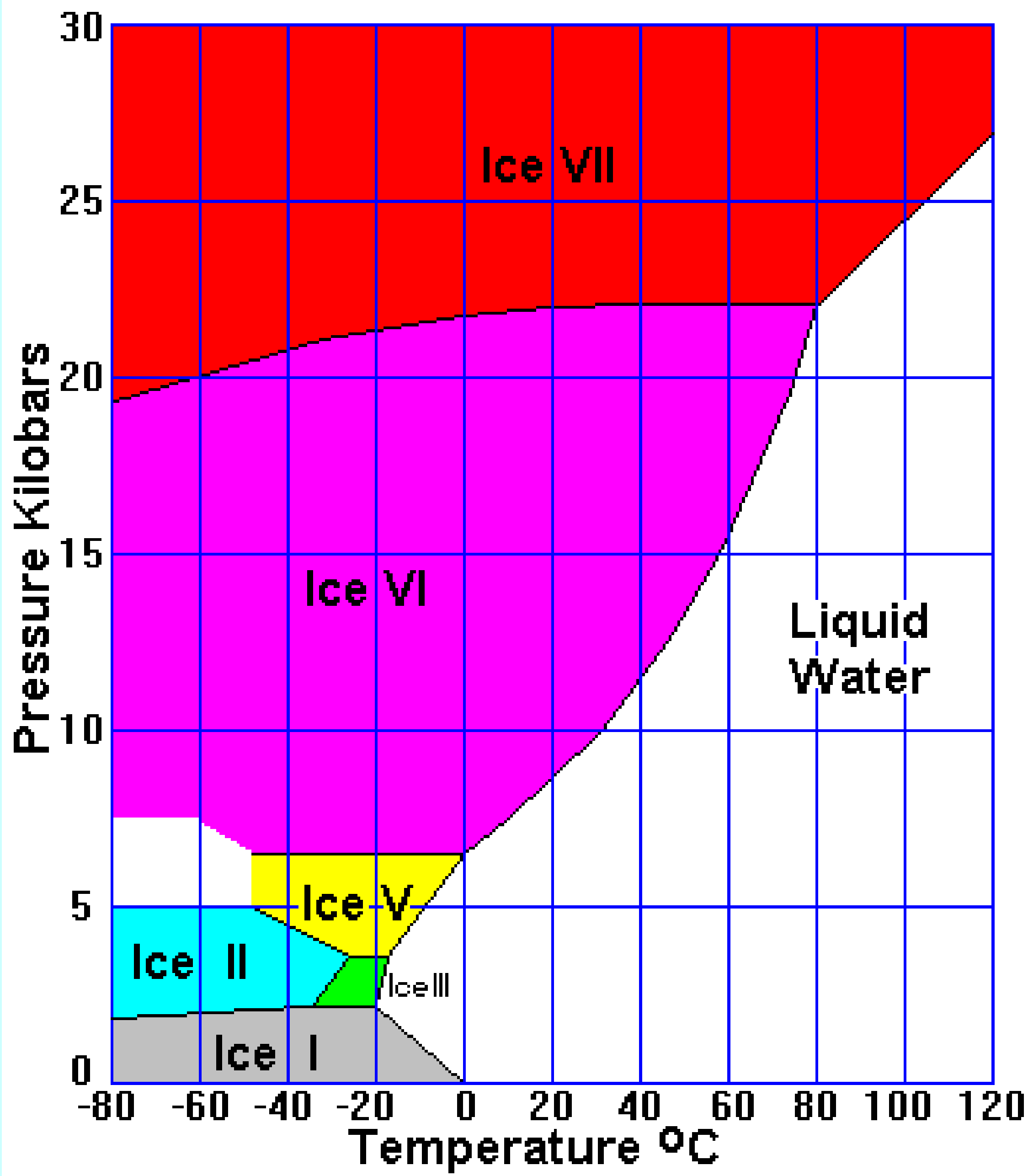
Dry High-Pressure Methods

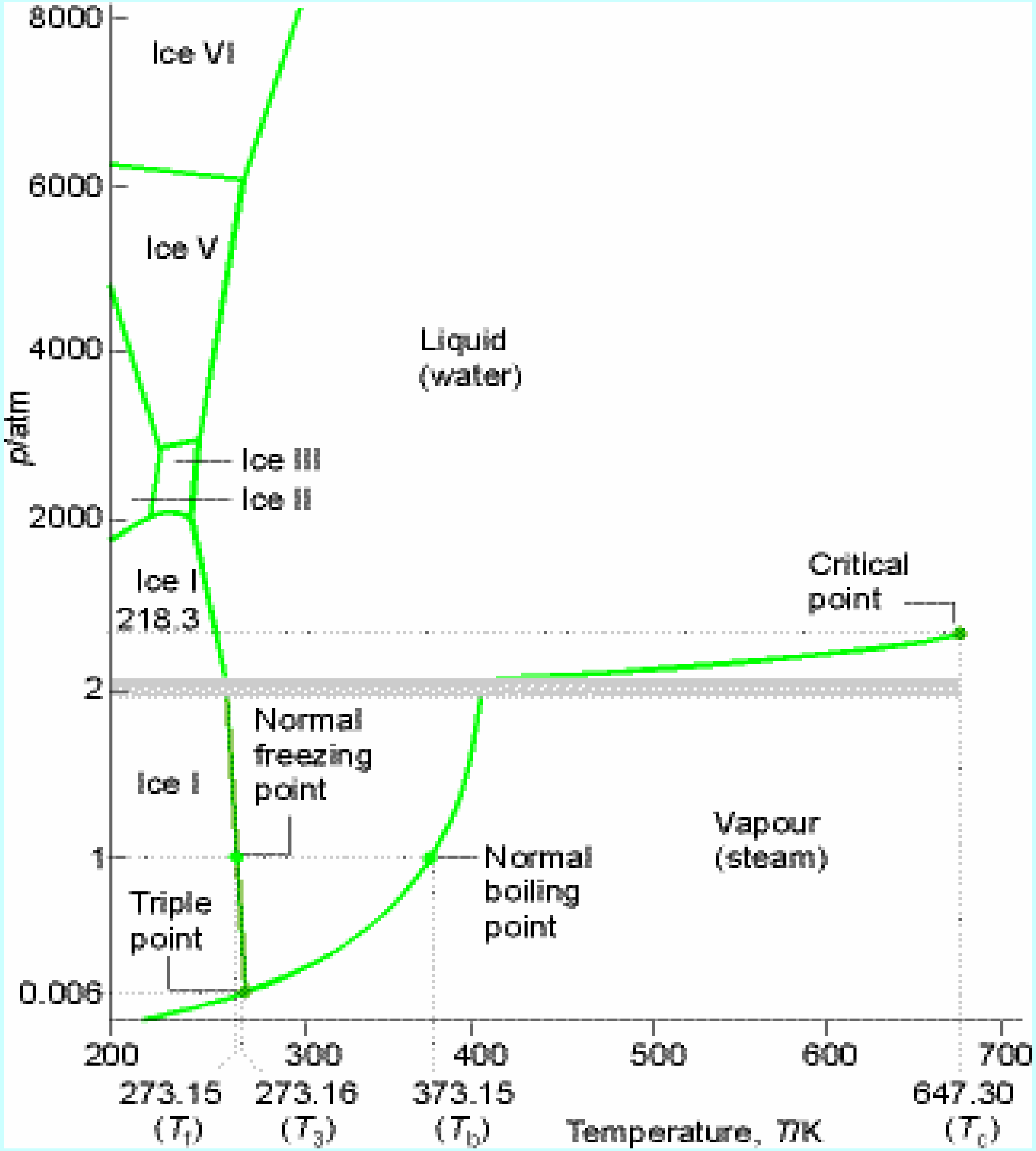
Examples of high pressure polymorphism for some simple solids

Solid	Normal structure and coordination number	Typical transformation conditions P(kbar)	Typical transformation conditions T(^oC)	High pressure structure and coordination number
C	Graphite 3	130	3000	Diamond 4
CdS	Wurtzite 4:4	30	20	Rock salt 6:6
KCl	Rock salt 6:6	20	20	CsCl 8:8
SiO_2	Quartz 4:2	120	1200	Rutile 6:3
Li_2MoO_4	Phenacite 4:4:3	10	400	Spinel 6:4:4
$NaAlO_2$	Wurtzite 4:4:4	40	400	Rock salt 6:6:6

Phase Diagrams




Ice VII
Ice VI
Liquid Water
Ice V
Ice II
Ice III
Ice I
Pressure Kilobars
30
25
20
15
10
5
0
-80
-60
-40
-20
0
20
40
60
80
100
120
Temperature °C



8000
6000
4000
2000
2
1
0.006
p/atm
Ice VI
Ice V
Ice III
Ice II
Ice I
218.3
Liquid
(water)
Critical
point
Normal
freezing
point
Ice I
Vapour
(steam)
Normal
boiling
point
Triple
point
200
300
400
500
600
700
273.15
(T_f)
273.16
(T_3)
373.15
(T_b)
Temperature, T/K
647.30
(T_c)

Water

12 phases of ice up to 8 GPa

Ice-VII   m.p. 100 °C

Ice-X   fluorite, ionically conductive above 10 GPa

Equalization of O-H covalent and hydrogen bonds above 60 GPa

Max pressure attained for water 210 GPa

Ca

ccp at ambient pressure

bcc (!) above 20 GPa   4s-3d mixing, Ca become a transition metal

$MgSiO_3$ most abundant silicate mineral within our planet !

pyroxene (silicate chains)

ilmenite > garnet > perovskite

Condensed gases

H_2 metallic conductivity in dense fluid hydrogen

H_2^+ H_2^-

$NO_2 + N_2O$ NO^+ NO_3^- calcite

CO_2 heating at 10-20 GPa sp^3 bonded CO_4 cristobalite, tridymite

40 GPa quartz (noncentrosymmetric)

N_2 semiconducting oligomers $(\text{-N-})_x$ at 100-240 GPa

Earth's Core

3.4 Mbar = 340 GPa,   6000 K

ε-Fe hcp

Diamond Anvil Cell

Diamond anvil cell

p = F/A

p = 40 GPa

A_{table} / A_{culet} = 10 : 1

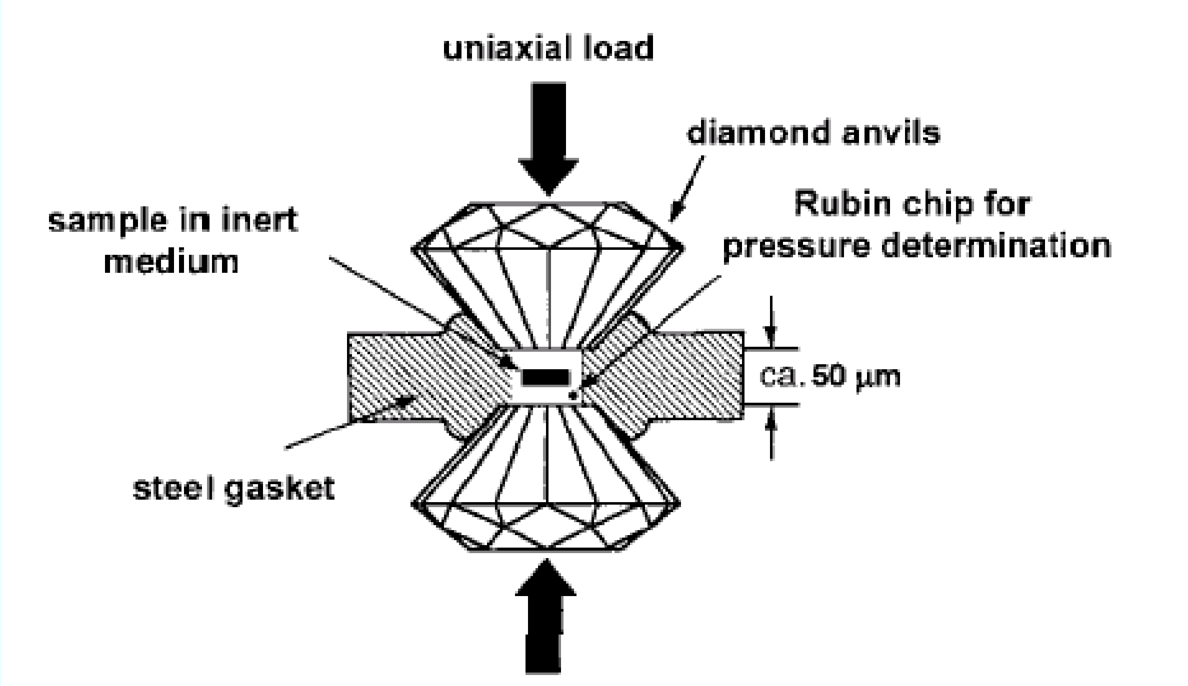
A_{culet} = 100-200 µm

laser heating T > 2500 °C

Re, steel gasket

transparent to radiation

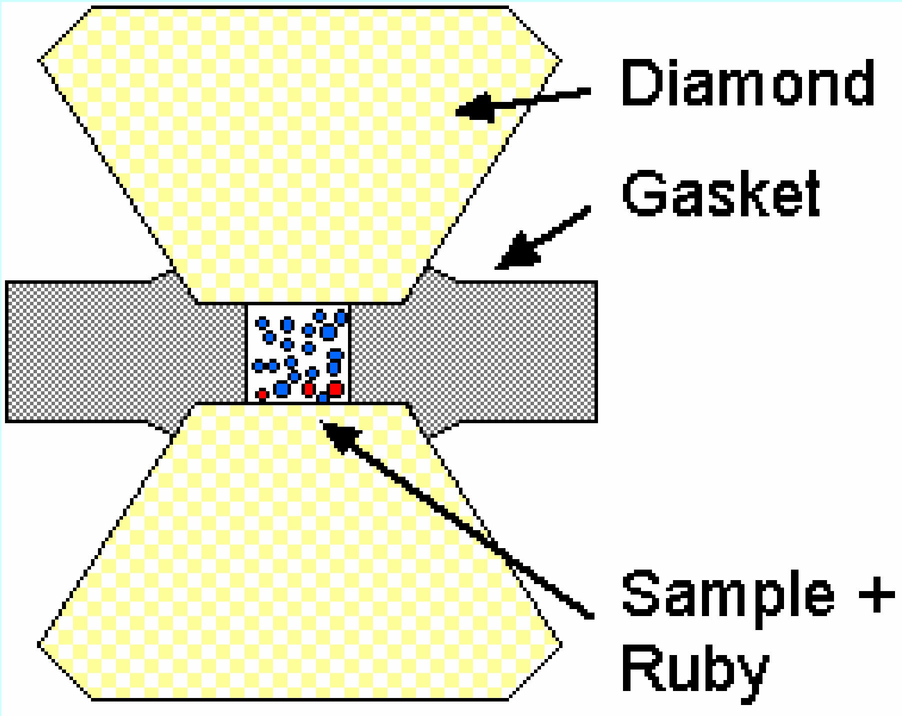
from IR to X-ray

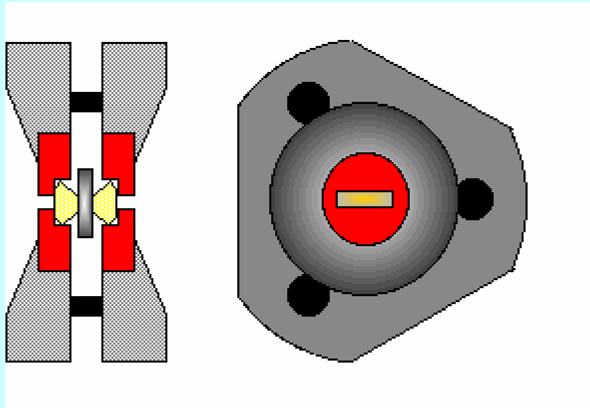


pressure transmitting medium:

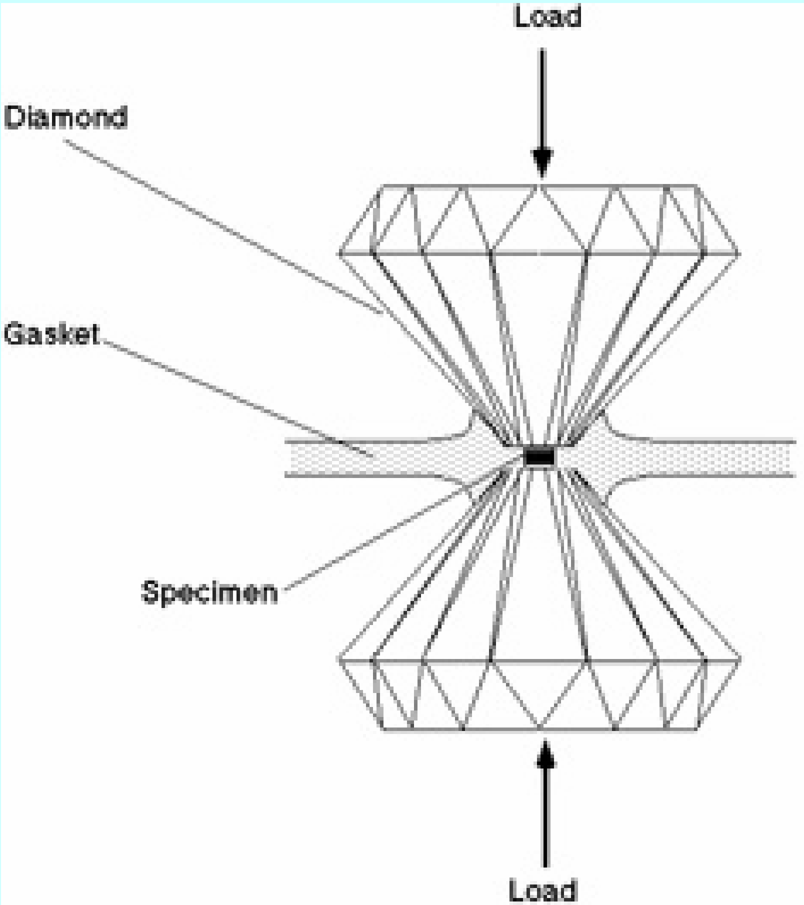
solid Ar, N_2, O_2,

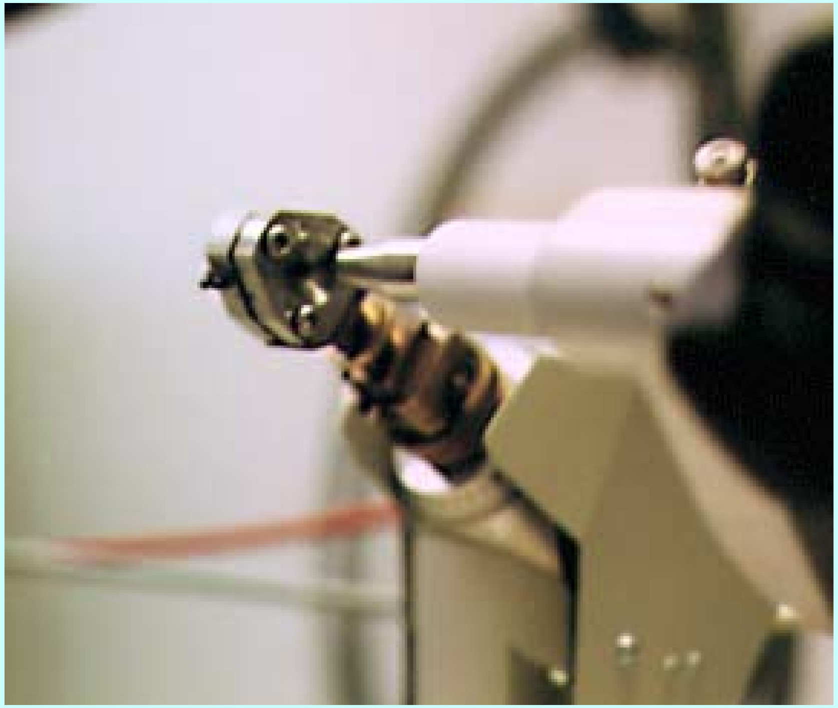
Diamond Anvil Cell





Diamond Anvil Cell





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Calibrating a high pressure diamond anvil

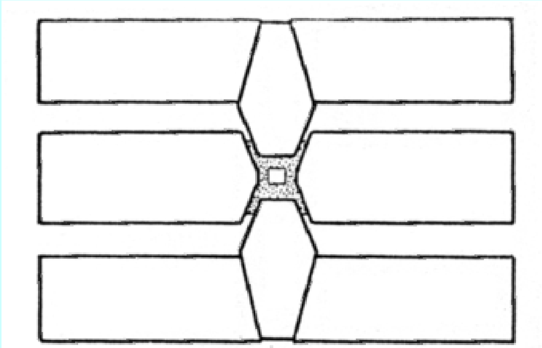
- **Ruby - fluorescence transition**
- **Bi, Tl, Ba pressure induced phase transition**

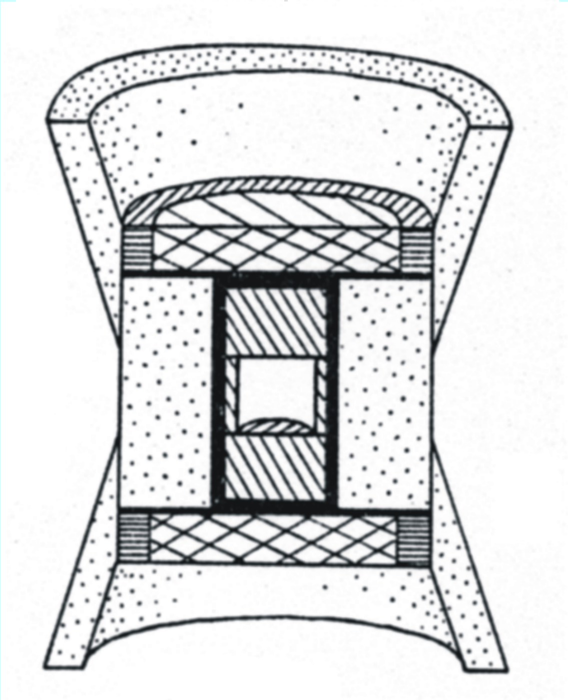
High pressure synthesis

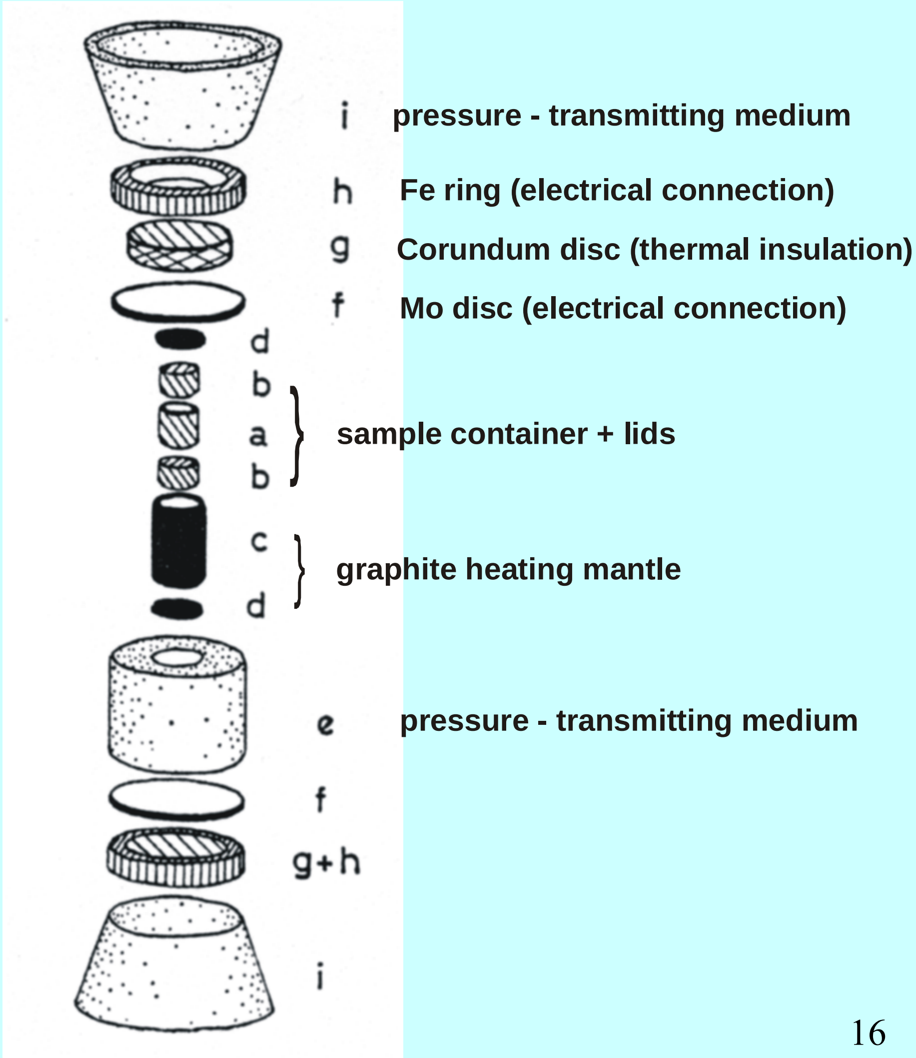
$SnO_2 + Pb_2SnO_4 \longrightarrow 2\ PbSnO_3$ perovskite   7 GPa, 400 °C

At ambient pressure only SnO_2 and PbO products

High Pressure Two-Die Belt-Type Apparatus



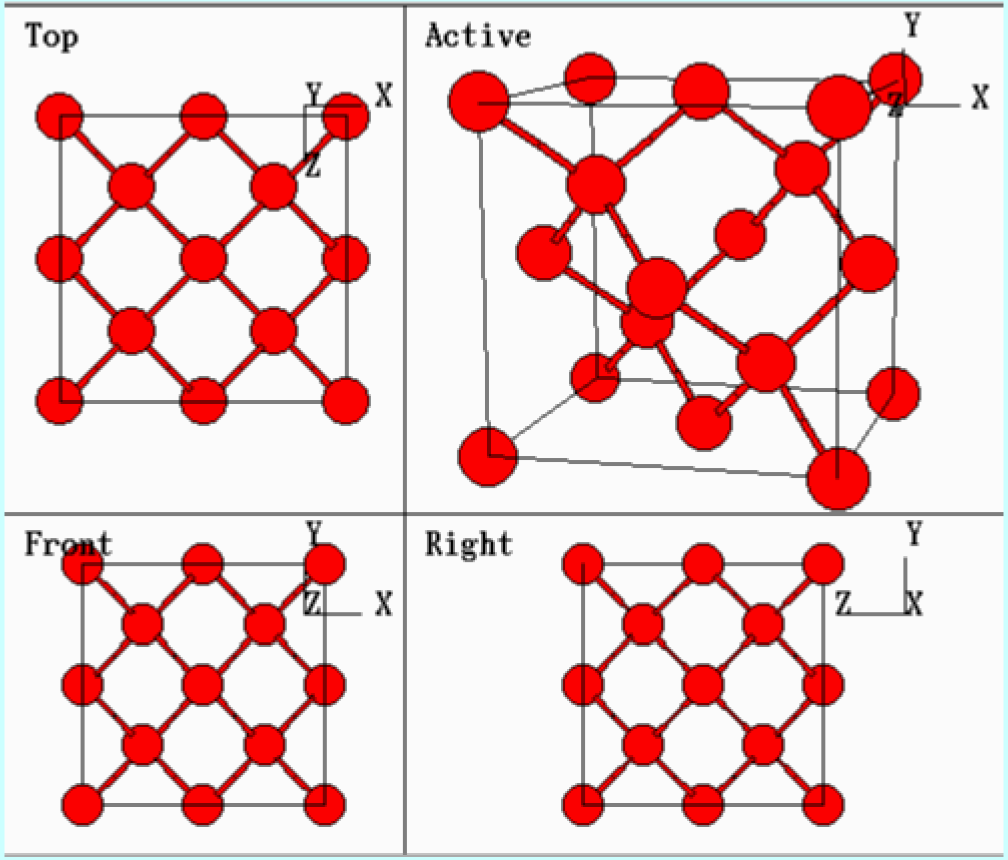




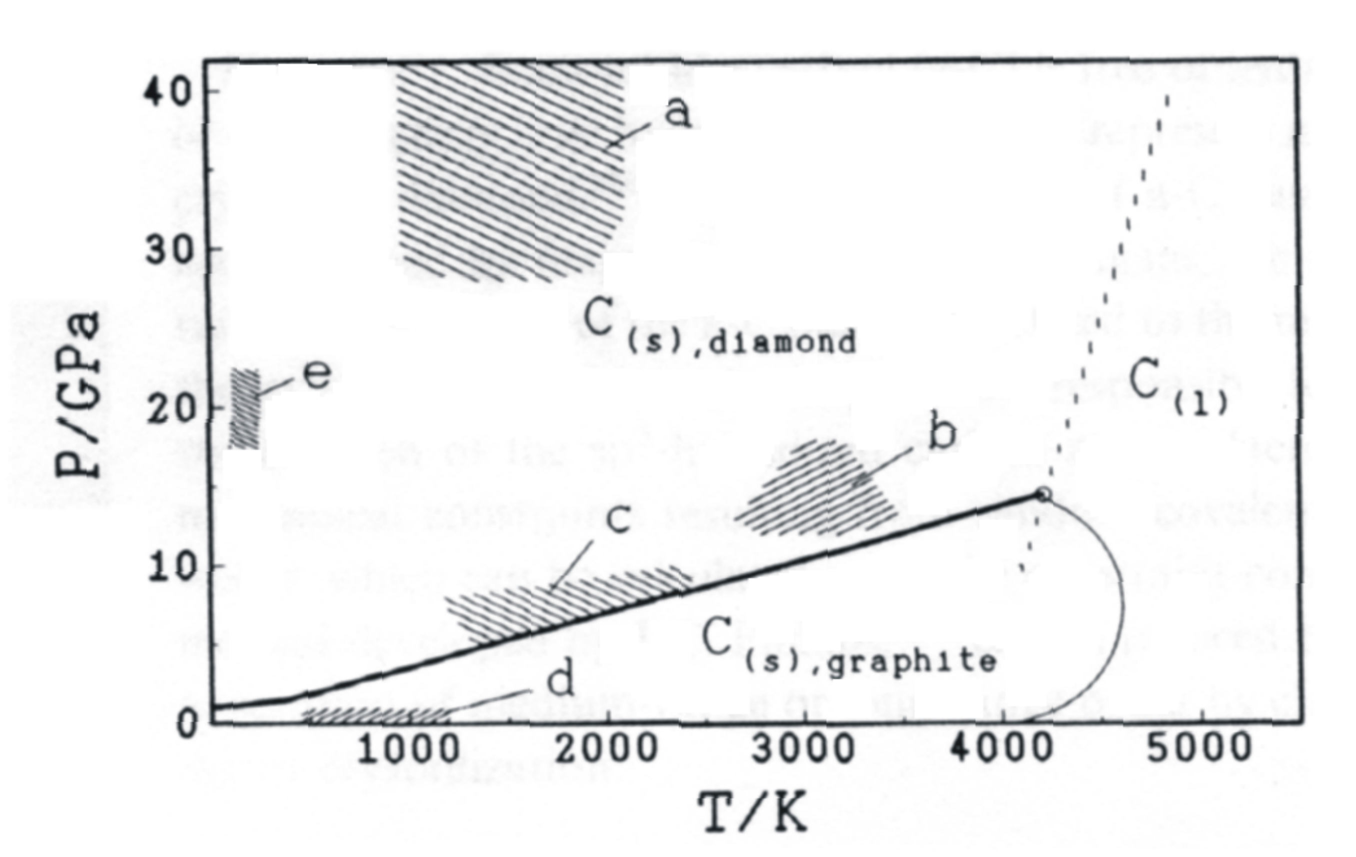
Diamonds

The hardest known substance, the highest thermal conductivity
Difficult to transform graphite into diamond

Industrial diamonds (GE) made from graphite around 3000 °C and 13 GPa



p, T diagram of carbon



a – shock wave production of diamond
b – high-temperature, high-pressure synthesis of diamond
c – catalytic region for diamond formation
d – CVD diamond
e – transformation of C_{60} into diamond

The activation energy required for a sp^2 3-coordinate to a sp^3 4-coordinate structural transformation is very high, so requires extreme conditions

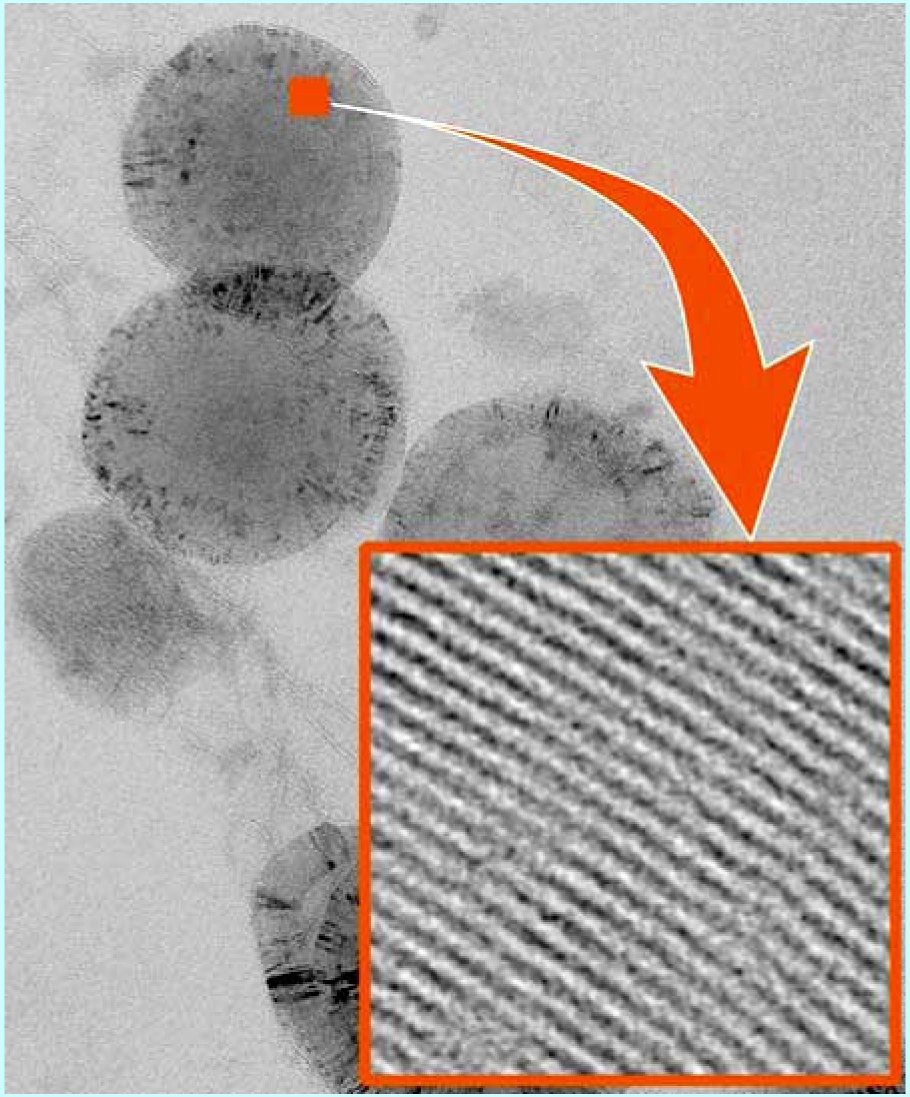
Ways of getting round the difficulty

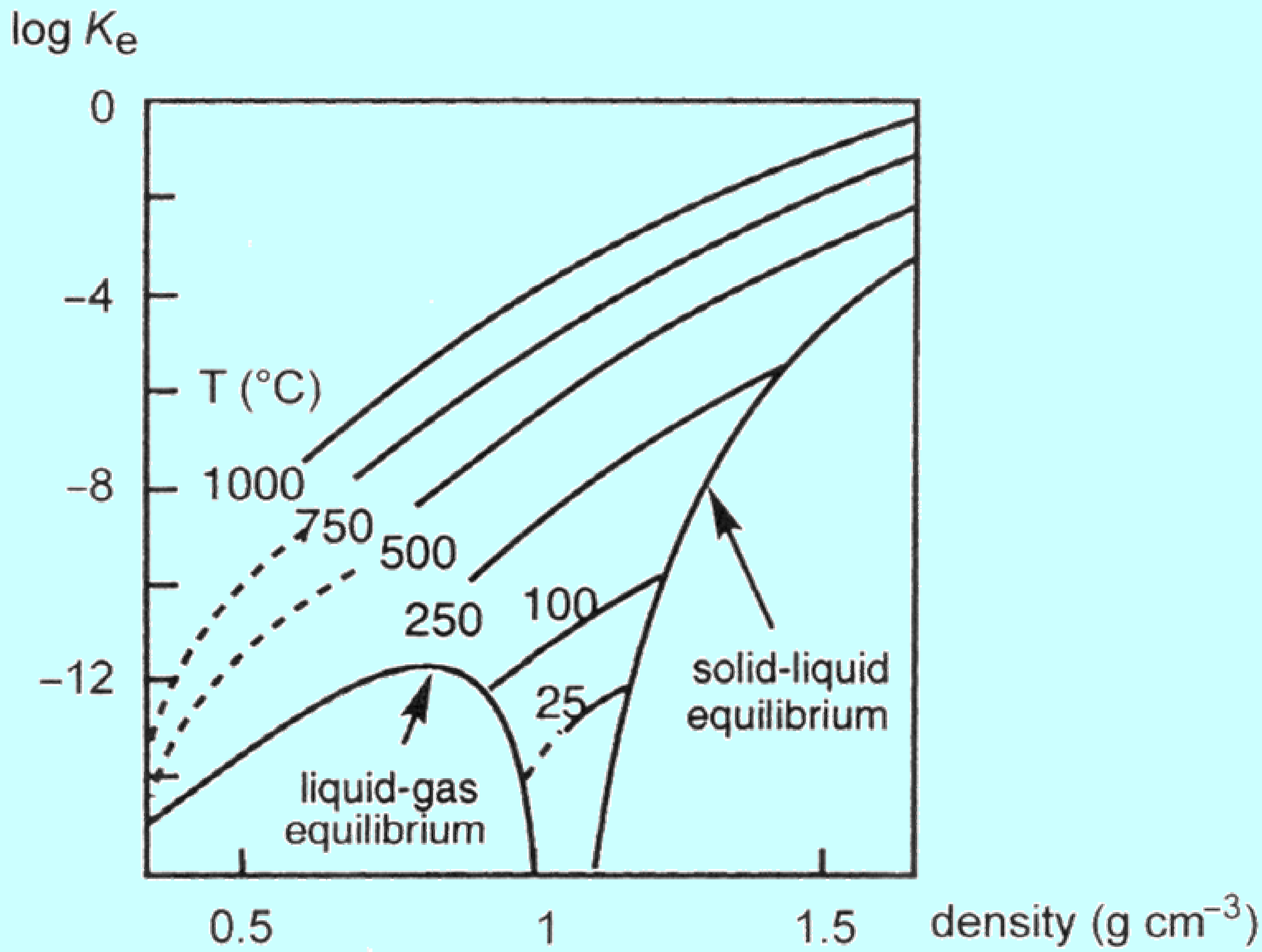
♦ **Catalyst: transition metals (graphite is dissolved in molten metal: Fe, Ni, Co, 6 GPa, 1000 °C), alloys (Nb-Cu), $CaCO_3$, hydroxides, sulfates, P (7.7 GPa, 2200 °C, 10 min),**

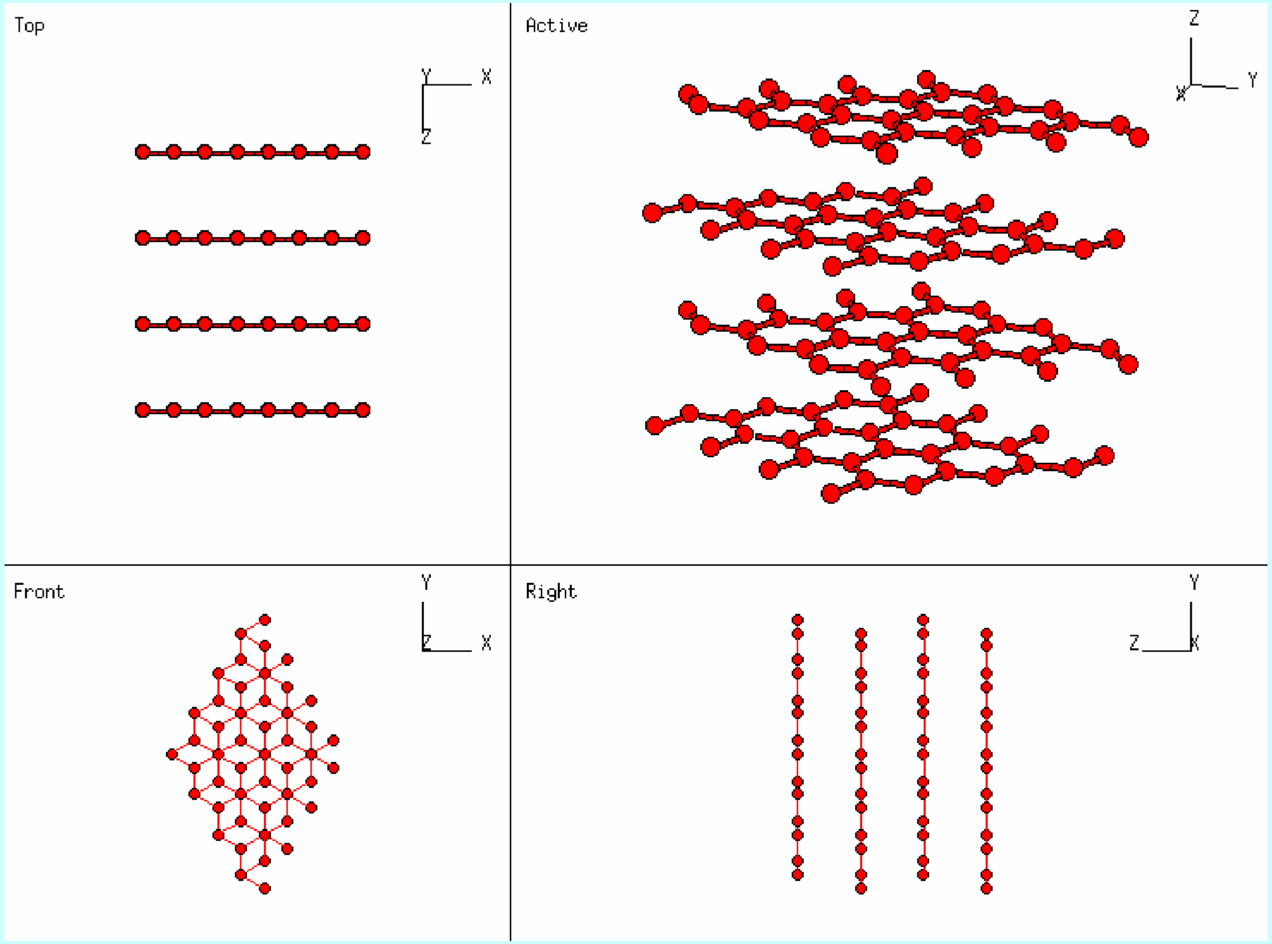
♦ **Squeezing (uniaxial not hydrostatic pressure), no heating, buckyball carbons are already intermediate between $sp^{2\text{-}3}$. C_{60}, diamond anvil, 25 GPa instantaneous transformation to bulk crystalline diamond, highly efficient process, fast kinetics**

♦ **Carbon onions, electron irradiation of graphite, concentric spherical graphite layers, spacing decreases from 3.4 Å to 2.2 Å in the onion center, 100 GPa, 200 keV beam, in several hours, pressureless conversion to diamond**

♦ **Using CH_4/H_2 microwave discharges to create reactive atomic carbon whose valencies are more-or-less free to form sp^3 diamond, atomic hydrogen saturates the dangling bonds, dissolves soot faster than diamond, a route for making diamond films, 50 μm**




log K_e
0
−4
−8
−12
T (°C)
1000
750
500
250
100
25
liquid-gas
equilibrium
solid-liquid
equilibrium
0.5
1
1.5
density (g cm^{-3})



Top
Y
X
Z
Active
Z
X
Y
Front
Y
Z
X
Right
Y
Z
X

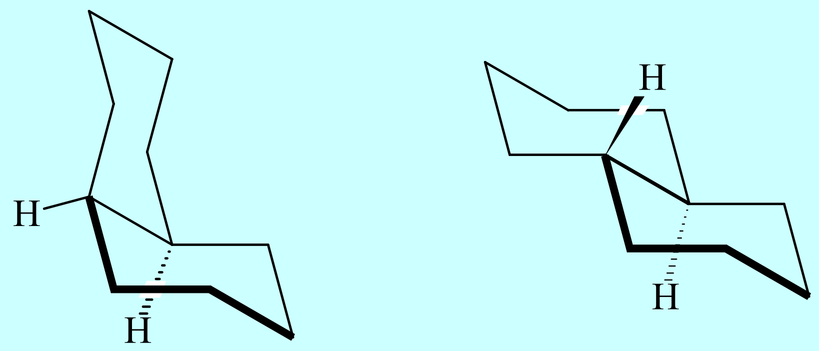
Organic molecule theory of diamond cleavage

The jeweler's chisel if placed correctly on a diamond, with a well oriented blow, always cause cleavage along {111} greater than 90% of the time, imagine the cost of a mistake with a large crystal

The number of bonds broken per unit area (that is, surface energies) for different planes does not explain the observations of preferential {111} cleavage!!!

Diamond viewed in terms of layers of polycondensed cyclohexane rings with axial bonds between layers and equatorial bonds within layers
Unfavorable axial-axial C-C bond interactions at 2.51 Å versus equatorial-equatorial at 2.96 Å

Model compounds like cis-decalin versus trans-decaline comprised of two fused cyclohexane rings
trans-decalin is 11-12 kJmol^{-1} more stable because cis-strain cannot be relieved by bond rotation as in cyclohexane itself,
cis can only isomerize to trans by bond cleavage followed by recombination, hence origin of the high activation energy for the cis-to-trans isomerization of decalin.



A breaking molecule theory: axial-axial unfavorable interactions cause the mechanical energy of the jeweler's chisel to be funneled into preferential breakage of an axial C-C bond
This then induces a kind of domino effect whereby the adjacent axial C-C bonds break and C-C bonds throughout the entire {111} plane are severed

- **Electrical conductivity increases with T. The change of conductivity with T is one way of measuring the band gap.**
- **Conductivity also increases with P, because atoms are pushed closer together.**
- **All elements eventually adopt metallic structures at high P.**
- **The interior of Jupiter is thought to contain metallic hydrogen!**