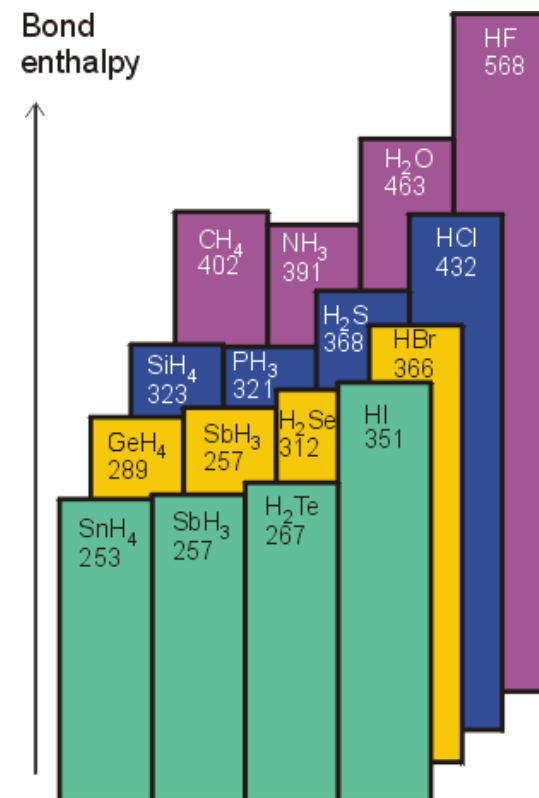


Stability of Hydrogen Compounds

Table 9.5 Standard Gibbs energy of formation, ΔG_f^\ominus /(kJ mol⁻¹), of binary *s*- and *p*-block hydrogen compounds at 25 °C

Period	Group						
	1 I	2 II	13 III	14 IV	15 V	16 VI	17 VII
2	LiH(s) - 68.4	BeH ₂ (s) (+ 20)	B ₂ H ₆ (g) + 86.7	CH ₄ (g) - 50.7	NH ₃ (g) - 16.5	H ₂ O(l) - 237.1	HF(g) - 273.2
3	NaH(s) - 33.5	MgH ₂ (s) - 35.9	AlH ₃ (s) (- 1)	SiH ₄ (g) + 56.9	PH ₃ (g) + 13.4	H ₂ S(g) - 33.6	HCl(g) - 95.3
4	KH(s) (- 36)	CaH ₂ (s) - 147.2	GaH ₃ > 0	GeH ₄ (g) + 113.4	AsH ₃ (g) + 68.9	H ₂ Se(g) + 15.9	HBr(g) - 53.5
5	RbH(s) (- 30)	SrH ₂ (s) (- 141)		SnH ₄ (g) + 188.3	SbH ₃ (g) + 147.8	H ₂ Te(g) > 0	HI(g) + 1.7
6	CsH(s) (- 32)	BaH ₂ (s) (- 140)					

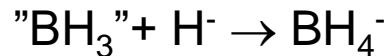
Data from *J. Phys. Chem. Ref. Data*, **11**, Supplement 2 (1982). Values in parenthesis are based on ΔH_f^\ominus data from this source and entropy contributions estimated by the method of W. M. Latimer, p. 359 of *Oxidation potentials*. Prentice Hall, Englewood Cliffs, NJ (1952).



Electron-Deficient Hydrides

Electron deficiency:

- Some say: electron deficient molecules are molecules with a central atom that does not have an electron octet
- BETTER: those molecules are called "electron poor"

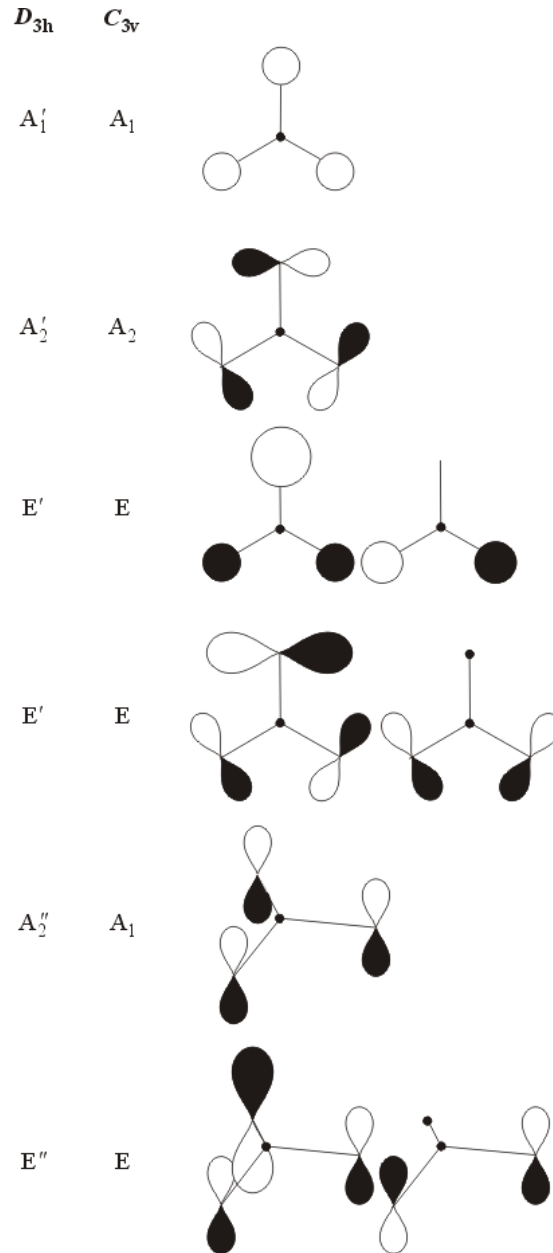


- **Electron-deficient compounds are compounds that cannot be explained by 'normal' 2-centre-2-electron bonds.**

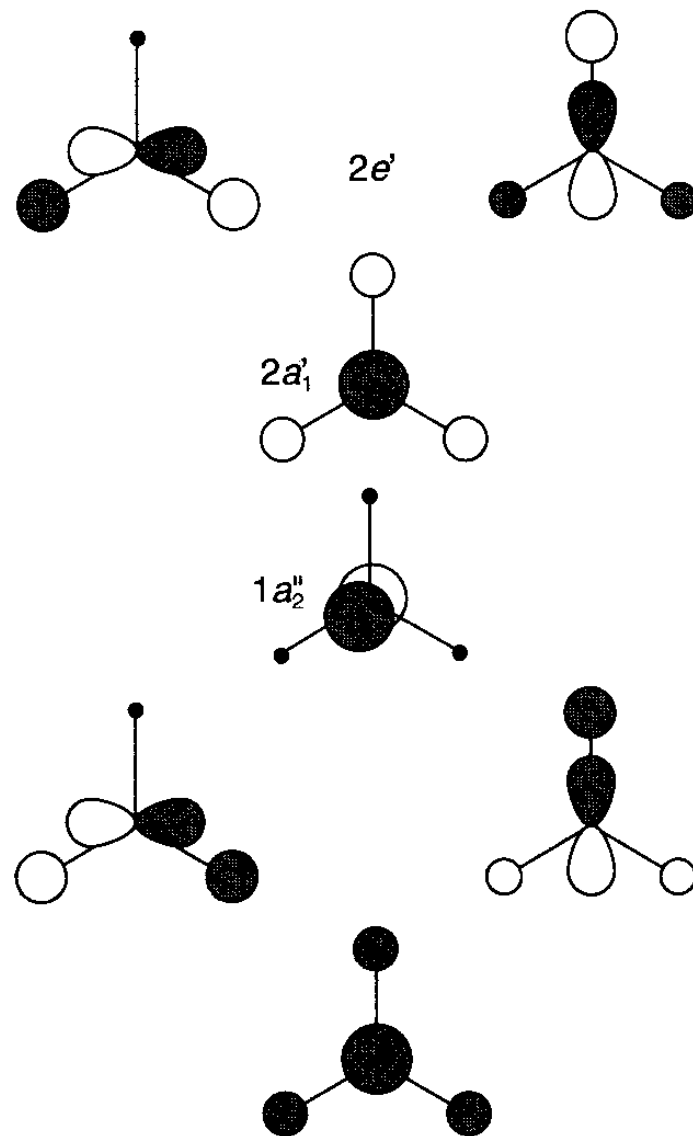
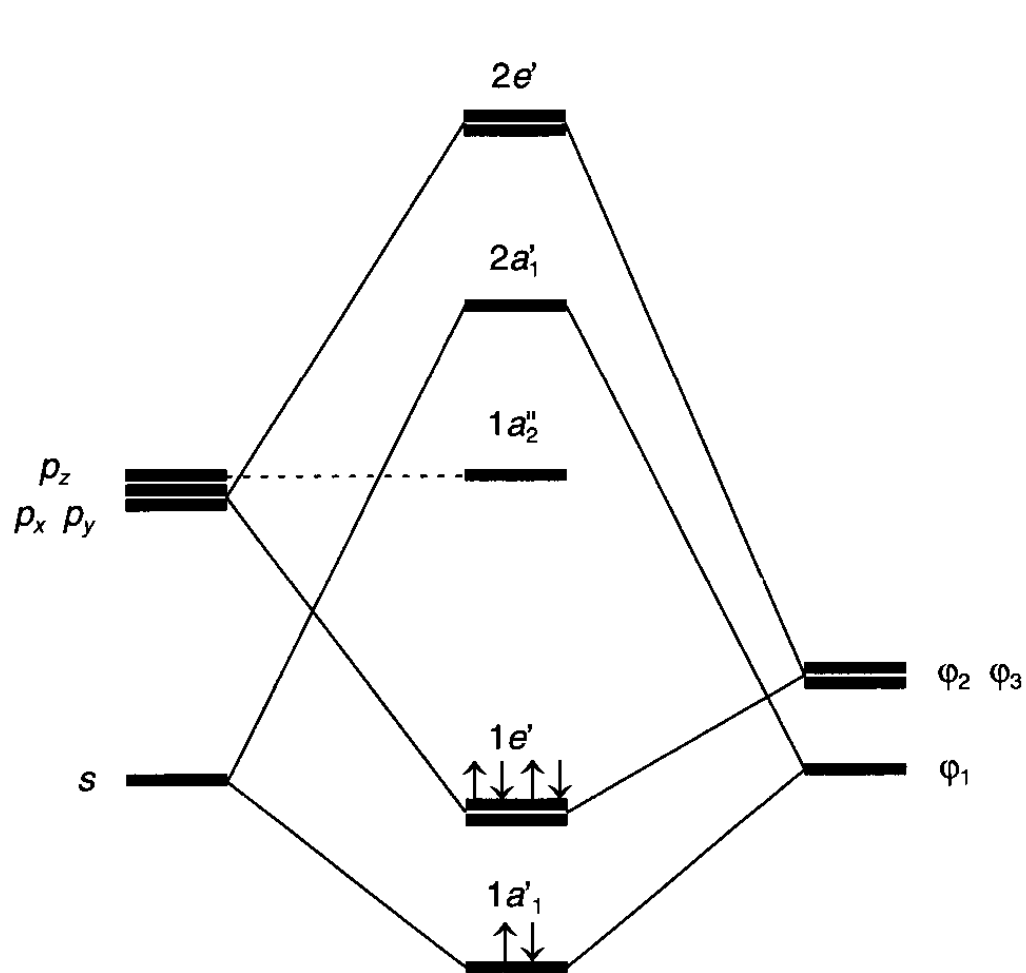
MO Diagram of BH₃

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

MO Diagram of BH₃

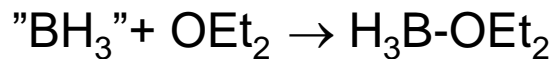
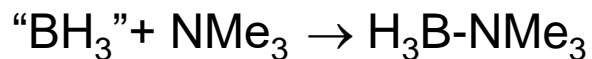
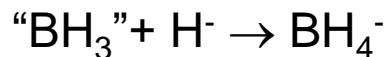


MO Diagram of BH₃



Reactivity of “BH₃”

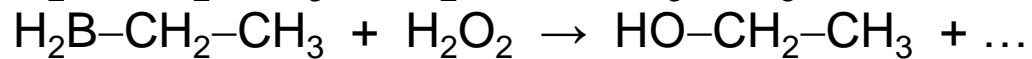
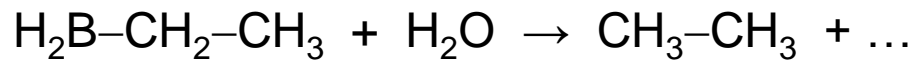
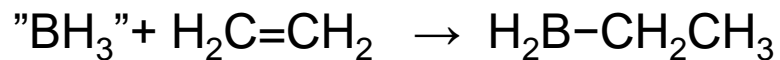
Lewis acid base reactions:



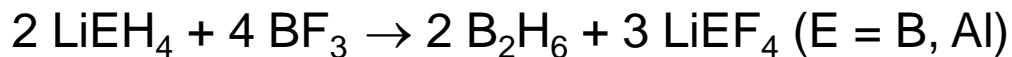
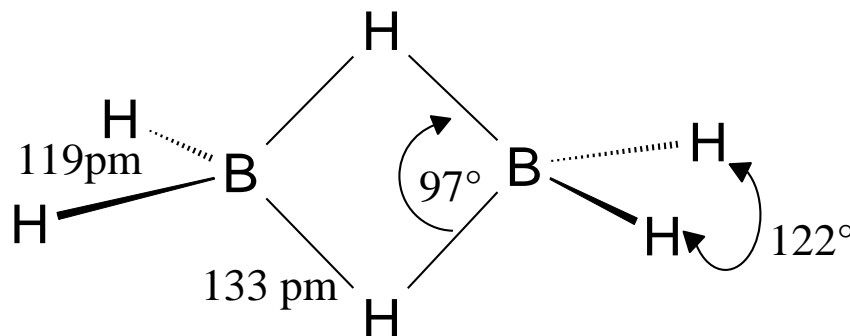
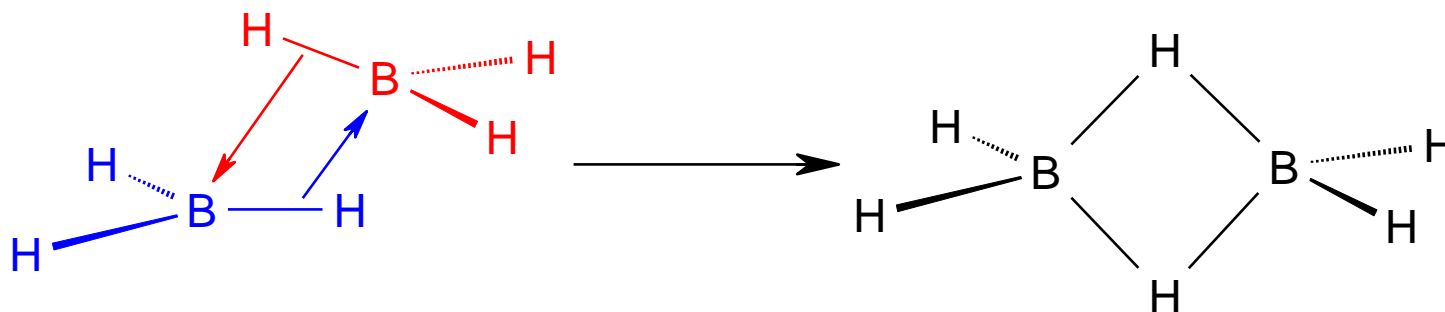
- BUT: BH₃ does not exist
- BH₃·OEt₂, an etherate of BH₃ is used as a reagent

Hydroboration

Hydroboration in organic chemistry:

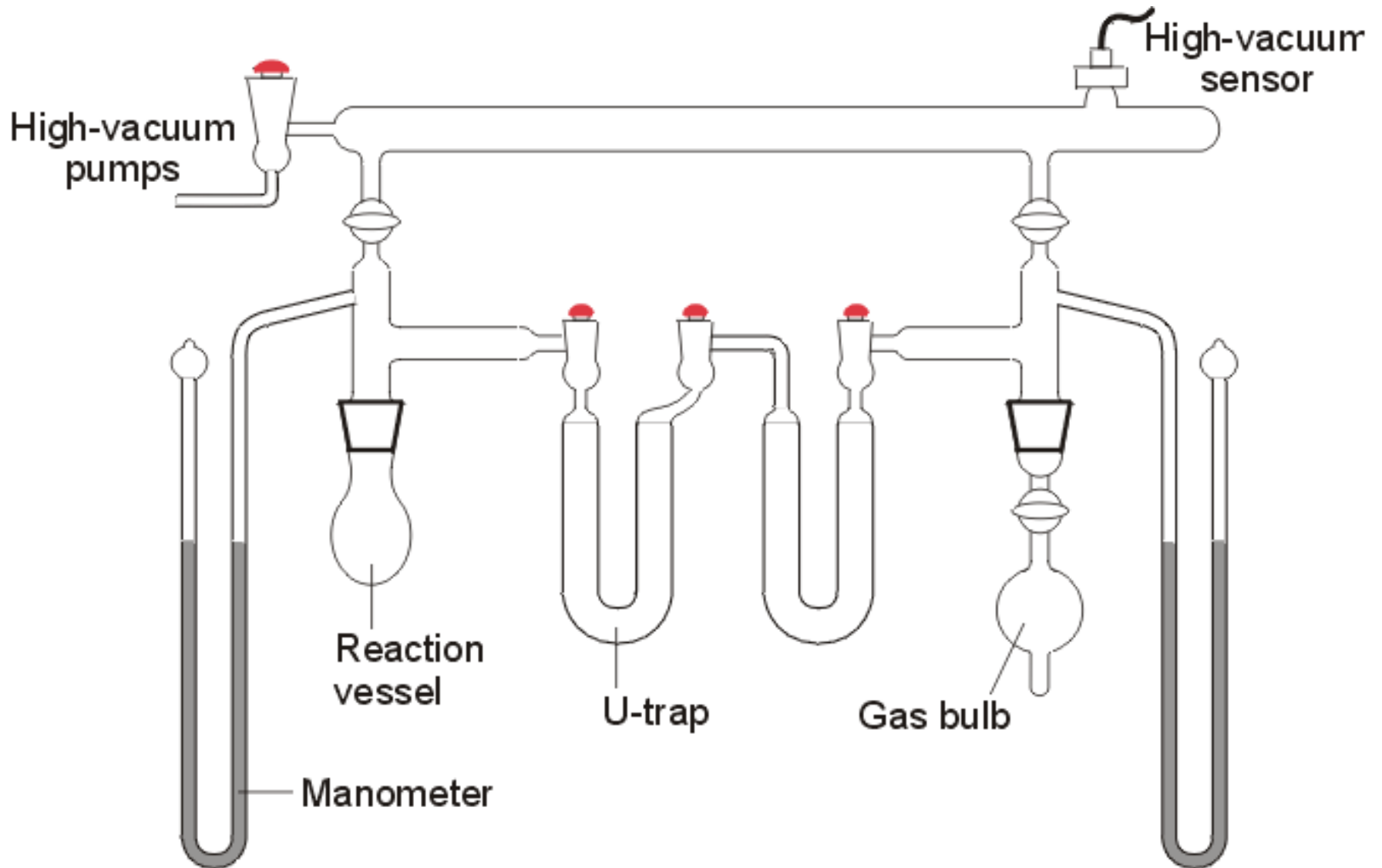


Diborane: B₂H₆



- Boranes are pyrophoric! They need to be handled under exclusion of air (oxygen).

Inert Atmosphere Techniques: Vacuum Lines



Inert Atmosphere Techniques: Vacuum Lines



Inert Atmosphere Techniques: Vacuum Lines



Inert Atmosphere Techniques: Vacuum Lines



Inert Atmosphere Techniques: Vacuum Lines



Inert Atmosphere Techniques: Glove Boxes



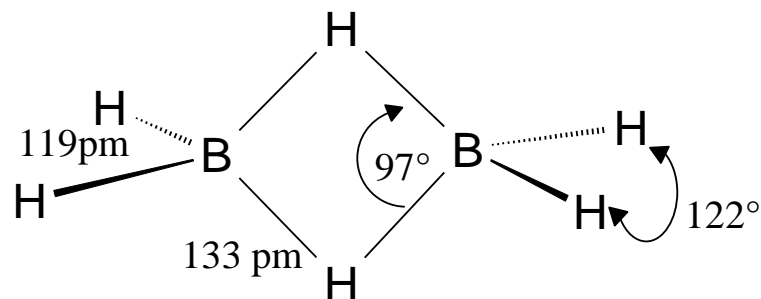
Inert Atmosphere Techniques: Glove Boxes



Inert Atmosphere Techniques



Diborane: B_2H_6

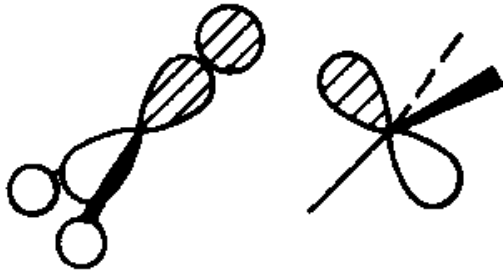


Electron count:

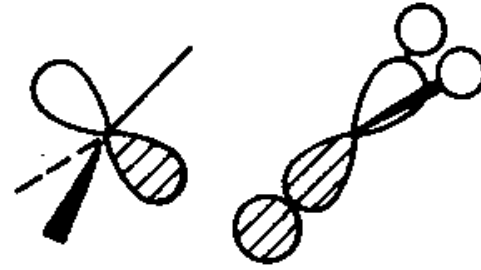
- B_2H_6 is electron deficient.

3-centre-2-electron bonding of bridging H:

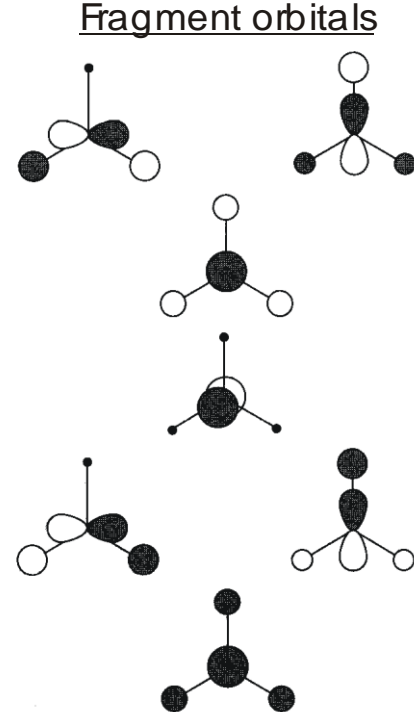
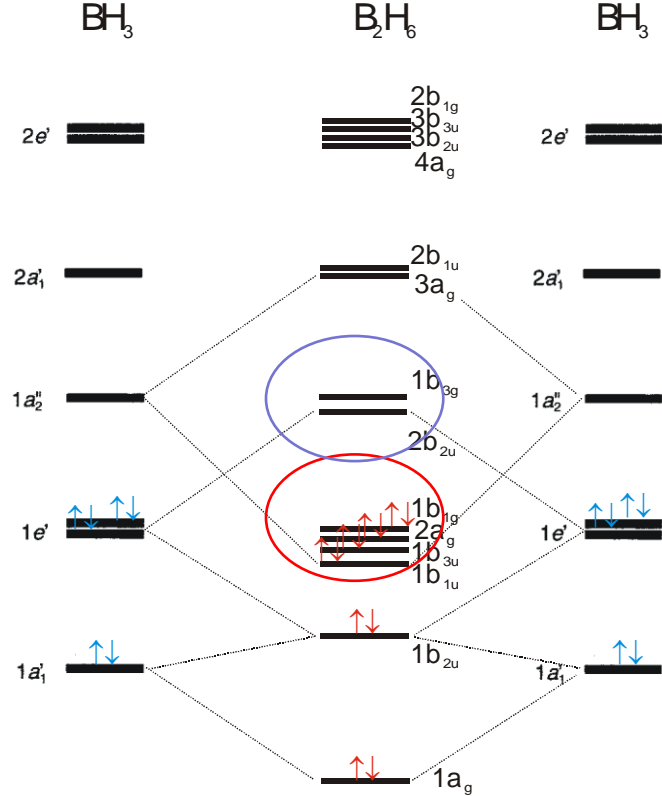
Diborane: B_2H_6



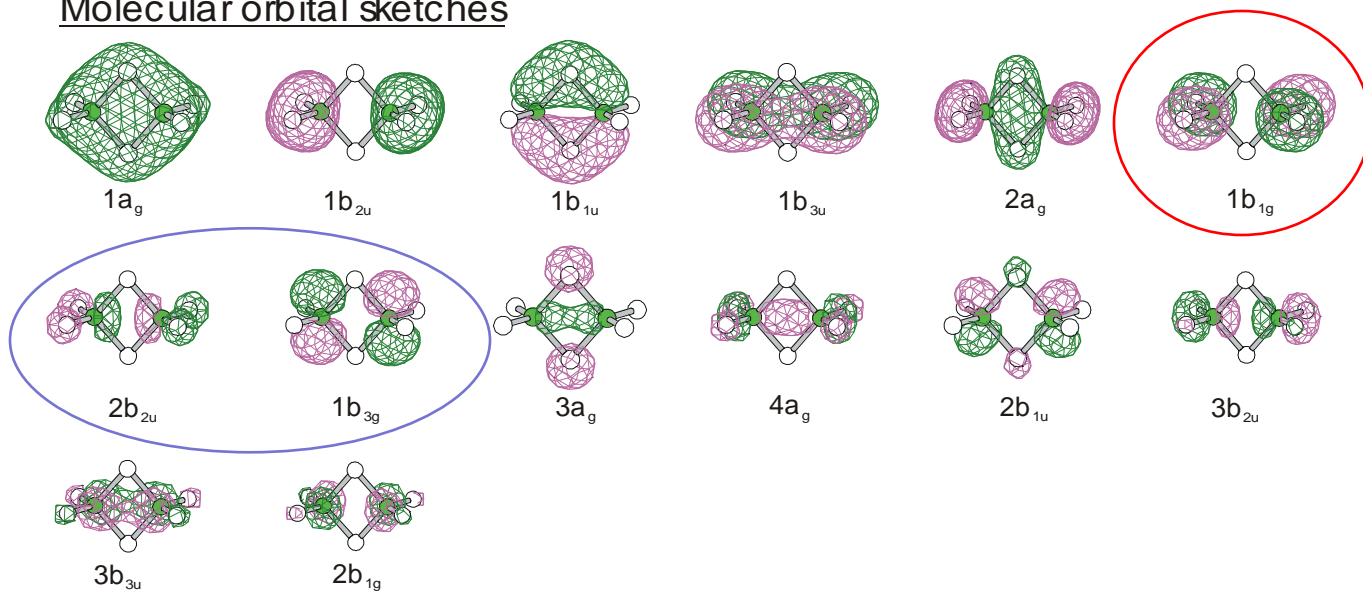
HOMO — LUMO



LUMO — HOMO



Molecular orbital sketches



HOMO

LUMO,
LUMO+1

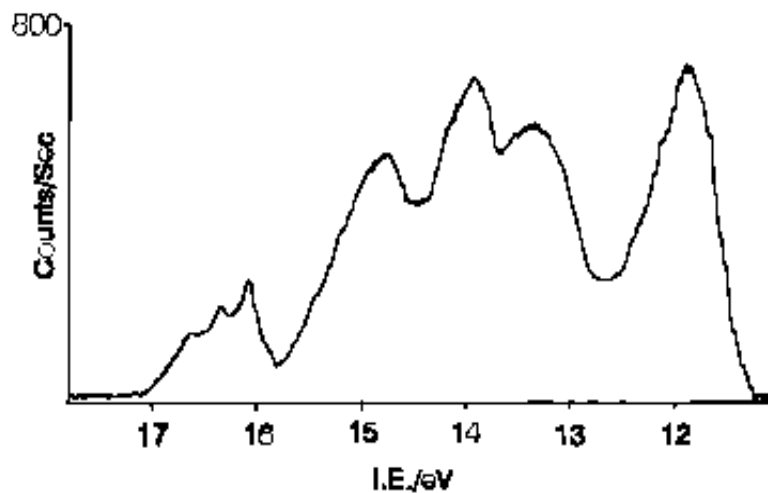
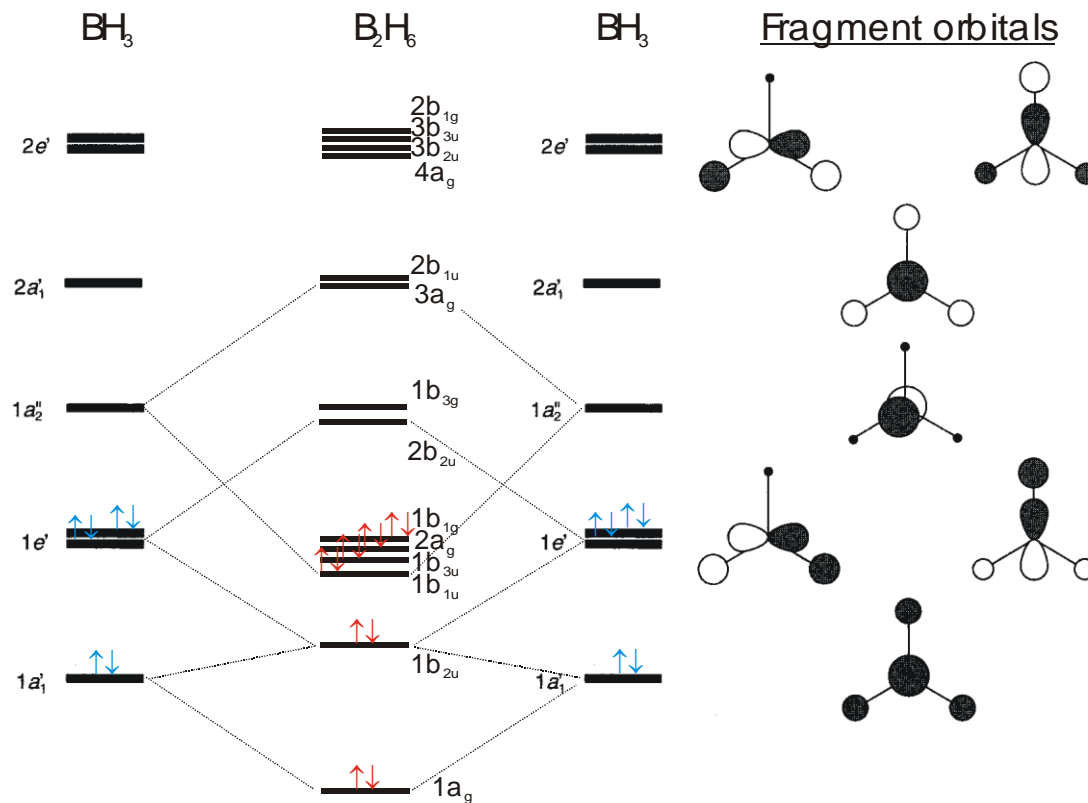


Figure 1. He I (21.22 eV) photoelectron spectrum of B_2H_6 . Ordinate: counts/s. Abscissa: ionization energy/eV.

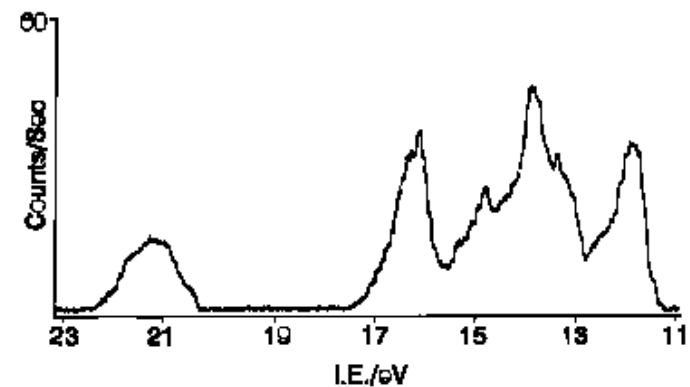
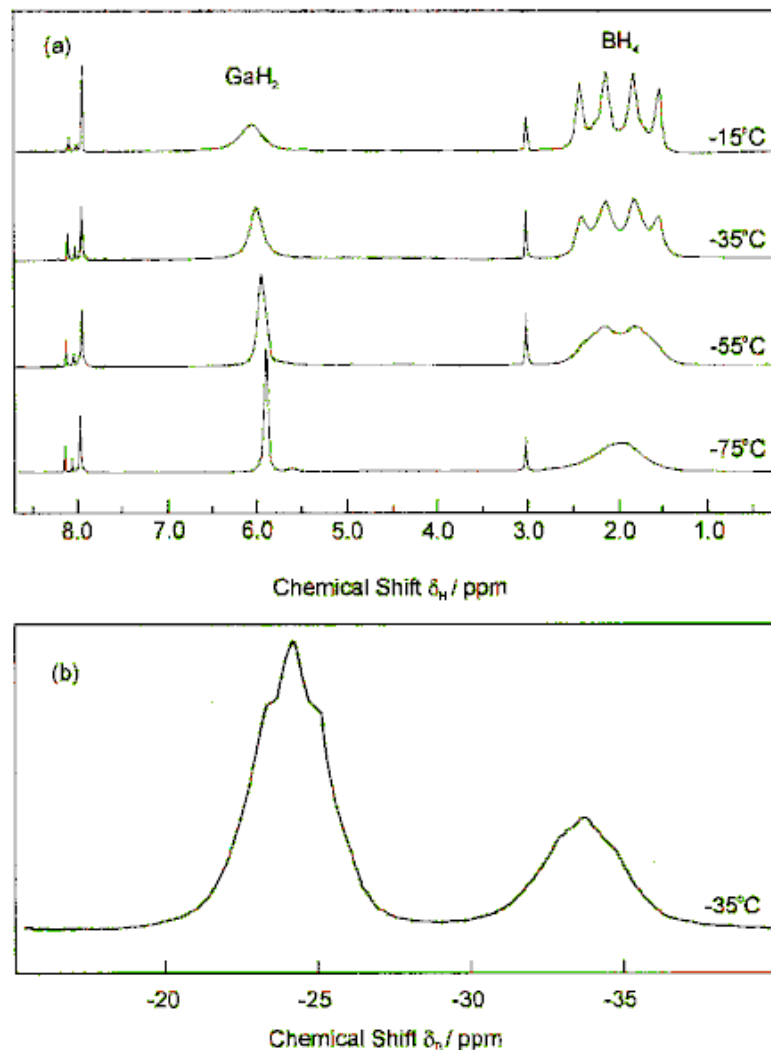


Figure 3. He II (40.81 eV) photoelectron spectrum of B_2H_6 recorded in the 11.0–23.0 eV ionization energy region. No other bands were observed at higher ionization energy. Ordinate: counts/s. Abscissa: ionization energy/eV.

Digallane: Ga₂H₆



⁶⁹Ga, I = 3/2, 60.4%

⁷¹Ga, I = 3/2, 39.6%

¹⁰B, I = 3, 19.53%

¹¹B = 3/2, 80.42%

Figure 5. ¹H and ¹¹B NMR spectra of a toluene-*d*₈ solution of gallaborane at different temperatures.

Digallane: Ga₂H₆

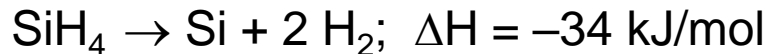
- Digallane is a volatile Ga compound
- Digallane can be 'decomposed' under the right conditions: Ga can be deposited
- Search for volatile metal/element compounds for **Chemical Vapour Deposition (CVD)**
- CVD can be used to deposit thin layers on a solid surface.
- CVD is important for semiconductors, e.g., GaAs.

Heavier Group 14 Hydrogen Compounds

- Silanes are structurally similar to alkanes, but the reactivity is very different.
- Si and B are related via a diagonal relationship in the periodic table.
- Silanes and boranes have similar properties: for example they are both pyrophoric.

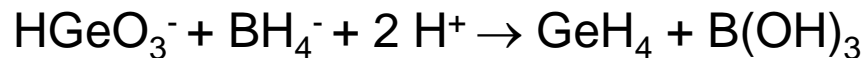
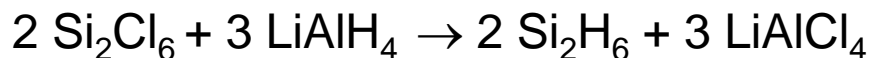
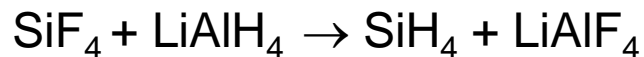


- Silanes and boranes are both endergonic compounds.
- Heating of SiH_4 above 500°C will cause decomposition into Si and H_2

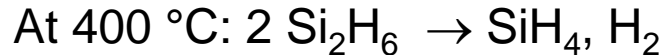


Silanes

Preparation (not from the elements!):



Higher silanes are easily cracked:



Properties:

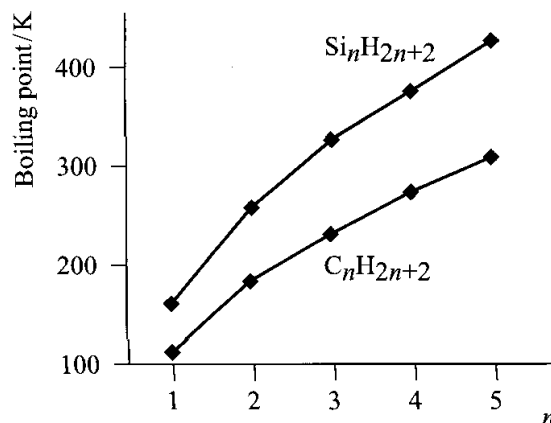


Fig. 13.8 Boiling points of the straight-chain silanes, $\text{Si}_n\text{H}_{2n+2}$, and hydrocarbons $\text{C}_n\text{H}_{2n+2}$.

Silanes

Bond energies:	C–H 416 kJ/mol	Si–H 326 kJ/mol
	C–Cl 327 kJ/mol	Si–Cl 391 kJ/mol
	C–O 359 kJ/mol	Si–O 466 kJ/mol

Properties:

- Methane is chlorinated with difficulty (radical reaction)
- Silanes react explosively with Cl_2

- Methane is kinetically stable towards oxygen
- Silanes react spontaneously with air

- Methane is stable with respect to hydrolysis
- Silanes are readily attacked by water

- Catenation is more common for alkanes
- Higher silanes, germanes, stannanes and plumbanes are less common

Bonding in Silanes

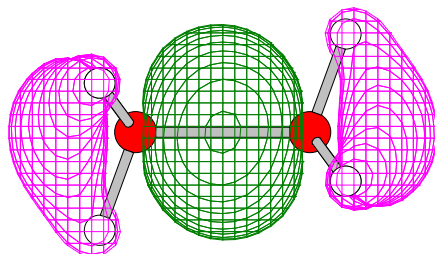
Energy levels of Ethane

Energy levels of Disilane

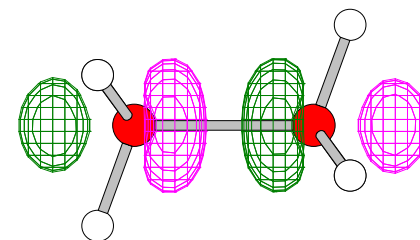
Energy levels in Ethene

LUMO	4.12 eV	-0.95 eV	1.44 eV
HOMO	-11.77 eV	-10.64 eV	-10.55 eV
ΔE	15.86 eV	9.69 eV	11.99 eV

- The C=C double bond is considered a functional group.
- One can consider the Si-Si bond to be a functional group because of the small HOMO-LUMO gap
- (absorption of light with wavelength >200 nm, which is the cut-off of transmission in air).



HOMO (σ), $2a_{1g}$



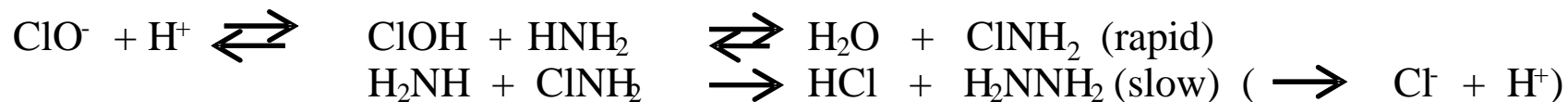
LUMO (σ^*), $2a_{2u}$

Group 15 Hydrogen Compounds

Ammonia, NH₃: Haber-Bosch process

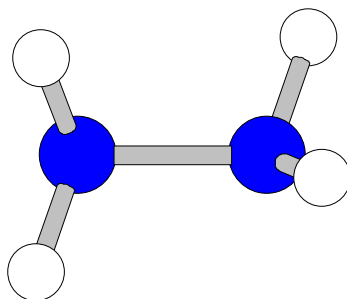
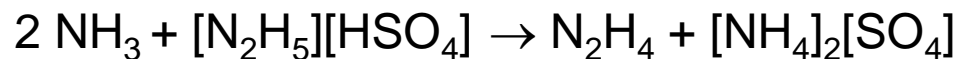
Hydrazine, N₂H₄: Olin Raschig Process in industry

- Preparation from a ca. 30-fold excess of ammonia and sodium hypochlorite



Hydrazine

- Hydrazine was used as a rocket fuel.
- The Apollo mission used a reaction between N_2H_4 and N_2O_4 (products H_2O and N_2)
- Hydrazine forms a stable monohydrate – dehydration is difficult.
- Anhydrous hydrazine is usually produced via reactions such as:

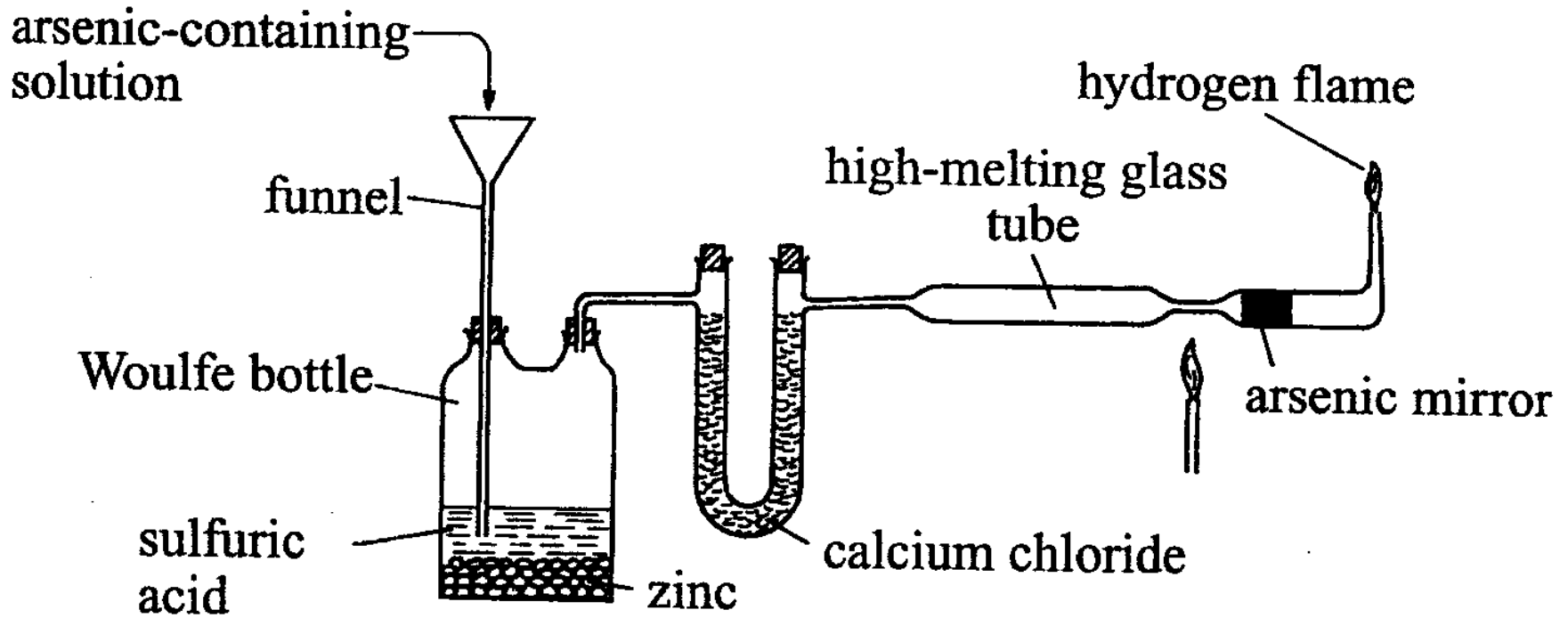


Gauche conformation

Heavier Group 15 Hydrogen Compounds

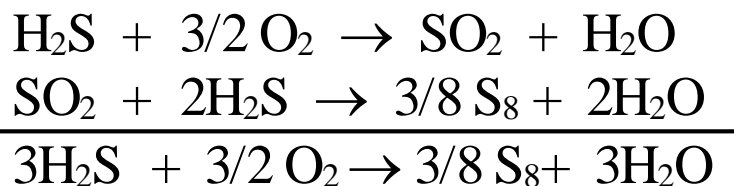
- Phosphine (PH_3), arsine (AsH_3), stibine (SbH_3)
- Phosphine is an extremely toxic, colourless gas
 - Lower solubility in water than ammonia
 - Neither Brønsted acidic or basic
 - Excellent Lewis base
 - Strong acids can protonate phosphine to PH_4^+
 - Alkali metals can reduce phosphine to PH_2^-

Marsh Test



Group 16 Hydrogen Compounds

- Sulfane (H_2S), hydrogen selenide (H_2Se), and hydrogen telluride (H_2Te)
- Toxic, foul-smelling gas, part of sour gas.
- It is used to prepare sulfur via the Claus Process



Combustion Chamber

1st reactor: 300 °C, Co/Mo catalyst

2nd reactor: 220 °C, Large surface area Al_2O_3