Gas Phase Reactions

Heating: furnace, laser, plasma, flame, arc

Gas-Metal Rxn

$Ti + N_2 \xrightarrow{1800\ K} TiN$

$3\ Si + 2\ N_2 \longrightarrow Si_3N_4$

$W + CH_4 \longrightarrow WC + H_2$ mp 2720 °C

WC dissolved in Co = cemented carbides

$Ti + CH_4 \longrightarrow TiC + H_2$ mp 2940 °C

cementite

steel + $H_2/CO + CH_4 + NH_3 \longrightarrow Fe_3C$ + nitrides

Gas Phase Reactions

Gas-Gas Rxn

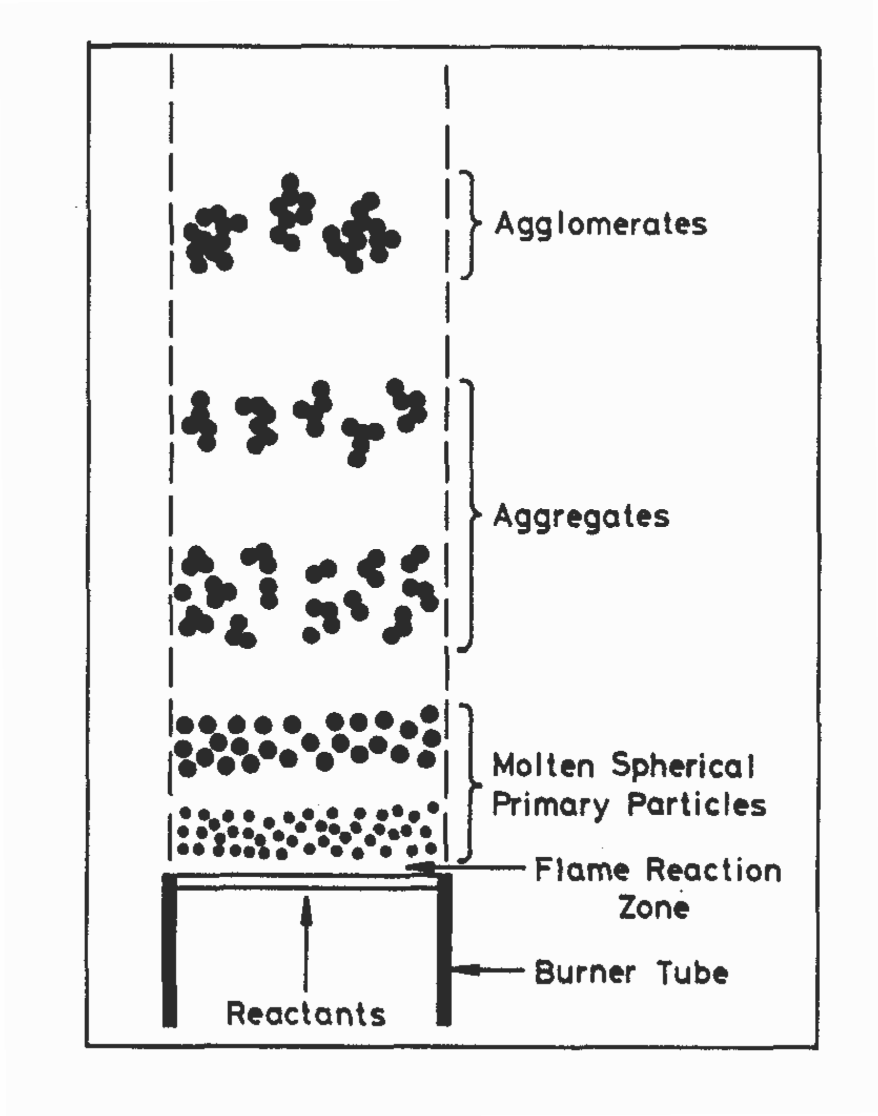
homogeneous nucleation from supersaturated vapor (nano)

Flame hydrolysis
volatile compounds are passed through an oxygen-hydrogen stationary flame:

$SiCl_4 + H_2 + O_2 \longrightarrow SiO_2 + HCl$ **fumed silica**

reagent	bp/°C	product
$SiCl_4$	57	SiO_2
$AlCl_3$	180 (subl.)	Al_2O_3
$TiCl_4$	137	TiO_2
CrO_2Cl_2	117	Cr_2O_3
$Fe(CO)_5$	103	Fe_2O_3
$GeCl_4$	84	GeO_2
$Ni(CO)_4$	42	NiO
$SnCl_4$	114	SnO_2
$ZrCl_4$	331 (subl.)	ZrO_2
$VOCl_3$	127	V_2O_5

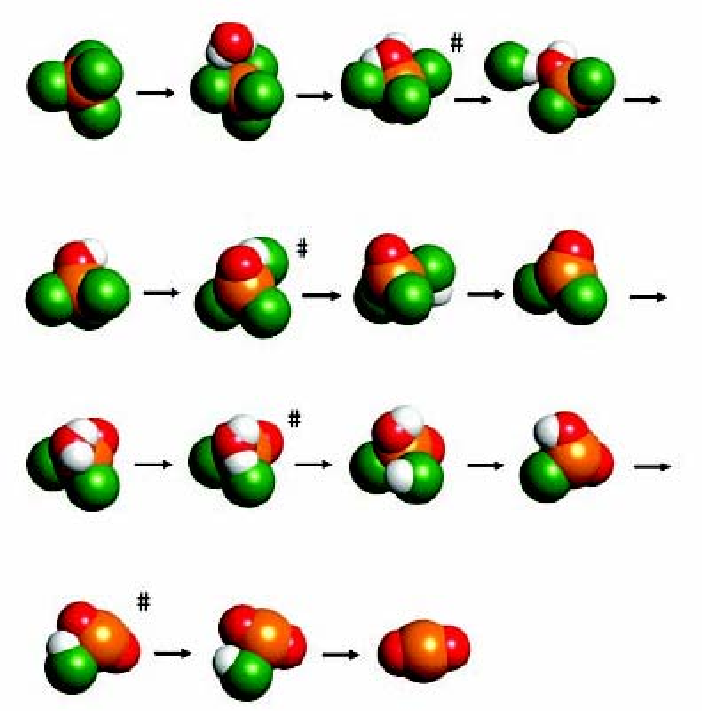
Gas Phase Reactions



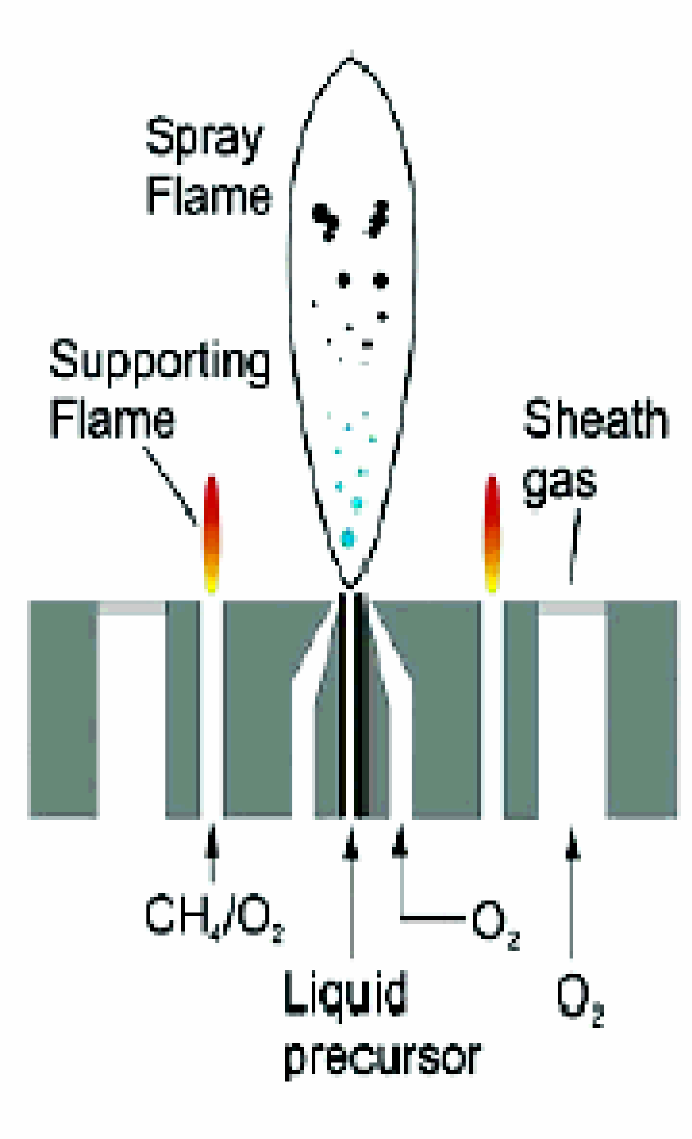
$SiCl_4 + H_2O \rightarrow OSiCl_2 + 2\,HCl$

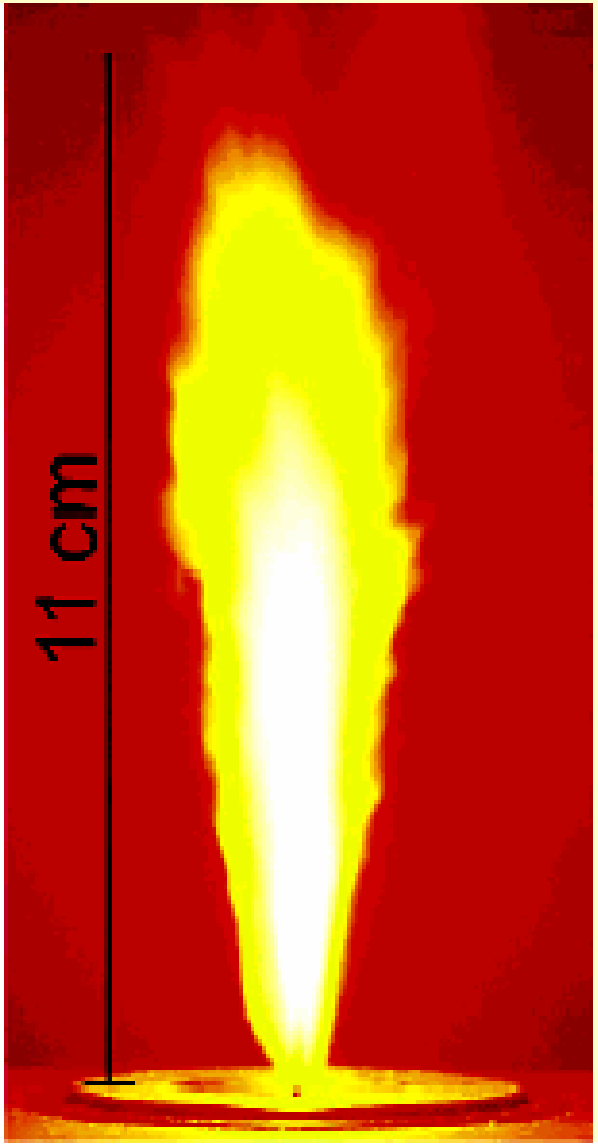
$OSiCl_2 + H_2O \rightarrow SiClOOH + HCl$

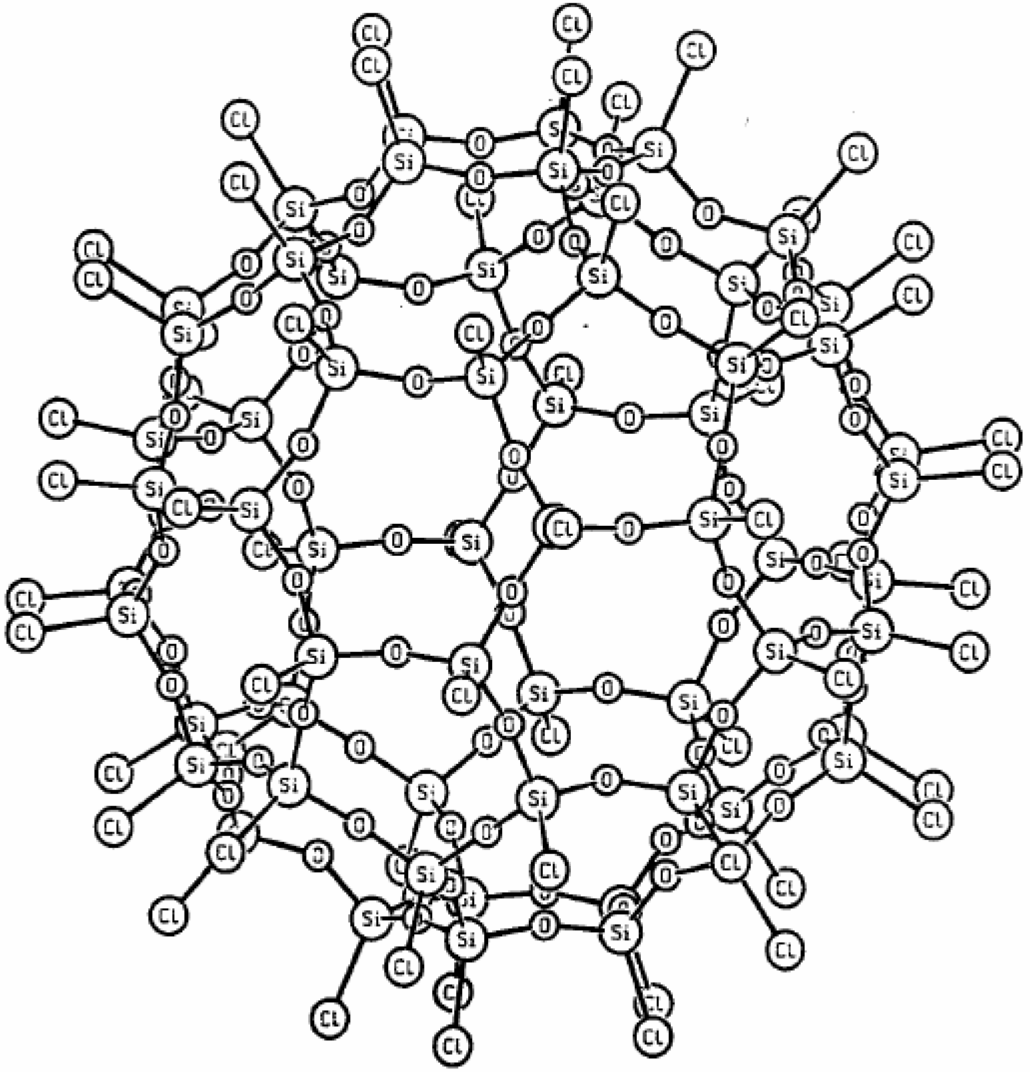
$SiClOOH \rightarrow SiO_2 + HCl$



Gas Phase Reactions







$Si_{60}O_{90}Cl_{60}$ (I_h)

Gas Phase Reactions

Calcium phosphate nanoparticles Ca/P molar ratios 1.43 to 1.67

synthesized by simultaneous combustion of
$Ca(OAc)_2 + OP(O^nBu)_3$ in a flame spray reactor

Fluoro-apatite and zinc or magnesium doped calcium phosphates
adding trifluoroacetic acid or metal carboxylates into the fuel.

Nanoparticle morphology

At a molar ratio of Ca/P < 1.5 promoted the formation of dicalcium pyrophosphate ($Ca_2P_2O_7$).

Phase pure tricalcium phosphate
obtained with a precursor Ca/P ratio of 1.52 after subsequent calcination at 900 °C

micropores and the facile substitution of both anions and cations
possible application as a biomaterial.

Gas Phase Reactions

High-power CO_2 lasers

$3\,SiH_4 + 4\,NH_3 \longrightarrow Si_3N_4 + 12\,H_2$

$HN(SiMe_3)_2 + NH_3 \longrightarrow Si_3N_4 + SiC$

DC-Ar Plasma

$TiCl_4 + NH_3 \xrightarrow{1300\ K} TiN + HCl$

Tarnishing of Metal Surfaces

oxide, hydroxide layers

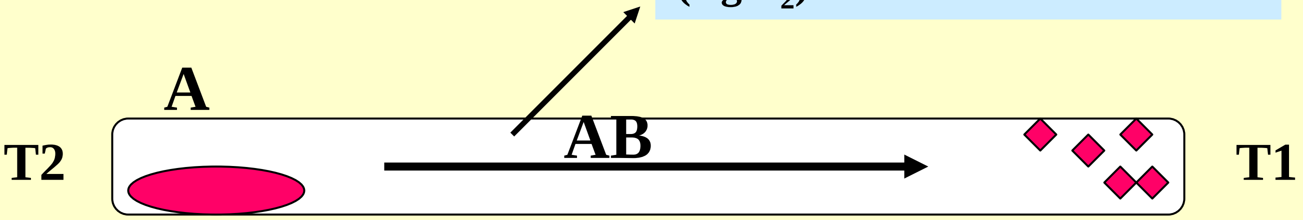
Arc

$\text{Graphite} \longrightarrow C_{60}$

Vapor Phase Transport Syntheses

Sealed glass tube reactors
Solid reactant(s) A + gaseous transporting agent B
Temperature gradient furnace $\Delta T \sim 50\ ^{o}C$

Equilibrium established $A(s) + B(g) \leftrightarrow AB(g)$
Equilibrium constant K
A + B react at T_2
Gaseous transport by AB(g)
AB(g) decomposes back to A(s) at T_1, crystals of pure A
Temperature dependent K
Equilibrium concentration of AB(g) changes with T
Different at T_2 and T_1
Concentration gradient of AB(g) = driving force for gaseous diffusion



traces of a transporting agent B (e.g. I_2)

Vapor Phase Transport Syntheses

Whether T1 < T2 or T1 > T2 depends on the thermochemical balance of the reaction !
Transport can proceed from higher to lower or from lower to higher temperature

Example: $Pt(s) + O_2(g) \leftrightarrow PtO_2(g)$

Endothermic reaction, PtO_2 forms at hot end, diffuses to cool end, deposits well formed Pt crystals, observed in furnaces containing Pt heating elements

Chemical vapor transport, $T_2 > T_1$, provides concentration gradient and thermodynamic driving force for gaseous diffusion of vapor phase transport agent AB(g)

Uses of VPT

- **synthesis of new solid state materials**
- **growth of single crystals**
- **purification of solids**

Vapor Phase Transport Syntheses

Thermodynamics of VPT

Reversible equilibrium needed: $\Delta G^o = -RT\ln K_{equ} = \Delta H^o - T\Delta S^o$

✋ Exothermic $\Delta H^o < 0$
Smaller T implies larger K_{equ}
AB forms at cooler end, decomposes at hotter end of reactor

$W + 3Cl_2 \leftrightarrow WCl_6$ 400/1400 (exo)
$Ni + 4CO \leftrightarrow Ni(CO)_4$ 50/190 (exo)

✋ Endothermic $\Delta H^o > 0$
Larger T implies larger K_{equ}
AB forms at hotter end, decomposes at cooler end of reactor

$2Al + AlCl_3 \leftrightarrow 3\,AlCl$ 1000/600 (endo)
$4Al + Al_2S_3 \leftrightarrow 3Al_2S$ 1000/900 (endo)

Vapor Phase Transport Syntheses

Estimation of the thermochemical balance (ΔH) of a transport reaction:

e.g.:

$ZnS_{(s)} + I_{2(gas)} \leftrightarrow ZnI_{2(gas)} + S_{(g)} \quad \Delta H = ??$

$Zn_{(s)} + I_{2(g)} \leftrightarrow ZnI_{2(gas)} \quad \Delta H = -88 \text{ kJ mol}^{-1}$

$ZnS_{(s)} \leftrightarrow Zn_{(s)} + S_{(g)} \quad \Delta H = +201 \text{ kJ mol}^{-1}$

$\sum \quad ZnS_{(s)} + I_{2(gas)} \leftrightarrow ZnI_{2(gas)} + S_{(g)} \quad \Delta H = +113 \text{ kJ mol}^{-1}$

endothrmic reaction, transport from hot to cold!

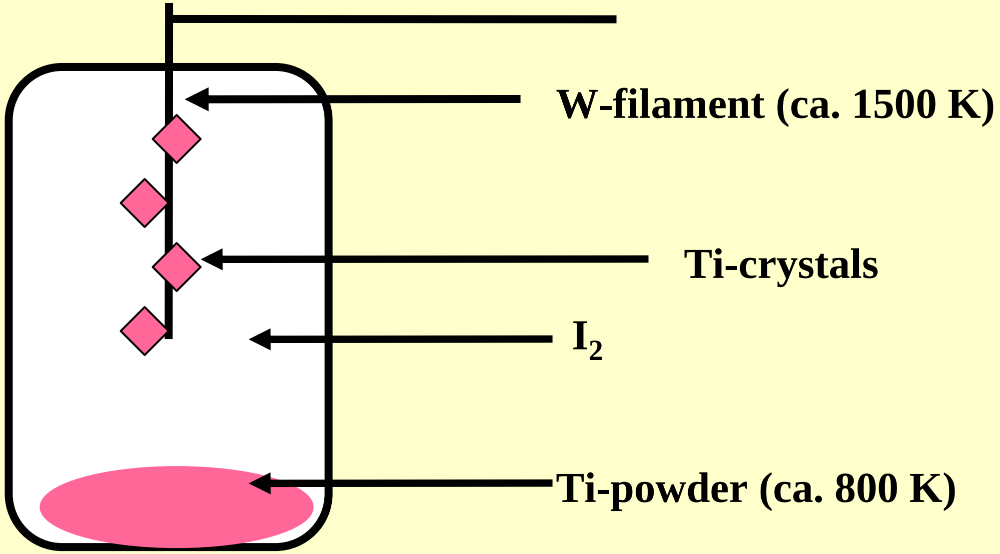
Applications of VPT Methods

💣 Purification of Metals: Van Arkel Method

$Cr(s) + I_2(g)\ (T_2) \leftrightarrow (T_1)\ CrI_2(g)$

Exothermic, $CrI_2(g)$ forms at T_1, pure Cr(s) deposited at T_2
Useful for Ti, Hf, V, Nb, Cu, Ta, Fe, Th
Removes metals from carbide, nitride, oxide impurities

$Ti + 2I_2 \leftrightarrow TiI_4 \quad \Delta H = -376\ kJ\ mol^{-1}$
exothermic: transport from <u>cold to hot</u>



Applications of VPT Methods

- **Double Transport Involving Opposing Exothermic-Endothermic Reactions**

Endothermic:

$WO_2(s) + I_2(g)\ (T_1\ 800^oC) \leftrightarrow (T_2\ 1000^oC)\ WO_2I_2(g)$

Exothermic:

$W(s) + 2H_2O(g) + 3I_2(g)\ (T_2\ 1000^oC) \leftrightarrow (T_1\ 800^oC)\ WO_2I_2(g) + 4HI(g)$

The antithetical nature of these two reactions allows W/WO_2 mixtures to be separated at different ends of the gradient reactor using H_2O/I_2 as the transporting VP reagents

Applications of VPT Methods

💣 **Vapor Phase Transport for Synthesis**

$A(s) + B(g)\ (T_1) \leftrightarrow (T_2)\ AB(g)$

$AB(g) + C(s)\ (T_2) \leftrightarrow (T_1)\ AC(s) + B(g)$

Concept: couple VPT with subsequent reaction to give overall reaction:

$A(s) + C(s)\ (T_2) \leftrightarrow (T_1)\ AC(s)$

Examples:

Direct reaction sluggish even at high T

$SnO_2(s) + 2CaO(s) \rightarrow Ca_2SnO_4(s)$

Useful phosphor, greatly speeded up with CO as VPT agent:

$SnO_2(s) + CO(g) \leftrightarrow SnO(g) + CO_2(g)$

$SnO(g) + CO_2(g) + 2CaO(s) \leftrightarrow Ca_2SnO_4(s) + CO(g)$

Applications of VPT Methods

Direct Reaction:

$Cr_2O_3(s) + NiO(s) \rightarrow NiCr_2O_4(s)$ Greatly enhanced rate with O_2

$Cr_2O_3(s) + 3/2O_2 \leftrightarrow 2CrO_3(g)$
$2CrO_3(g) + NiO(s) \leftrightarrow NiCr_2O_4(s) + 3/2O_2(g)$

Overcoming Passivation Through VPT

$Al(s) + 3S(s) \rightarrow Al_2S_3(s)$ passivating skin stops reaction

In presence of cleansing VPT agent I_2:

Endothermic:
$Al_2S_3(s) + 3I_2(g)\ (T_1\ 700^oC) \leftrightarrow (T_2\ 800^oC)\ 2AlI_3(g) + 3/2S_2(g)$

Applications of VPT Methods

💣 Vapor Phase Transport for Synthesis

$Zn(s) + S(s) \rightarrow ZnS(s)$

passivation prevents reaction to completion

Endothermic:

$ZnS(s) + I_2(g)\ (T_1\ 800^oC) \leftrightarrow (T_2\ 900^oC)\ ZnI_2(g) + 1/2S_2(g)$

VPT Synthesis of $ZnWO_4$:

A Real Phosphor Host Crystal for Ag^+, Cu^+, Mn^{2+}

$WO_3(s) + 2Cl_2(g)\ (T_1\ 980^oC) \leftrightarrow (T_2\ 1060^oC)\ WO_2Cl_2(g) + Cl_2O(g)$

$WO_2Cl_2(g) + Cl_2O(g) + ZnO(s)\ (T_2\ 1060^oC) \leftrightarrow ZnWO_4(s) + Cl_2(g)$

Growing Epitaxial GaAs Films by VPT Using Convenient Starting Materials

$GaAs(s) + HCl(g) \leftrightarrow GaCl(g) + 1/2H_2(g) + 1/4As_4(g)$

$AsCl_3(g) + Ga(s) + 3/2H_2 \leftrightarrow GaAs(s) + 3HCl(g)$

Serves to establish initial equilibrium