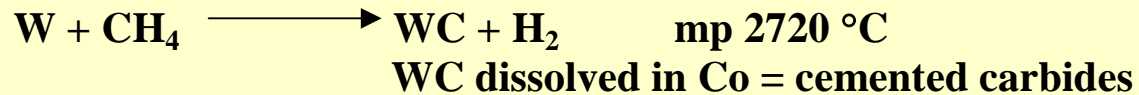
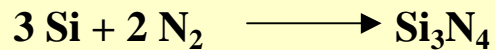
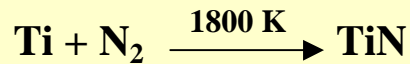


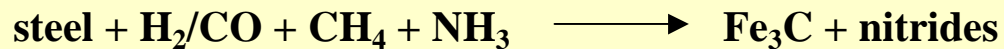
Gas Phase Reactions

Heating: furnace, laser, plasma, flame, arc

Gas-Metal Rxn



cementite



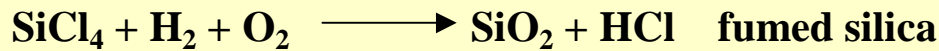
Gas-Phase Reactions

Gas-Gas Rxn

homogeneous nucleation from supersaturated vapor (nano)

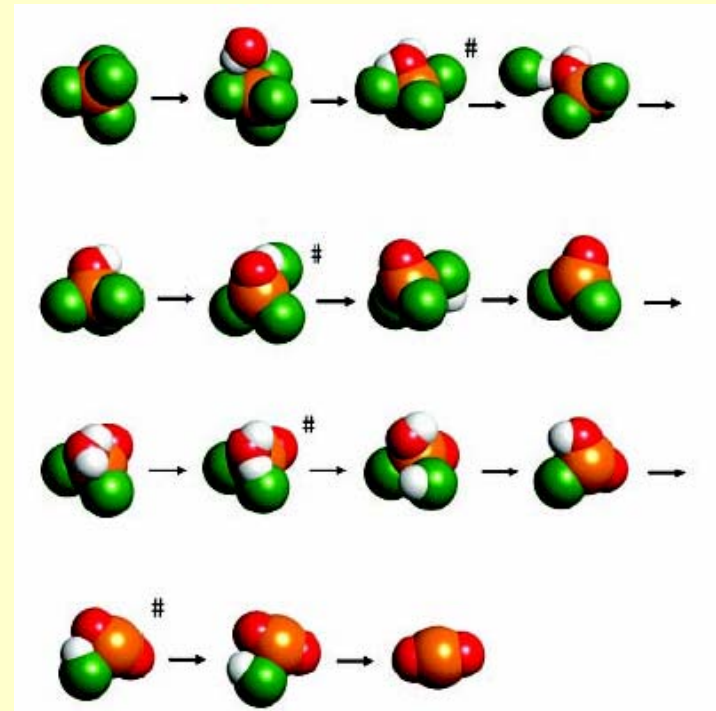
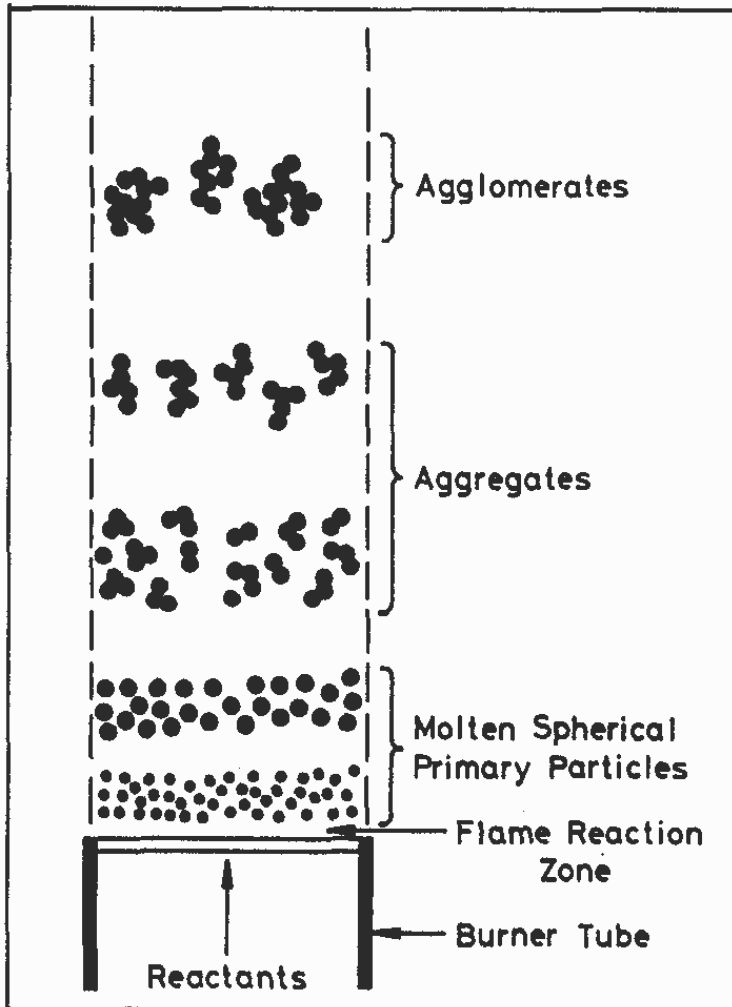
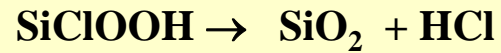
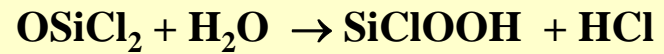
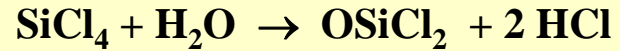
Flame hydrolysis

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

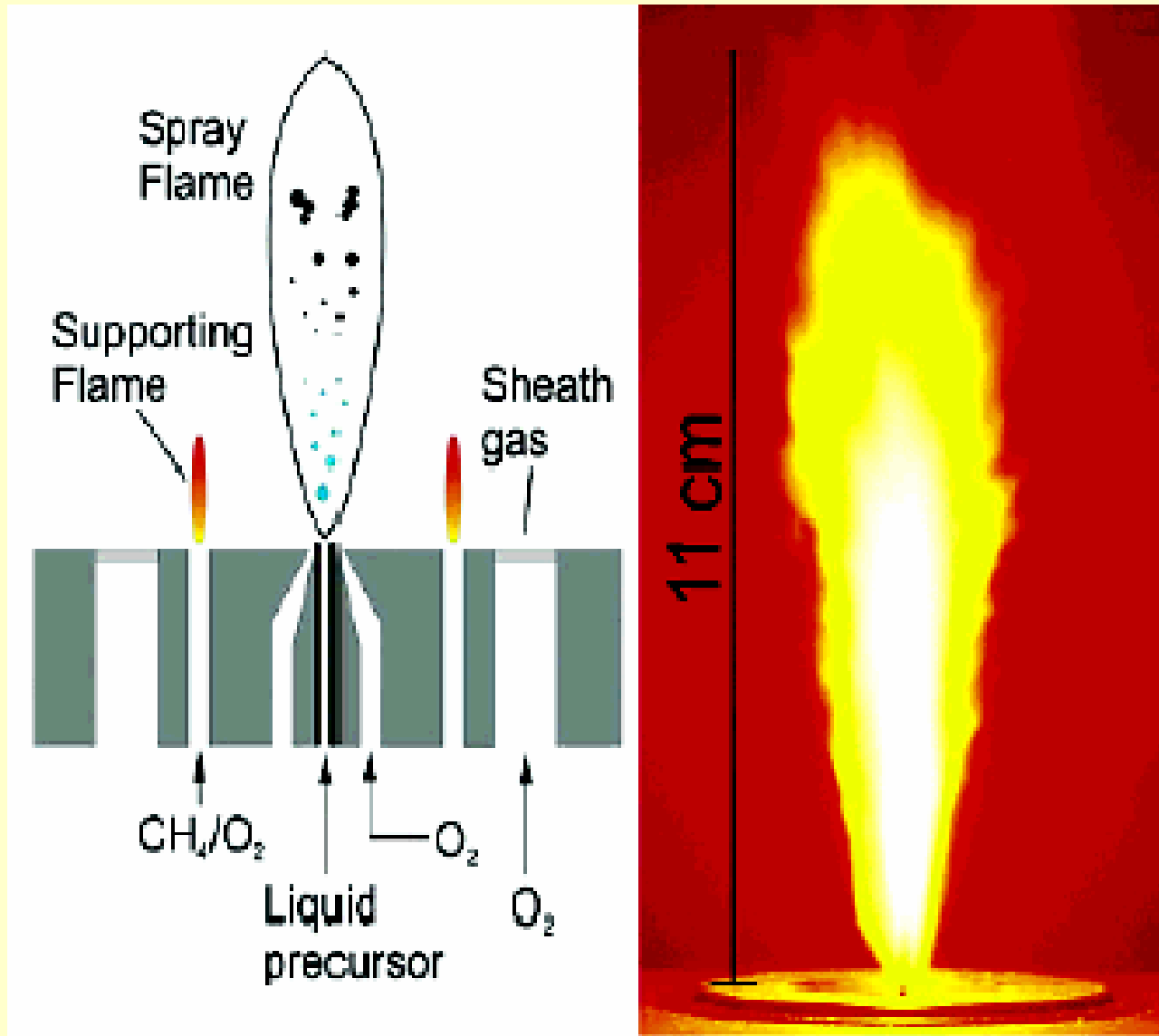


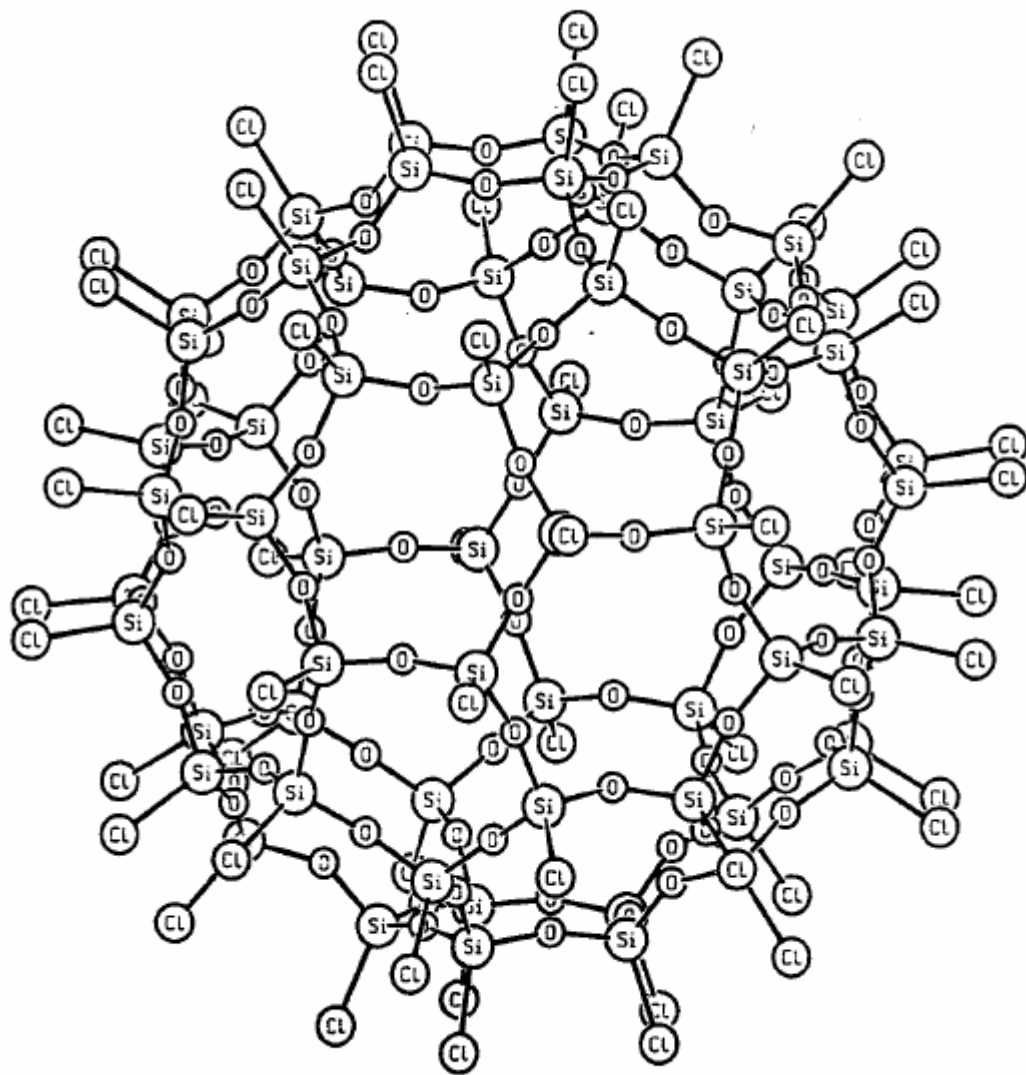
reagent	bp/°C	product
SiCl_4	57	SiO_2
AlCl_3	180 (subl.)	Al_2O_3
TiCl_4	137	TiO_2
CrO_2Cl_2	117	Cr_2O_3
$\text{Fe}(\text{CO})_5$	103	Fe_2O_3
GeCl_4	84	GeO_2
$\text{Ni}(\text{CO})_4$	42	NiO
SnCl_4	114	SnO_2
ZrCl_4	331 (subl.)	ZrO_2
VOCl_3	127	V_2O_5

Gas Phase Reactions



Gas Phase Reactions





$\text{Si}_{60}\text{O}_{90}\text{Cl}_{60} (I_h)$

Gas Phase Reactions

Calcium phosphate nanoparticles Ca/P molar ratios 1.43 to 1.67

**synthesized by simultaneous combustion of
 $\text{Ca}(\text{OAc})_2 + \text{OP}(\text{O}^n\text{Bu})_3$ 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

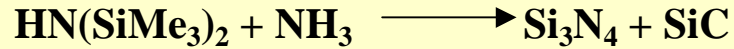
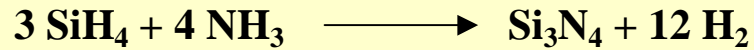
**At a molar ratio of $\text{Ca}/\text{P} < 1.5$ promoted the formation of dicalcium pyrophosphate
($\text{Ca}_2\text{P}_2\text{O}_7$).**

**Phase pure tricalcium phosphate
obtained with a precursor Ca/P ratio of 1.52 after subsequent calcination at $900\text{ }^\circ\text{C}$**

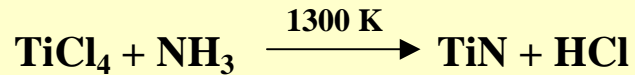
**micropores and the facile substitution of both anions and cations
possible application as a biomaterial.**

Gas Phase Reactions

High-power CO₂ lasers



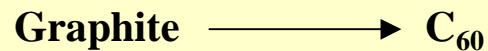
DC-Ar Plasma



Tarnishing of Metal Surfaces

oxide, hydroxide layers

Arc



Vapor Phase Transport Syntheses

Sealed glass tube reactors

Solid reactant(s) A + gaseous transporting agent B

Temperature gradient furnace $\Delta T \sim 50 \text{ }^\circ\text{C}$

Equilibrium established $\text{A(s)} + \text{B(g)} \leftrightarrow \text{AB(g)}$

Equilibrium constant K

A + B react at T_2

Gaseous transport by AB(g)

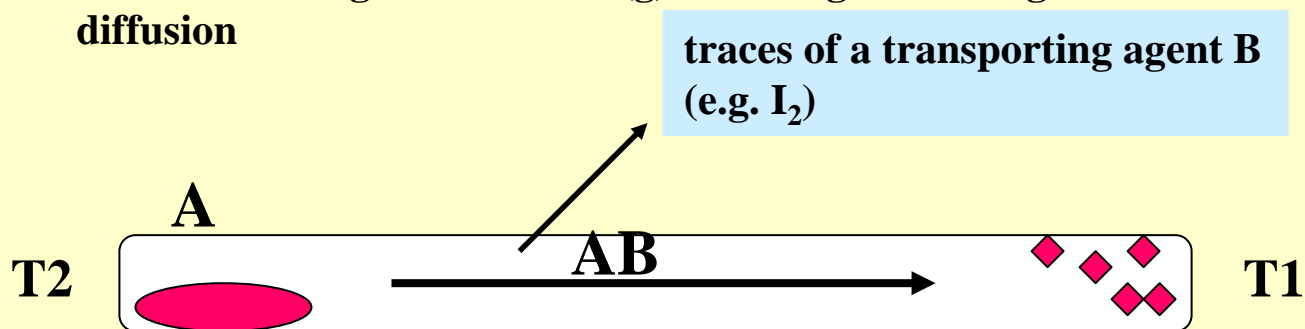
AB(g) decomposes back to A(s) at T_1 , crystals of pure A

Temperature dependent K

Equilibrium concentration of AB(g) changes with T

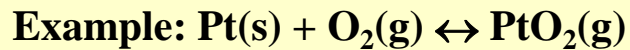
Different at T_2 and T_1

Concentration gradient of AB(g) = driving force for gaseous diffusion



Vapor Phase Transport Syntheses

Whether $T_1 < T_2$ or $T_1 > T_2$ depends on the thermochemical balance of the reaction !
Transport can proceed from higher to lower or from lower to higher temperature



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

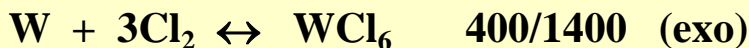
Thermodynamics of VPT

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

✎ Exothermic $\Delta H^{\circ} < 0$

Smaller T implies larger K_{equ}

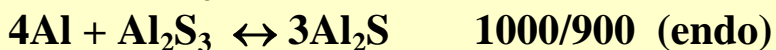
AB forms at cooler end, decomposes at hotter end of reactor



✎ Endothermic $\Delta H^{\circ} > 0$

Larger T implies larger K_{equ}

AB forms at hotter end, decomposes at cooler end of reactor



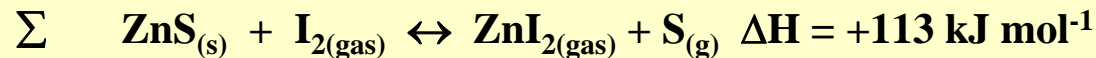
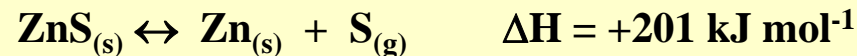
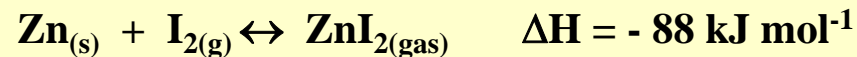
van't Hoff equation

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Vapor Phase Transport Syntheses

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

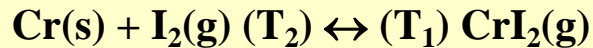
e.g.:



endothermic reaction, transport from hot to cold!

Applications of VPT Methods

●* Purification of Metals: Van Arkel Method



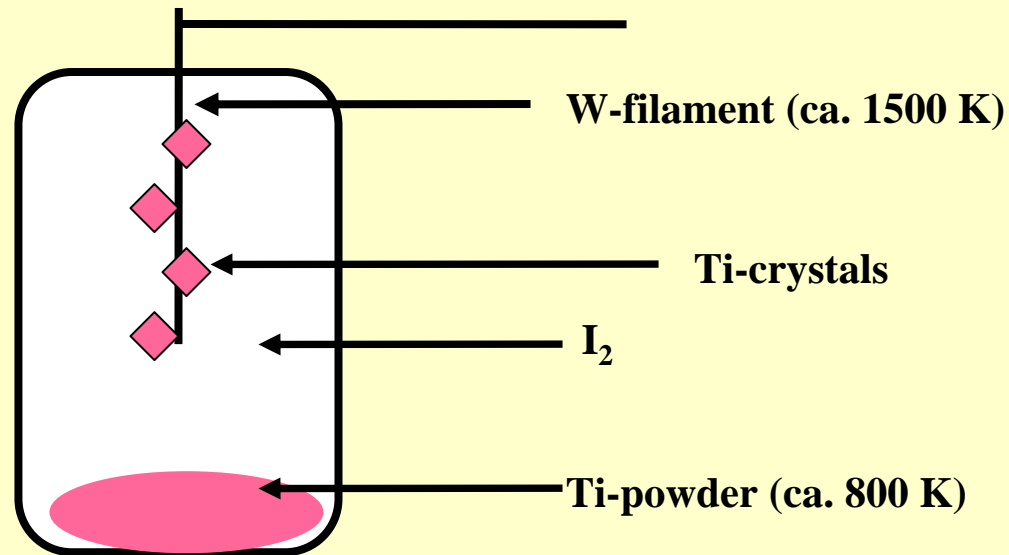
Exothermic, $\text{CrI}_2(\text{g})$ forms at T_1 , pure Cr(s) deposited at T_2

Useful for Ti, Hf, V, Nb, Cu, Ta, Fe, Th

Removes metals from carbide, nitride, oxide impurities



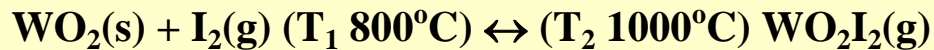
exothermic: transport from cold to hot



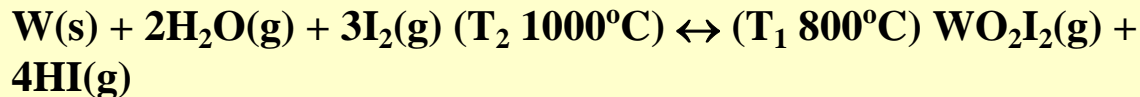
Applications of VPT Methods

●* Double Transport Involving Opposing Exothermic-Endothermic Reactions

Endothermic:



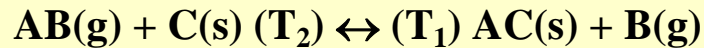
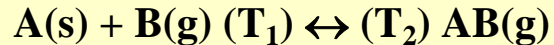
Exothermic:



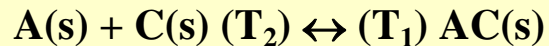
The antithetical nature of these two reactions allows W/WO₂ mixtures to be separated at different ends of the gradient reactor using H₂O/I₂ as the transporting VP reagents

Applications of VPT Methods

☛ Vapor Phase Transport for Synthesis

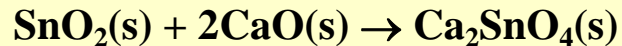


Concept: couple VPT with subsequent reaction to give overall reaction:

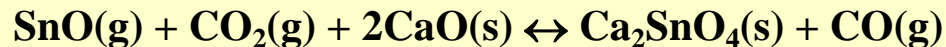
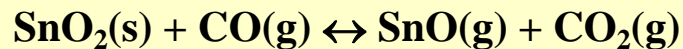


Examples:

Direct reaction sluggish even at high T

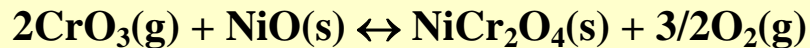
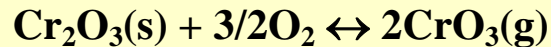
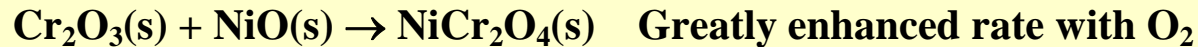


Useful phosphor, greatly speeded up with CO as VPT agent:



Applications of VPT Methods

Direct Reaction:

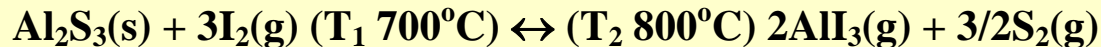


Overcoming Passivation Through VPT



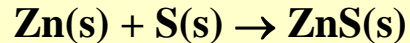
In presence of cleansing VPT agent I₂:

Endothermic:



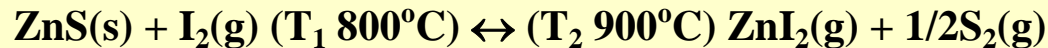
Applications of VPT Methods

●* Vapor Phase Transport for Synthesis



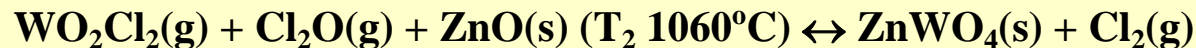
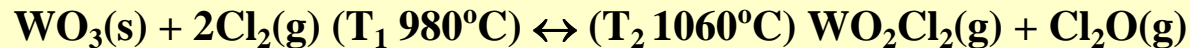
passivation prevents reaction to completion

Endothermic:

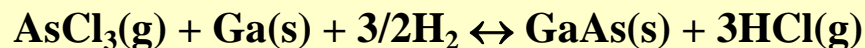


VPT Synthesis of ZnWO₄:

A Real Phosphor Host Crystal for Ag⁺, Cu⁺, Mn²⁺



Growing Epitaxial GaAs Films by VPT Using Convenient Starting Materials



Serves to establish initial equilibrium