CHAPTER 4:

PREPARATION, CHARACTERIZATION AND SENSING PROPERTIES OF WO$_3$ MODIFIED FOR LPG
ABSTRACT:

This chapter discusses the results of our experiments to study the effect of concentration of gas, response time and operating temperature on the sensitivity of the sensor element. The gas sensing measurements of pure WO₃ and also with different additives have been used to find out their effect on the gas-sensing phenomenon. Addition of metal oxides and noble metals to WO₃ not only make the element highly sensitive to LPG but significantly enhance the sensitivity of the sensor element to LPG and also reduce the response time. The sensor element has been tested for cross sensitivity to other reducing gases and confirmed unambiguously to be specifically sensitive to LPG gas.
4.1 CHARACTERIZATION:

The tungsten oxide powder obtained has been characterized for its structural properties by studying the temperature of decomposition of ammonium tungstate, with the help of Differential Thermal Analysis (DTA), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) are used for structural and morphological studies.

4.1.1 DIFFERENTIAL THERMAL ANALYSIS:

Simultaneous TG - DTG - DTA was performed in air on a Mettler Toledo Star TGA/SDTA 851° system apparatus (Pt crucibles, Pt - Pt / Rh thermocouples) with the heating rate of $10 \degree C \text{ min}^{-1}$ from $25 \degree C$ to $900 \degree C$ on the (a) ammonium tungstate, (b) ammonium tungstate mixed with citric acid, confirm the results given below.

Fig. 4.1 shows the thermogravimetry patterns of all the samples prepared from ammonium tungstate, citric acid. The mass decrease observed for this sample below $200 \degree C$ is due to the loss of water of hydration, that between $50 \degree C$ and $450 \degree C$ to the elimination of both constitutional water (from the six $\text{OH}^-$ groups bounding to W) and $\text{NH}_3$. The latter observation is more visible in the DTA
Fig. 4.1 DTA Spectrum of the Sample of WO₃
patterns reported in Fig 4.1 (a-b). The endothermic peak observed around 270°C is attributed to the loss of both constitutional water and ammonia.

4.1.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR):

The analysis of the vibrational spectra in the skeletal region has been performed with FT-IR. The IR spectrum of WO₃, WO₃: In₂O₃ prepared from (a) Ammonium Tungstate, (b) Phospho - Tungstic acid (c) Ammonium Tungstate and Indium Oxide (5 wt. %) (d) Commercial Sample (Riedel - De Haen Ag.). All are calcined at 650 for 5 hrs are reported in Fig. 4.2(a-d).

The spectra 4.2(a-d) show the presence of monoclinic WO₃. They show the IR bands at 980 cm⁻¹ which falls in the region typical of the stretching of W=O bonds having a double bond character, such as those characteristic of WO₃ hydrates. The very broad IR absorptions at 900-700 cm⁻¹ fall in the regions corresponding to the vibrations of the type W-O-M (M=W or in Fig. 4.2(c) M = In) stretching and deformation modes, respectively, as in the case of different polymorphic forms of crystalline WO₃ and tungstic poly oxo anions. In the high frequency region all the spectra show a broad adsorption centered near 3500 cm⁻¹ attributed to H-bonded OH⁻ groups.
Fig. - 4.3. FTIR Spectra of (a) WO₃ (Prepd. from ammo, tung.)
    b) WO₃ (Prepd. from phospho tungstic acid)
    c) WO₃ : In₂O₃ (5 Wt. %) d) WO₃ Commercial
In comparison to the spectrum of commercial WO₃ (Fig 4.2 d) which shows a sharp absorption in the region between 700-900 cm⁻¹, the spectra of WO₃ prepared from ammonium tungstate and phospho-tungstic acid (Fig. 4.2 a-b) are much broader. The sharper absorption spectra could be attributed to a better resolution. This may be ascribed to the higher crystallinity in the commercial samples as compared to the synthesized ones.

4.1.3 X-RAY DIFFRACTION (XRD):

X-ray diffractometer (model: SIEMEN D.5000) with copper target, Kα radiation (λ=1.5406 Å) was used for phase identification, where the diffracted intensities were recorded as a function of 2θ. In order to obtain high resolution and low noise, the measurements have been performed in Bragg Brentano mode using 0.6 mm/ Ni/ 0.1 mm slits. Fig. 4.3(a-c) is the X-ray diffraction pattern of the a) WO₃ powder prepared from ammonium tungstate calcined at 650 °C for 5 hrs. b) WO₃ powder prepared from ammonium tungstate with 5 wt. % loading of In₂O₃ calcined at 650 °C, c) WO₃ powder prepared from phospho tungstic acid calcined at 650 °C. Fig. 4.3(a) is the spectrum of WO₃ prepared from ammonium tungstate which shows the complete formation and all the lines agree with those of reported values.
Fig. - 4.3 XRD Pattern of the a) $\text{WO}_3$ Prepared from Ammonium tungstate. b) $\text{WO}_3 : \text{In}_2\text{O}_5$ (5 Wt. %) c) $\text{WO}_3$ Commercial
Fig. 4.3(b) is the spectrum of WO₃ : In₂O₃ (5 wt. %) which shows an extra peak which typically found in the region of 2θ = 20.8 Å which corresponds with that of In₂O₃ and is in good agreement with the reported values (JCPDS data No. 71-2195).

Similarly Fig 4.3(c) is the X-ray diffraction pattern of the WO₃ powder prepared from phospho tungstic acid calcined at 650 °C for 5 hrs. It is seen that the peaks are of low intensity and broad indicating not well crystallinity. Even the peak at 2θ-22⁰ and 2θ-34⁰ resolved in the WO₃ prepared from phosphotungstic acid. On the other hand, sharp and intensive peaks are observed for the samples where the unit cell dimensions are found to be a = 7.297 Å, b = 7.539 Å, C = 7.688 Å which are in good agreement with the reported values (JCPD data NO. 43 - 1035).

4.1.4 SCANNING ELECTRON MICROSCOPY (SEM):

Scanning Electron Microscopy (SEM) was used to establish the morphology and to evaluate the particle size distributions. Calcination leads to the formation of agglomerates due to the establishment of electrical contact between themselves.

SEM pictures of pure WO₃ obtained commercially from Aldrich Chemical Co., and Riedel - De Haen AG., and also the material prepared in our laboratory
are taken is shown in Fig. 4.4. WO\textsubscript{3} is prepared from ammonium tungstate (Fluka), Phospo tungstic acid (BDH). The method employed for this involves calcination from 550-950 °C. The observations from all these micrographs are summarized as follows.

(a) The WO\textsubscript{3} sample as received from Aldrich chemical company is uniform (average size is about 0.2 μm). The ultimate particle size is 0.1 μm and the aggregation is loose.

(b) WO\textsubscript{3} received from the Riedel - De Haen AG. Company is in the form of lumps with a wide range of sizes. The average size ranges from 0.2 μm to nearly 4 μm, the ultimate size is about 0.2 μm.

(c) In the case of WO\textsubscript{3} prepared from ammonium meta tungstate (Fig. 4.5), calcined at

(i) 550 °C the aggregates are small spheres ranging between 0.1 to 0.4 μm dia. The ultimate particle size is less than 0.1 μm and the particles are loosely aggregated.

(ii) Calcination at 650 °C shows a slight agglomeration and the ultimate particle size increases to about 0.3 to 0.5 μm.

(iii) At 750 °C the crystallites take the shape of rods. This is very different from the WO\textsubscript{3} prepared starting with phospo tungstic acid.
Fig. 4.4. SEM Micrographs of (a) $\text{WO}_3$ (Aldrich),
(b) $\text{WO}_3$ (Riedel-De haen A.G.)
Fig. 4.5. SEM Micrographs of $\text{WO}_3$ Prepd. from Ammo. tung. Calcined at (a) 550 (b) 650 (c) 750 (d) 850 & (e) 950°C
(iv) Calcination at 850 °C and above showed a drastic change and these rod shaped crystallites transformed into spherical ones. The average size is form 2 to 3 μm. The ultimate particle size is 2 μm.

(v) At 950 °C, the characteristic multifaced spherical crystallites appeared. These crystallites are similar to those reported earlier [40]. The average crystallite size is anywhere between 2-5 μm.

From all the above pictures it is observed that increase in calcination temperature, the WO₃ composition changes from amorphous to crystalline at different temperatures.

SEM pictures of WO₃ prepared from phospho tungstic acid (H₃PO₄·12 WO₃·X H₂O) and similarly in the case to WO₃ calcined at temperatures ranging from 450 to 950 °C are shown in Fig.4.6. The observation from the micrographs can be summarized as follows,

a) Calcination at 550 °C results in small lumps. No individual crystallites are visible. All the lumps seem to be connected to each other.

b) Calcination at 850 °C results in releasing these lumps. Smaller aggregates are formed with the appearance of individual crystallites. The ultimate particle size is comparatively very small (0.01 μm).
Fig. 4.6. SEM Micrographs of $\text{WO}_3$ Prepd. from Phospo Tungstic Acid
Calcined at (a) 550 (b) 650 (c) 750 (d) 850 & (e) 950°C
c) For WO₃ calcined at 750 °C, the individual crystallites are separated further and we can determine the ultimate particle size, which is about 0.2 μm with an average size around 0.5 μm.

d) Further calcination at 850 °C and further 950 °C tend to bring the crystallites closer and from agglomerates. The average size of the clusters in the 850 °C calcined sample is about 0.5 μm to 1 μm and in the 950 °C calcined sample it is μm and more.

The next section deals with the SEM micrographs of WO₃ : InₓO₃ (5 wt. %) prepared from ammonium meta tungstate. The mixture was also calcined at different temperatures from 550 °C to 950 °C.

If we compare WO₃ : InₓO₃ prepared from ammonium tungstate with that of pure WO₃ prepared from the same starting material, there are a few differences. Fig. 4.7. shows the SEM micrographs of WO₃ with loading of InₓO₃.

(a) For WO₃ : InₓO₃ (5 wt. %) calcined at 550 °C and 650 °C, the aggregates are loose. At 550 °C calcination the particles are well dispersed and the ultimate particle size is 0.1 μm. In case of 650 °C calcination composition, the ultimate particle size does not seem to increase but the particles are coming closer. Individual crystallites are clearly visible and the ultimate particle size is 0.2 μm.

This observation is similar to that of pure WO₃ prepared from ammonium meta tungstate.
Fig. 4.7. SEM Micrographs of $\text{WO}_3 : \text{In}_2\text{O}_3$ (5 wt.%)
Calcined at (a) 550 (b) 650 (c) 750 (d) 850 & (e) 950°C
(b) Calcination at 750 °C makes the particle size uniform, and spherical. Whereas in case of pure WO₃ (Ammonium meta tungstate) particles are needle shaped. This may be the effect of addition of In₂O₃. The average crystallite size is 0.2 µm.

(c) At 850 °C the SEM micrographs are clear with well-defined crystallites. The ultimate particle size is above 0.5 µm and each of the agglomerates is of an average size of 2-3 µm.

(d) At 950 °C calcination shows well-formed crystallites of WO₃ which are characterized by the multifaced spherical crystallites.

Another observation is that the crystallite sizes in WO₃ : In₂O₃ (5 wt. %) is smaller than that of pure WO₃ even though the physical appearance of each is qualitatively similar. This means the presence of In₂O₃ in WO₃ may be preventing the grain growth of WO₃ and thereby acting as a grain growth inhibitor.

4.2 GAS SENSING PROPERTIES OF PURE WO₃:

Experiments have been carried out on WO₃ without any additives and without calcination of material for sensitivity to various reducing gases such as LPG, H₂, CO, CO₂ and NO₂.

Fig - 4.8 shows the sensitivity versus operating temperature for the sensor element of commercially available WO₃ without calcination. It is seen that the
Fig. 4.8. Sensitivity Vs Operating Temperature for Commercial WO₃ Sample Without Calcination for a) LPG, b) H₂, c) CO, d) CO₂, e) NO₂

Fig. 4.9. Sensitivity Vs Operating Temperature for WO₃ Prepared from Phosphoric Acid Without Calcination for a) LPG, b) H₂, c) CO, d) CO₂, e) NO₂
sensor does not show any significant selectivity to any of the test gases up to 250 °C. It is to be made clear at the outset itself that all the test gases are taken with 1% dilution in air. Above 250 °C all the gases have sensitivity between 0 to 0.31. The maximum sensitivity of 0.35 and 0.31 is observed for LPG and H₂ at about 325 °C respectively. The sensitivity to other gases such as CO, CO₂, and NO₂ is 0.18, 0.1 and 0.16 at 325 °C and above respectively.

Fig - 4.9 shows the gas sensing characteristics of WO₃ prepared from phosphoric tungstic acid (H₃PO₄·12 WO₃). This material was used without calcination. Here it is observed that sensitivity to LPG and H₂ is improved compared to other gases. LPG has sensitivity of 0.39 at 300 °C, while H₂ shows maximum of 0.36 at 325 °C. The other gases i.e. CO, CO₂, and NO₂ shows maximum sensing somewhere between 0.13 to 0.3.

Fig - 4.10 shows the sensitivity versus operating temperature for the sensor element of WO₃ prepared from ammonium tungstate, without calcination. Here there is a remarkable improvement in the sensitivity for LPG and H₂. The sensor shows 0.33 for LPG at 250 °C and goes on increasing to 0.49 at 300 °C. Similarly sensitivity for H₂ is 0.38 at 300 °C while CO and NO₂ shows maximum sensing of 0.16 and 0.28 at 250 °C and above. CO₂ shows maximum sensitivity of 0.1 at 300 °C.

From these studies it is concluded that WO₃ prepared from ammonium tungstate has an advantage in the gas sensing character over the other two.
Fig. 4.10. Sensitivity Vs Operating Temperature for WO$_3$ Prepared from Ammonium Tungstate Without Calcination for
   a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$
materials viz commercially available $\text{WO}_3$ and $\text{WO}_3$ prepared from phosphotungstic acid. Kipping this in view we have narrowed down to using only $\text{WO}$ prepared from ammonium tungstate in all our further work. This included the studies on effect of calcination temperature, sintering temperature, different oxide addition, noble metal additives etc in an effort to improve the gas sensitivity. All these studies are directed towards a goal of designing and developing materials for selective gas sensor detection.

The next step was to try and improve the sensitivity. For this purpose, the material has been studied further to see the effect of calcination temperature on the sensitivity to different test gases like LPG, $\text{H}_2$, CO, $\text{CO}_2$ and $\text{NO}_2$.

Fig. 4.11 is a representation of the variation of sensitivity for $\text{WO}_3$ prepared from ammo-tungstate for a series of samples calcined at different temperature. This is to bring out the dependence of the calcination temperature on sensitivity. The operating temperature is chosen at 300 °C. It is clear from the 4.11 that the sensitivity is significantly increased with calcination for all the test gases. The elements calcined at 650 °C shows high sensitivity for all gases. The sensitivity of LPG is 0.67, while $\text{H}_2$, CO, $\text{CO}_2$ and $\text{NO}_2$ shows maximum sensing of 0.48, 0.38, 0.1 and 0.29 at 300 °C respectively. The elements subjected to high calcination temperature at 750 °C and above do not show an appreciable sensitivity at 300 °C. This is an expected observation because lower calcination temperature implies better dispersion and also smaller crystallite size and
Fig. 4.11. Sensitivity Vs Calcination Temperature for WO$_3$ Prepared from Ammonium Tungstate at 300 °C Operating Temperature for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$

<table>
<thead>
<tr>
<th>Sintering Temperature ($°C$)</th>
<th>Operating Temperature ($°C$)</th>
<th>Maximum Sensitivity</th>
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<tbody>
<tr>
<td></td>
<td>LPG</td>
<td>H$_2$</td>
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<tr>
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<td>300</td>
<td>0.55</td>
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<td>650</td>
<td>300</td>
<td>0.63</td>
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<tr>
<td>750</td>
<td>300</td>
<td>0.71</td>
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<tr>
<td>850</td>
<td>300</td>
<td>0.61</td>
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</tbody>
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Table. 4. Effect of Sintering Temperature on Sensitivity for WO$_3$ Prepared from Ammonium Tungstate.
indirectly higher surface area. All these parameters most suitable for an efficient gas sensing reaction.

4.3 EFFECT OF SINTERING TEMPERATURE AND BINDER ON SENSITIVITY:

Here we studied the effect of sintering temperature and binders on the sensitivity of WO₃ to LPG, H₂, CO, CO₂, and NO₂ gases.

Table 4 shows the effect of sintering temperature on the sensitivity of various gases. WO₃ element is mixed with 2 wt.% of Tetra Ethyl Ortho Silicate (TEOS) as a binder and pasted on alumina tube. This element is dried in air and then sintered in a furnace at various temperatures from 550-850 °C for 2 hrs. The gas-sensing characteristics were studied on this compound with LPG, H₂, CO, CO₂ and NO₂. It was found that at 550 °C the sensitivity is very less because at this temperature the binder (TEOS) is not completely decomposed. The maximum sensitivity for optimum binding strength is observed at 750 °C. At sintering temperature of 750 °C. LPG shows the sensitivity of 0.71, while H₂, CO, CO₂ and NO₂ shows maximum sensitivity of 0.51, 0.41, 0.1 and 0.31 at 300 °C operating temperature respectively.

At 750 °C TEOS decomposes and the strength of the final element increases markedly. So we optimized the sintering temperature at 750 °C for 2 hrs for all WO₃ compounds.
Fig - 4.12 shows the sensitivity versus operating temperature for the sensor element of WO₃ prepared from ammonium tungstate. The WO₃ powder prepared from ammonium tungstate is calcined at 650 °C is mixed with 2 wt.% TEOS binder, the resulting paste is applied on an alumina tube. The element is sintered at 750 °C for two hrs and gas sensing properties are measured. Here there is a significant improvement in the sensitivity for LPG, H₂, and CO. The sensor starts detecting LPG at an operating temp. as low as 150 °C and at 250 °C it is 0.6 reaches to maximum of 0.74 at 350 °C. H₂ and CO shows maximum sensitivity of 0.6 and 0.49 at an operating temperature of 350 °C and 325 °C respectively. While CO₂ and NO₂ shows maximum of 0.09 and 0.41 at 270 °C and onwards.

The next step was to try and improve the sensitivity and impart selectivity by addition of different metal oxides. In this direction we have tried different oxides such as lanthanum oxide (La₂O₃), stannic oxide (SnO₂) and Indium oxide (In₂O₃). All these oxides were taken in different weight percentages like 5, 10 and 15 wt% into the base WO₃, all of these compounds are calcined at 650 °C for 5 hrs.

Fig - 4.13 to 4.22 shows the variation of sensitivity as a function of operating temperature for each of these compositions to different test gases. The preparation of sensor element is same as described in the chapter 1. A general trend that is observed is that the inclusion of these metal oxides increase the
Fig. 4.12. Sensitivity Vs Operating Temperature for WO$_3$, Prepared from Ammonium Tungstate Calcined at 650 °C and Sintered at 750 °C for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$. 
sensitivity and reduce the operating temperature. The specific observations for each of these systems is described below.

4.4 SYSTEM : \( \text{WO}_3 : \text{La}_2\text{O}_3 \):

4.4.1 EXPERIMENTAL DETAILS :

Calculated quantity of \( \text{WO}_3 \) powder prepared from ammonium tungstate is mixed with different weight percentage of \( \text{La}_2\text{O}_3 \) in an agate mortar. The mixture is thoroughly ground by using distilled alcohol as solvent, followed by evaporation to dryness under IR lamp and calcined at \(650^\circ\text{C} \) for 5 hrs. The calcined powder is sieved to obtain fine particles and examined for gas sensing properties.

4.4.2 GAS SENSING CHARACTERISTICS OF \( \text{WO}_3 - \text{La}_2\text{O}_3 \)

( 5%, 10%, 15% BY WEIGHT) :

Fig. 4.13 is for \( \text{WO}_3, \text{La}_2\text{O}_3 \) 5 wt% powder calcined at \(650^\circ\text{C} \) for 5 hrs. This sensor element shows sensitivity versus operating temperature to sense LPG, \( \text{H}_2 \) and \( \text{CO} \) to a large extent as compared to the other gases like \( \text{CO}_2, \text{NO}_2 \). This graph shows that LPG detection starts at very low operating temperature of about \(150^\circ\text{C} \) and reaches to a maximum of 0.7 at about \(300^\circ\text{C} \). \( \text{H}_2 \) and \( \text{CO} \) detection improves from \(200^\circ\text{C} \) onward and reaches a maximum at about the same temperature of \(300^\circ\text{C} \).
Fig. 4.13. Sensitivity Vs Operating Temperature for $\ce{WO_3 : La_2O_3}$ (5 wt. %) for a) LPG, b) $\ce{H_2}$, c) CO, d) $\ce{CO_2}$, e) $\ce{NO_2}$

Fig. 4.14. Sensitivity Vs Operating Temperature for $\ce{WO_3 : La_2O_3}$ (10 wt. %) for a) LPG, b) $\ce{H_2}$, c) CO, d) $\ce{CO_2}$, e) $\ce{NO_2}$
Fig. 4.15. Sensitivity Vs Operating Temperature for WO₃ : La₂O₃ (15 wt. %) for a) LPG, b) H₂, c) CO, d) CO₂, e) NO₂
Fig - 4.14 shows the gas sensing characteristics of WO$_3$ - La$_2$O$_3$ (10 wt %) powder calcined at 650 °C for 5 hrs. In this composition sensitivity of NO$_2$ and H$_2$ is increased while LPG shows the similar trend as that of earlier. H$_2$ and NO$_2$ shows maximum sensing of 0.61 and 0.54 at 300 °C. While LPG show 0.7 at 300 °C. Other gases i.e. CO and CO$_2$ shows 0.5 and 0.2 at 300 °C respectively.

Fig - 4.15 shows the gas sensing characteristics of WO$_3$: La$_2$O$_3$ (15 wt %) powder. This sensor element detects LPG with a sensitivity of 0.6 to 0.8 from 225 °C onwards. Sensitivity to NO$_2$ is decreases. Hydrogen shows the next highest sensitivity of 0.63 at an operating temperature of 250 °C followed by CO with 0.53 at 275 °C.

4.5 SYSTEM : WO$_3$ : SnO$_2$ :-

4.5.1 EXPERIMENTAL DETAILS :

Calculated quantity of WO$_3$ powder prepared from ammonium tungstate is mixed with different weight percentages of SnO$_2$ in an agate mortar. The mixture is thoroughly ground by using distilled alcohol as solvent, followed by evaporation to dryness under IR lamp and calcined at 650 °C for 5 hrs. The calcined powder is sieved to obtain fine particles and examined for gas sensing properties.
4.5.2 GAS SENSING CHARACTERISTICS OF WO₃ - SnO₂

(5%, 10%, 15% BY WEIGHT.):

Fig - 4.16 shows the sensitivity versus operating temperature to gas sensing characteristics of WO₃ - SnO₂ (5 wt. %) powder. This sensor element also senses LPG and H₂. The sensitivity of this system to LPG and H₂ at 275 °C is 0.7 and 0.6 respectively. On the other hand, maximum CO detection with sensitivity of 0.5 is reached at a comparatively higher operating temperature of 300 °C. Maximum sensitivity of NO₂ is 0.5 at 275 °C. CO₂ does not show any significant sensitivity up to 300 °C.

Fig - 4.17 shows the gas sensing characteristics of WO₃ - SnO₂ (10 wt. %) sensor element. Here we observed that the sensitivity to LPG increases and it reaches to a maximum of 0.8 at 325 °C. H₂ shows the maximum sensing of 0.8 at 275 °C beyond 275 °C sensitivity goes on decreasing. While other gases like CO, CO₂ and NO₂ shows maximum of 0.47, 0.27 and 0.2 at 275 °C and onwards respectively.

Fig - 4.18 shows the operating temperature versus sensitivity for the sensor element of WO₃ : SnO₂ (15 wt. %). This sensor element also does not show any kind of selectivity. At 275 °C it senses LPG to 0.75, H₂ to 0.45 and NO₂ to 0.6. While CO shows maximum sensing of 0.43 at 350 °C. CO₂ does not show any remarkable sensitivity.
Fig. 4.16. Sensitivity Vs Operating Temperature for WO$_3$: SnO$_2$ (5 wt. %)
for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$

Fig. 4.17. Sensitivity Vs Operating Temperature for WO$_3$: SnO$_2$ (10 wt. %)
for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$
Fig. 4.18. Sensitivity Vs Operating Temperature for WO$_3$ : SnO$_2$ (15 wt. %) for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$
4.6 SYSTEM: WO$_3$ : In$_2$O$_3$ :-

4.6.1 EXPERIMENTAL DETAILS:

Calculated quantity of WO$_3$ powder prepared from ammonium tungstate is mixed with different weight percentages of In$_2$O$_3$ in an agate mortar. The mixture is thoroughly ground by using distilled alcohol as solvent, followed by evaporation to dryness under IR lamp and calcined at 650 °C for 5 hrs. The calcined powder is sieved to obtain fine particles and examined for gas sensing properties.

4.6.2 GAS SENSING CHARACTERISTICS OF WO$_3$ : In$_2$O$_3$

(5%, 10% and 15% BY WEIGHT):

Fig - 4.19 shows the gas sensing characteristics of WO$_3$ : In$_2$O$_3$ (5 wt. %) . This sensor element shows a sufficient selectivity towards LPG even at 200 °C. The sensitivity of the WO$_3$ - In$_2$O$_3$ (5 wt. %) sensor to LPG is about 0.7 which is much above the sensitivity of 0.31, 0.22, 0.19 to H$_2$, CO, CO$_2$ and NO$_2$ respectively even at 200 °C.

Fig - 4.20 shows the sensitivity versus operating temperature for the sensor element of WO$_3$ - In$_2$O$_3$ (10 wt. %). From this graph it is observed that sensitivity to LPG at 200 °C is 0.5 and it goes on increasing to 0.74 at 275 °C and
Fig. 4.19. Sensitivity Vs Operating Temperature for WO$_3$ : In$_2$O$_3$ (5 wt. %) for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$.
Fig. 4.20. Sensitivity Vs Operating Temperature for \( \text{WO}_3 \cdot \text{In}_2\text{O}_3 \) (10 wt. %) for a) LPG, b) \( \text{H}_2 \), c) CO, d) \( \text{CO}_2 \), e) \( \text{NO}_2 \)

Fig. 4.21. Sensitivity Vs Operating Temperature for \( \text{WO}_3 \cdot \text{In}_2\text{O}_3 \) (15 wt. %) for a) LPG, b) \( \text{H}_2 \), c) CO, d) \( \text{CO}_2 \), e) \( \text{NO}_2 \)
remains constant up to 325 °C. While CO₂ and NO₂ shows 0.16 and 0.33 at 300 °C and 350 °C respectively.

Fig - 4.21 shows the variation of sensitivity of WO₃ - In₂O₃ (15 wt. %) as function of the operating temperature to LPG, H₂, CO, CO₂ and NO₂. The qualitative observation is that the sensor shows partial selectivity towards LPG at 250 °C as compared to the other gases. This system detects LPG with a selectivity of about 0.7 at 250 °C operating temperature. On the other hand the sensitivity to other test gases i.e. H₂, CO, CO₂ and NO₂ is 0.38, 0.35, 0.1 and 0.19 respectively, at 250 °C.

Thus from the above study we carry out some observations as below.

(1) Among all the metal oxides incorporated in to WO₃, in different weight percentages, Indium oxide, In₂O₃ (5 wt. %) is seems to definitely improve the gas sensing characteristics of WO₃ sensor by imparting some degree of selectivity towards LPG.

(2) In other combinations such as WO₃ : La₂O₃ (15 wt. %) shows good sensing properties towards LPG and H₂ at 250 °C also WO₃ -SnO₂ (15 wt. %) sensor element sense LPG and NO₂ to a good extent. But both of these systems failed to achieve the selectivity.
Further we have carry out an experiment for WO$_3$ with addition of (3 wt. %) of In$_2$O$_3$ for the sensitivity to various reducing gases.

Fig - 4.22 shows the gas sensing characteristics for the composition of WO$_3$ : In$_2$O$_3$ (3 wt. %) system. The qualitative observation is that the sensor does not show any kind of selectivity. In other words it senses all the gases except LPG with a sensitivity value defined as $\Delta R_A/R_g$ between 0.1 to 0.75 between 100 °C - 275 °C. Only at sufficiently high temperatures i.e. at about 300 °C and above the sensitivity to LPG is seen to increase to 0.9 whereas the sensitivity to H$_2$, CO, NO$_2$ decreases.

For the lower composition of In$_2$O$_3$, 3 wt. % the sensitivity to LPG is observed only above 275 °C. As also the higher composition of 10 wt. % and 15 wt. % In$_2$O$_3$, sensor element shows a lesser sensitivity at operating temperature when compared to 5 wt. % In$_2$O$_3$ in WO$_3$.

In WO$_3$ : In$_2$O$_3$ (5 wt. %), the maximum sensitivity to LPG rises from 200 °C onwards and maintain this even upto 350 °C. Hence this optimum composition has been studied further to see the effect of incorporation of noble metals.
Fig. 4.22. Sensitivity Vs Operating Temperature for $\text{WO}_3: \text{In}_2\text{O}_3$ (3 wt. %)
for a) LPG, b) $\text{H}_2$, c) CO, d) $\text{CO}_2$, e) $\text{NO}_2$
4.6.3 EFFECT OF NOBLE METAL ON SENSITIVITY:

The next step was to incorporate noble metal to increase the sensitivity and also selectivity at lower operating temperature. The next few results are directed towards this goal. Electrical measurements have been carried out to see the effect of variation of platinum concentration and Indium Oxide concentration in the base material WO₃.

Fig - 4.23 shows the operating temperature versus sensitivity for the sensor elements of WO₃ with different wt. % of platinum and Indium oxide (5 wt. %) sintered at 750 °C for 2 hrs. The sensor element was checked for only LPG at different operating temperature. It is seen that the sensor response to LPG at 200 °C is 0.97 for 0.5 wt. % of Pt while that of 1 wt. % and 1.5 wt. % of Pt it shows sensitivity of 0.79 and 0.73 respectively at 200 °C.

From the above experiment, it is evident that the best composition for maximum sensitivity for LPG is found to be WO₃ - In₂O₃ (5 wt. %) : Pt (0.5 wt. %) sintered at 750 °C for 2 hrs.

The above sensor element was checked for cross sensitivity at different operating temperatures for other gases.

Fig - 4.24 shows the sensitivity versus operating temperature for the sensor element WO₃ - In₂O₃ (5 wt. %) Pd (0.2, 0.5 and 1 wt %). It is observed
Fig. 4.23. Sensitivity Vs Operating Temperature for WO$_3$ : In$_2$O$_3$ (5 wt. %) With Different wt. % of Pt for LPG.

Fig. 4.24. Sensitivity Vs Operating Temperature for WO$_3$ : In$_2$O$_3$ (5 wt. %) With Different wt. % of Pd for LPG.
that there is a sharp increase in sensitivity (0.9) to LPG for 0.5 wt % of Pd. At 225 °C while 0.2 and 1 wt. % of Pd it is 0.8 at the same operating temperature respectively.

Fig - 4.25 shows the cross sensitivity at different operating temperatures for other gases of the WO₃ - In₂O₃ (5 wt. %) - Pt (0.5 wt %) sensor element. It is observed that there is a sharp increase in sensitivity (0.97) to LPG at an operating temperature of 200 °C. Also it shows good selectivity towards LPG as compared to the other gases. In other words it senses LPG with a remarkably high sensitivity value between 0.97 -0.98 right from 200 °C upto 350 °C. In comparison the response of the sensor to the other gases is very low. That means the sensor reveals the saturation sensitivity at an operating temperature of 200 °C.

All the results bring out a very definite conclusion. We started with the aim of developing a highly selective and sensitive sensor based on WO₃ for the detection of LPG. It can be concluded that WO₃ based composition of WO₃ : In₂O₃ (5 wt. %). Pt (0.5 wt. %) gives us the best results. It shows the sensitivity of 0.97 at a temperature of 200 °C.
Fig. 4.25. Sensitivity Vs Operating Temperature for \( \text{WO}_3 \): \( \text{In}_2\text{O}_3 \) (5 wt. %) : Pt (0.5 wt. %) for a) LPG, b) \( \text{H}_2 \), c) CO, d) \( \text{CO}_2 \), e) \( \text{NO}_2 \)
4.6.4 EFFECT OF CONCTRATION OF LPG IN AIR:

LPG, which has been used for the studies of sensitivities as a function of concentration, is diluted as follows.

Assuming the filled air balloon to be spherical we have measured its circumference whose radius ‘r’ has then been calculated. The volume of the balloon was fixed (5 lit.) in which the circumference value was 66.6 cm (r = 10.26 cm). If 5 ml of LPG is injected by using gas syringe into a Balloon containing 5 lit. of air it becomes 1000 ppm (5 / 5000 × 10^6 = 1000 ppm). Similarly we have measured for other concentrations of LPG in air.

Fig. 4.26 shows the plot of sensitivity versus gas concentration in air for sensor element of WO₃ with 5 wt. % In₂O₃ and 1 wt. % Pt sintered at 750 °C for 2 hrs. The sensor element exhibits significant increase in sensitivity upon exposure to low concentration of LPG (600 ppm) in air. The sensor is able to detect 200 ppm LPG with reasonable sensitivity.
Fig. 4.26. Sensitivity as a Function of Concentration of LPG in Dry Air of the 
WO₃ : In₂O₃ (5 wt. %) : Pt (0.5 wt. %) Sensor Element at 200 °C.
4.6.5 RESPONSE CHARACTERISTICS:

The time taken to reach the saturation value is apparent from its response characteristics, which gives the rise time in presence of gas and fall time once the gas leaves the system. The typical response characteristic of the sensor element is shown in the Fig. 4.27. It is observed that the response to LPG shows a steep rise followed by steep fall in response to the presence and absence of gas respectively. The element reaches its maximum value of sensitivity (0.97), also defined as the saturation value in less than 1 minute. And it comes to its original position in less than 10 minutes. Number of experiments have been carried out for the sensor element under similar conditions at an operating temperature of 200 °C. All the time the sensitivity of sensor element is constant indicating the reliability of the sensor for long life.
Fig. 4.27. Response Characteristics of $\text{WO}_3 : \text{In}_2\text{O}_3$ (5 wt. %) : Pt (0.5 wt. %) for LPG