Edu. Chem. Sci. Tech.,
Vol. 2, August 2022, pp. 35-40

Thermochromism property of dichromate in liquid nitrogen

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Abstract : Thermochromism is the reversible colour change of a compound when it is heated or cooled. The thermochromic colour change is distinguished by being quite noticeable, often dramatic and occurring over a small or sharp time interval. It is one of the important phenomena as it has bright future for industrial and practical use. North Bengal Science Centre regularly conducts Liquid Nitrogen Show to show the behavior of materials at low temperature to the visitors. During this time it is observed that ammonium dichromate shows thermochromism in liquid nitrogen.

What is Chromism?

Chromophore is a group of atoms within a larger molecule which are principally responsible for the absorption of visible light to give the compound, its colour. The colour we observe is formed from the visible light that is transmitted or reflected by the chromogen. Chromogenic materials change colour in response to an electrical, optical (light intensity), thermal changes or with the changes of pH of the solvent. This property of materials is known as Chromism.

Accordingly we can sub-categories the chromogenic materials as –

Electro-chromic materials

These are the materials which changes their colour or opacity on the application of a voltage.

- We use this effect in liquid crystal displays.
- It is also known as electroluminescence.
- Electroluminescent materials can produce brilliant colours if stimu-

lated by A.C. current. So these can be used for decorating buildings and for industrial and public vehicles displays e.g. of safety notices.

Thermo-chromic materials

Here change in color depends on temperature.

- Thermochroism is the change in colour of a material with change in temperature which is reversible in nature.
- They can be designed to change colour happens at a particular temperature, which can be varied by doping the material with other compounds.
- Thermochromic materials are used to make paints, inks or are mixed to molding or casting materials for different applications.

Photo-chromic materials

When colour changing depends to the intensity of light.

- The term photochromic is applied to materials whose transmittance to light varies with the intensity of the incident light on it.
- Photochromic materials reversibly change colour with change in light intensity.
- Light sensitive sunglasses darken in response to increased intensity/ brightness of sunlight and so reducing glare e.g. when driving a car or when skiing at high altitude when the snow reflects extra light into your eyes.
- Light sensitive photochromic materials are used in optical memory devices.

Halo-chromic materials

When colour change depends on acidity or basicity of the solvent.

- Halo-chromic materials change colour according to the pH of the solvent.
- One possible application is to use paints that can change colour in response to corrosion in the metal underneath them e.g. in the rusting of iron or steel the pH of the water in contact with the metal changes in pH.

More details on thermochromism?

History

Systematic of thermochromism was investigated in 1971 at first by two New York inventors, Josh Reynolds and Maris Ambats. In 1975 they bonded liquid crystals with quartz stones and set into rings named as "Mood Ring" and claimed that the ring can monitor one's State of Mind. The theory behind the idea was the ring indicates the wearer's mood is based on a claim that body heat fluctuates with the emotional state of the wearer. Human body temperatures are known to vary by small amounts (less than 0.5 °C) when the body is fighting an infection or even in excitement. But the idea became flop as the variations in ambient air temperature appear to have a larger effect on the temperature of the ring than changes in the body temperature. Whatever may be, since then the application of themochromism starts. Scientists became interested to know the specific mechanisms according to which these materials working. Following 4 materials are used as thermochromism

(I) Organic compound

(II) Inorganic compound

(III) Polymer

(IV) Sol-gel

(I) Organic compound thermochromism

Advantages of thermochromism for these organic compounds are that color change takes place sharply and that there are many factors to control temperature easily. It has wide applications for fiber, optical science, photo storage instrument, optical sensor, and so on. The mechanism responsible for thermochromism varies with molecular structure. It may be due to an equilibrium between two molecular species, acid-base, keto-enol, lactim-lactam, or between stereoisomers or between crystal structure. On the basis of structure mechanism the colour changes happens for the following reasons :

(i) Variation in crystal struture

(ii) Stereoisomer

(iii) Moelcular rearrangement

ISBN : 978-81-954339-7-1

(II) Inorganic thermochromism

Many metals and inorganic compounds are known to exhibit thermochromic behavior either as solids or in solution. It has been suggested that such thermochromic behavior arises from one of the following mechanisms :

(i) Phase transition

(ii) Change in ligand geometry

(iii) Equilibrium between different molecular structure

(iv) Change in the number of solvent molecules in the coordination sphere

(v) Change in the gap between valance band and conduction band

(III) Polymer thermochromism

Polymer thermochromism arises from polymer planar-non-planar conformation transition. Specially, poly-acetylene is famous for polymer thermochromic material, therefore it has been researched. Generally poly-acetylene can be synthesized in solid state. Color change is happened to transform acetylene structure to buta-triene structure

(IV) Sol-gel thermochromism

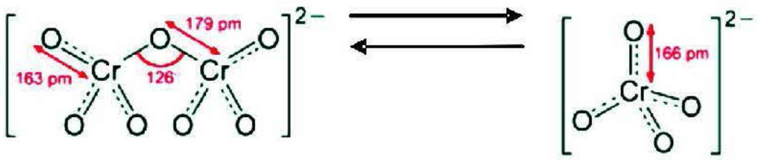
Interactions between macromolecules fall into four categories : ionic, hydrophobic, Van der Waals and hydrogen bonding. Phase transition in polymer gels provides a means of studying these interactions. Many gels will undergo reversible, discontinuous volumes changes in response to changes in temperature. This transition result from the competition between repulsive intermolecular forces, usually electrostatic in nature, which act to expand the polymer network, and an attractive force that acts to shrink it.

What exactly happens to dichromate in liquid nitrogen

Ammonium dichromate is usually orange in colour as its oxidation state +6. It is observed that if we put a test tube containing aqueous solution of ammonium dichromate in liquid nitrogen the colour turned to yellow. The yellow state of chromium is +4 i.e. chromate. It is also observed that the reaction is reversible. On withdrawing it from liquid nitrogen the colour again turned to orange after sometime.

Initially it was though that it is a chemical reaction in aqueous solution, as chromate and dichromate anions exist in a chemical equilibrium

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$



But the question is, according to Le Chatelier's Principle at low temperature the water will be freeze so we should get more dichromate than chromate ion.

Ammonium chromate is also stable compound at room temperature so the reaction should not be a revisable one.

Again we have carried out the same experiment with solid ammonium dichromate instead of aqueous solution. The same result obtained. In this case too solid orange coloured materials turn to yellow in low temperature and after some time it again turns in to orange when came to normal temperature.

Not only that if we pour liquid nitrogen directly to the solid (which means we carried out the reaction in inert medium, as nitrogen is almost inert in nature) it has shown the same behavior.

Ammonium dichromate

Ammonium chromate (?) or
Ammonium dichromate
(Courtesy : Wikipedia)

ISBN : 978-81-954339-7-1

So the primary conclusion is that it is not a chemical phenomenon rather it may be a physical change and the yellow substance though looks like ammonium chromate but actually ammonium dichromate.

To be sure that it is a physical change not chemical one I have taken the sample in a test tube and sealed it with grease to make it air tight. Same result shown in this case too. Again I have poured LN in to the sample and sealed the test tube, so that entire change can take place in inert atmosphere. Same experiments have carried out with two different solvents alcohol and acetone. In all cases we I have seen the same results. Potassium dichromate also shows the same result. So it is confirm that dichromate shows thermochromism at low temperature.

Conclusion

Virtually all inorganic compounds are thermochromic to some extent. Most examples however involve while we heat the compounds. For example, titanium dioxide and zinc oxide are white at room temperature but when heated change to yellow. Similarly indium(III) oxide is yellow darkens to yellow-brown when heated. Lead(II) oxide exhibits a similar color change on heating. Here the dichromate compounds show distinct colour changes when cooled. Secondly, in most of the cases thermochromic behavior shows due to phase transition or changes in ligand geometry, but here the most probable cause is due to change in energy gap between valance band and transition band or due to inner orbital electron rearrangement.

Bibliography

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