Nanomaterials for Hydrogen Storage

The van 't Hoff Connection

C S Sunandana

After highlighting the fundamental contributions of van 't Hoff to the emergence of modern physical chemistry, we bring out the relevance of his ideas to a problem of great contemporary interest – storage of hydrogen in nanomaterials.

Introduction

The seminal work of van 't Hoff, recognized by the award of the first Nobel Prize in Chemistry in the year 1901, laid the foundations of chemical thermodynamics. Some of the classic contributions from van 't Hoff include the famous equations that bear his name [1], systematization of a whole class of osmotic phenomena and development of an understanding of the solution state using concepts transferred from the gaseous state.

Separation of a solution from the pure solvent by a porous partition that is impermeable to the solute leads to predominant motion of the solvent molecules towards the solution. Equilibrium in the solvent–membrane–solution system is maintained by the osmotic pressure developed by the solute in the solution. van 't Hoff showed that the osmotic pressure (π) is related to the number of moles i of the solute in a volume V of the solution at a temperature T, by an equation analogous to the ideal gas law:

$$\pi V = iRT. \tag{1}$$

R is the gas constant and the van 't Hoff factor i is the number of moles of solute actually present in the solution, per mole of the solid solute added. Equivalently, i refers to the ratio of true molecular mass to that calculated by colligative methods. It is important in quantitative analysis of colligative properties such

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as vapour pressure, freezing point depression and boiling point elevation. Reverse osmosis has recently formed the basis of large-scale production of mineral water that is an indispensable part of life today. Some text books refer to equation (1) as the van 't Hoff equation.

Besides the physical equilibrium scenario noted above, van 't Hoff has also investigated the equilibrium state that arises in chemical reaction processes. The ratio of the rates of forward and backward reactions, the so-called equilibrium constant *K* for a chemical reaction has a temperature dependence controlled by the standard enthalpy change (ΔH^o) associated with the reaction. This relation is enshrined in the following equation, usually referred to as the van 't Hoff equation or van 't Hoff isochore.

$$\frac{\partial (\ln K)}{\partial T} = \frac{\Delta H^{\,o}}{RT^{2}} \, .$$

(2)

This equation implies that for a system in equilibrium, an increase of temperature increases the rate of the reaction absorbing heat.

Splitting Water to get Hydrogen

Beyond its fundamental relevance to basic chemical thermodynamics and kinetics, van 't Hoff's work continues to impact upon various areas of current research; a particularly fascinating one relates to problems such as the production and storage of non-conventional energy. Hydrogen as a source of energy offers an attractive solution. Future cars could be fuelled by hydrogen 'tanks' which contain typically 5–10 % by volume of gas. Hydrogen is projected as a compact, light-weight and affordable storehouse of energy. It is generated, among other methods, by photo-electrochemical conversion of water using semiconductors such as titanium dioxide (TiO_2). In 1971, Fujishima and Honda showed that by irradiating single crystal TiO_2 electrode connected with a platinum black electrode, using light of higher energy than the band-gap energy of TiO_2, it is possible to bring about the splitting

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of water into hydrogen and oxygen. This reaction is considered similar to photosynthesis, and the possibility of construction of artificial photosynthetic systems for conversion of solar light into chemical energy has been suggested [2]. Hydrogen is the ultimate clean fuel.

Materials for Hydrogen Storage

A major bottleneck in the ongoing research in this area is the effective and efficient storage of hydrogen. Nanomaterials offer great promise. Storage and retrieval of hydrogen involves an important phenomenon called 'sorption'. Adsorption and desorption are the two processes involved and the associated thermodynamics is vital in the design and optimization of the materials for hydrogen storage. We shall focus briefly on the basic issues of hydrogen adsorption in nanomaterials, the thermodynamics involved at the nanolevel and the van 't Hoff connection.

As early as in 1932, Lennard-Jones found [3] that the potential energy for useful molecular hydrogen physisorption on say, a metal surface at low temperature, falls in the range 10–60 kJ/mol. This is much lower than the energy required for chemisorption of atomic hydrogen that usually occurs at high temperatures (*Figure* 1). Among the metals/materials that can effectively adsorb and desorb hydrogen, are Li, Al, Mg and their alloys

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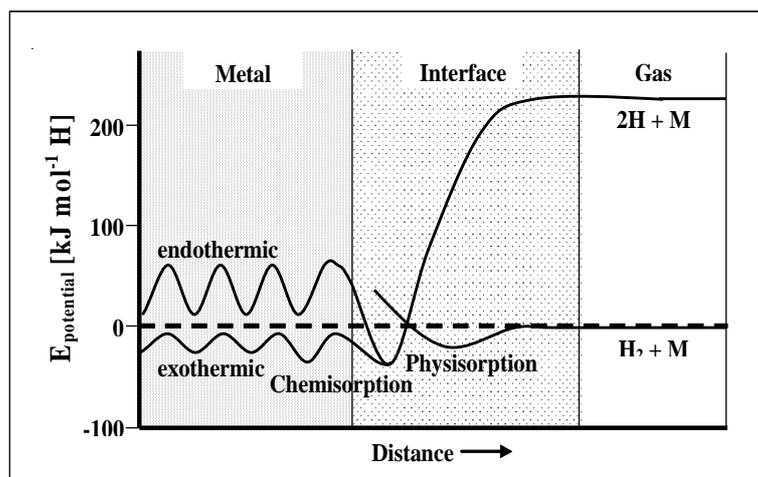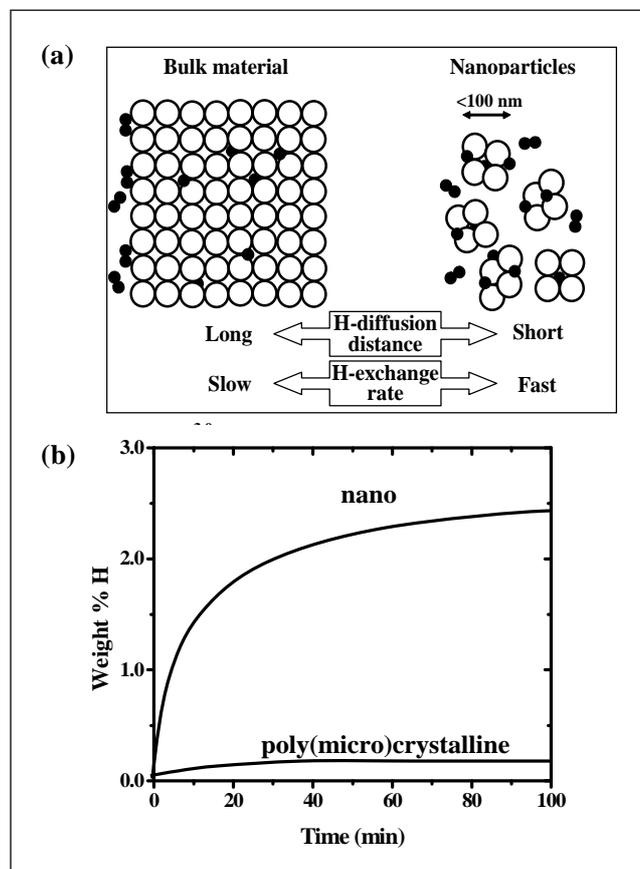

Figure 1. Potential energies of 2H+M and H$_2$+M reactions at a gas-metal interface (adapted from [4]).

Figure 2. *(a) Schematic diagram showing the impact of nanosizing on the H diffusion distance and exchange rate; (b) Adsorption kinetics in nano and bulk polycrystalline forms of Mg₂Ni at 200°C (adapted from [4,5]).*

whose hydrides can store 4–6 MJ/kg gravimetric energy density or 2–3 MJ/L volumetric energy density.

Nanomaterials are Superior for Storing Hydrogen

Major obstacles in the development of materials for hydrogen storage are the low rate of bulk hydride sorption and the high temperatures required for gas release. Poor heat transfer characteristics of bulk storage materials that results in interrupted gas release process is a further impediment, especially in transport vehicular applications. Nanomaterials are a natural choice for increasing the kinetics of uptake and release; the sorption characteristics can be fine-tuned by controlling the particle sizes. *Figure* 2a clarifies why nanomaterials are superior to macroscopic bulk materials. Nanoparticles help promote fast hydrogen

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exchange by shortening diffusion distances for hydrogen. This is facilitated by the increased porosity and smaller size leading to increased diffusion-limited rates. Surface energies and materials properties at the nanoscale help tune the energetics of adsorption and desorption to reduce the release temperature and hasten the release process. The case of Mg_2Ni shown in *Figure* 2b illustrates the advantage of nano over bulk as far as absorption kinetics is concerned [5].

The Thermodynamics of Hydrogen Storage – van 't Hoff Relation

We now face the question: how does thermodynamics work at the nanoscale? To begin answering it, let us consider the reaction:

$$M + H_2 \rightleftarrows MH_2, \tag{3}$$

where M is a metal. p_{H_2}, the equilibrium pressure of hydrogen is related to the adsorption process through the van 't Hoff relation

$$\ln p_{H_2} = \frac{\Delta H^o}{RT} - \frac{\Delta S^o}{R}, \tag{4}$$
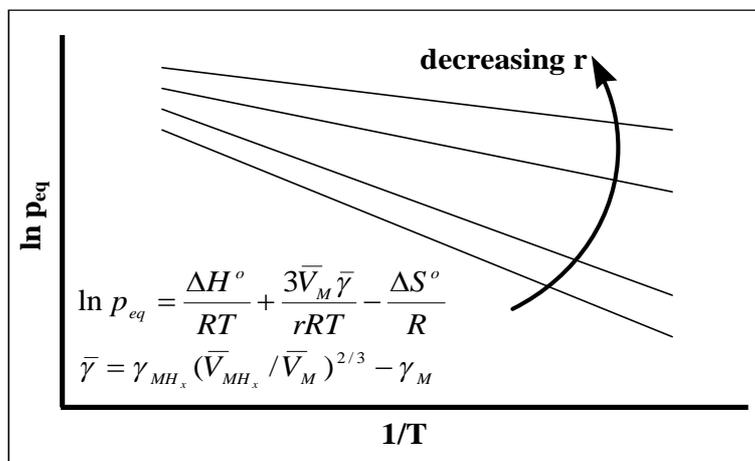
where ΔH^o and ΔS^o are the equilibrium enthalpy and entropy changes respectively, R the gas constant and T the absolute temperature. The reaction enthalpy is modified at the nanoscale due to surface and size effects. The basis for this is the increased surface to volume ratio which increases the adsorption sites and the low coordination of the surface atoms. Small metal clusters have weaker binding energies relative to bulk and the thermodynamic stability of such clusters depends on the number of atoms present, both electronic and geometric shells playing vital roles. Thus we are led to the nanoscale thermodynamics of adsorption. The most important changes that occur at the nanoscale are the significant contribution due to the surface free energy and consequently, the dependence of free energy on r, the size (radius) of the nanocluster. The van 't Hoff relation (equation (4)) now gets an additional term due to the surface energy (equation (5)), and the enthalpy and entropy terms are dependent on the particle size.

Suggested Reading

[1] **J H van 't Hoff, Osmotic pressure and chemical equilibrium,** *Nobel Lecture,* **December 13, 1901; W J Hornix, S H W M Mannaerts,** *van 't Hoff and the Emergence of Chemical Thermodynamics,* **Centennial of the First Nobel Prize for Chemistry 1901–2001, Delft University, December 2001.**

[2] **A Fujishima, K Honda, Electrochemical Evidence for the Mechanism of the Primary Stage of Photosynthesis,** *Bull. Chem. Soc. Japan,* **Vol.44, No.4, p.1148, 1971; A Fujishima, K Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode,** *Nature,* **Vol.238, No.5358, p.37, 1972.**

[3] **J E Lennard-Jones, Processes of adsorption and diffusion on solid surfaces,** *Trans. Faraday Soc.,* **Vol.28, p.333, 1932.**

[4] **A Zaluska, L Zaluski, J O Ström-Olsen, Structure, catalysis and atomic reactions on the nano-scale: a systematic approach to metal hydrides for hydrogen storage,** *Appl. Phys. A,* **Vol.72, p.157, 2001.**

[5] **M Dresselhaus, Overview of the Hydrogen Initiative, American Physical Society Meeting, March 2006 (http://www.aps.org/meetings/multimedia/upload/Overview_ o f _ t h e _ H y d r o g e n _ Inititative_Dresselhaus.pdf)**

Figure equations shown in plot:

$$\ln p_{eq} = \frac{\Delta H^{o}}{RT} + \frac{3\overline{V}_M\overline{\gamma}}{rRT} - \frac{\Delta S^{o}}{R}$$

$$\overline{\gamma} = \gamma_{MH_x}(\overline{V}_{MH_x}/\overline{V}_M)^{2/3} - \gamma_M$$

with axes ln p_{eq} versus $1/T$ and annotation "decreasing r".

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$$\ln p_{H_2} = \frac{\Delta H^{o}(r)}{RT} + \frac{3\overline{V}_M\overline{\gamma}}{rRT} - \frac{\Delta S^{o}(r)}{R}, \qquad (5)$$

$3\overline{V}_M/r$ signifies the average surface area. Its product with $\overline{\gamma}$, the change in surface tension (see *Figure* 3 for details), represents the contribution from the surface energy upon hydride formation. For hydrided nanoparticles in equilibrium with nonhydrided ones, any system with an extra positive surface energy term will cause reduction of the magnitude of the effective enthalpy of formation and cause release of hydrogen at a lower temperature. Variation of the van 't Hoff plot with the size of the nanocluster (*Figure* 3) offers a means to optimize nanostructured hydrogen storage systems.

van 't Hoff's seminal work provides scope for finding optimized nanomaterials that could serve as functional hydrogen storage subsystems for automotive fuel cells, consumer electronics and stationary electricity/heat generation [4]. One can clearly see that the impact of van 't Hoff's contributions goes far beyond what we read in basic textbooks.