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Hydrogen Purification and Storage Using Lithium Borohydride



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Objective

- To develop a system for H₂ storage and delivery based on lithium borohydride, LiBH₄
- Demonstrate control of H₂ evolution process by combination of solution conditions and by heterogeneous catalysts
- Develop a new family of catalysts, consisting of fused ring heteroaromatic pigments

Introduction

Borohydrides

- Tetrahydroborates, or borohydrides: general formula $M(\text{BH}_4)_x$
- Anion forms a salt with any of a number of electropositive metals
- Alkali and alkaline earth metals of greatest interest
- Borohydride compounds studied early on as rocket fuels

Lithium borohydride, LiBH_4

- Intrinsic gravimetric hydrogen density of 18.5%
- Discovery of LiBH_4 part of a World War II research program on developing agents for rapid deployment of signal balloons in the field
- Begins to decompose at 275°C ; decomposition proceeds to lithium hydride and diborane, which further condenses to make $\text{B}_{10}\text{H}_{14}$ and H_2

Water + Borohydride Approach to Hydrogen Generation

Aqueous chemistry of LiBH_4 :

- One mole of lithium borohydride reacts with 4 moles of water to generate lithium hydroxide and boric acid plus hydrogen gas:



- By this mechanism, one gram of LiBH_4 liberates 4.11 liters of hydrogen gas at STP.

H₂ evolution rate is pH dependent

- At high pH (11-14): BH₄⁻ ion essentially inert material- could be stored for an indefinite period of time
- At neutral pH (6-8), mildly effervescent solution obtained (steady outgassing of H₂) - special precautions necessary to store LiBH₄ solutions under these conditions
- At acidic pH (1-4), effervescence quite vigorous; additionally, H₂ production reaction sufficiently exothermic that, unless solution is protected from air, there is risk of igniting evolving gas.

Results

- **Catalytic H₂ Evolution**
 - To demonstrate H₂ recovery in a safe, economical manner, it is most desirable to use plain water for regeneration.
- **Two problems with plain water:**
 1. Solid LiBH₄ initially mixed with water produces gas evolution difficult to control.
 2. Reaction progresses, solution becomes progressively more alkaline, and reaction winds down to nothing well before stoichiometric amount of H₂ is collected.

Figure 1: Time Dependence of H₂ Evolution From NaBH₄ in Pure Water.

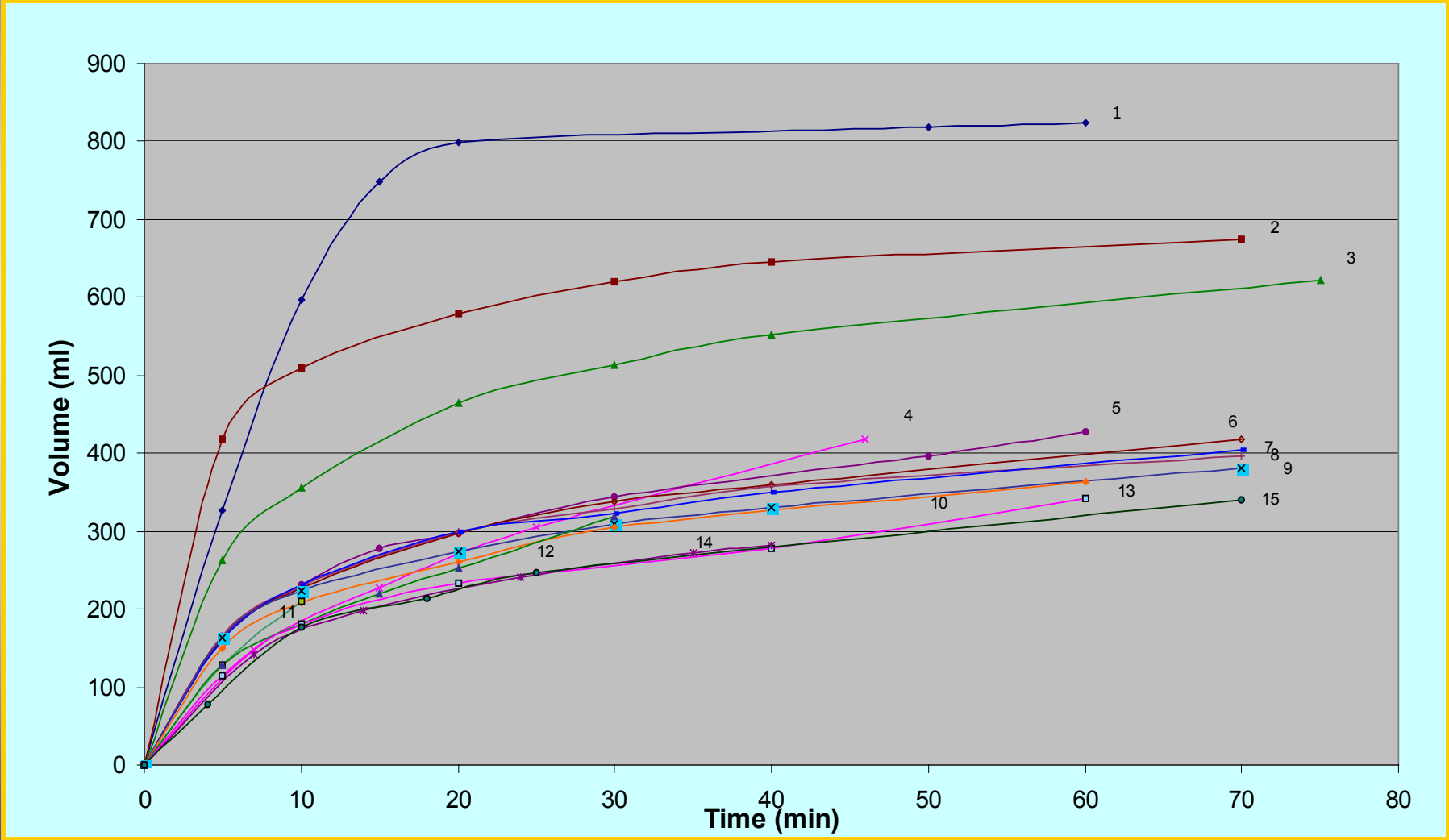


Figure 1, Time dependence of H₂ evolution from NaBH₄ in pure water

- 1) Indanthrene Gold Orange
- 2) Perylene TCDA;
- 3) Perylene diimide;
- 4) Co powder;
- 5) Indanthrene Yellow;
- 6) Zn phthalocyanine;
- 7) Indanthrene Black;
- 8) Quinacridone;
- 9) Pyranthredione;
- 10) Isoviolanthrone;
- 11) Indigo;
- 12) Indanthrone;
- 13) Ni phthalocyanine;
- 14) No catalyst;
- 15) Cu phthalocyanine.

Table I. Ranking of pigment catalysts; pH 11 phosphate buffer, 1.0 M ionic strength

Rank	Catalyst	Rate ml/min
1	Pyranthredione	6.5
2	Indanthrene Gold Orange	5.0
3	Cobalt powder	5.0
4	Ditridecyl-3,4,9,10-perylenetetracarboxylic diimide	4.9
5	Indanthrene Black	4.2
6	Dimethoxyviolanthrone	4.0
7	Poly(methylmethacrylate)	4.0
8	Quinacridone	3.9

Table I. Cont'd

Rank	Catalyst	Rate ml/min
9	1,4-Di-keto-pyrrolo(3,4-C) pyrrole	3.8
10	Indanthrene Yellow	3.5
11	Copper phthalocyanine	3.4
12	3,4,9,10, perylenetetracarboxylic dianhydride	3.3
13	Isoviolanthrone	3.3
14	Perylenetetracarboxylic diimide	3.2
15	Indigo	2.8
16	Phosphate buffer pH 11	1.0

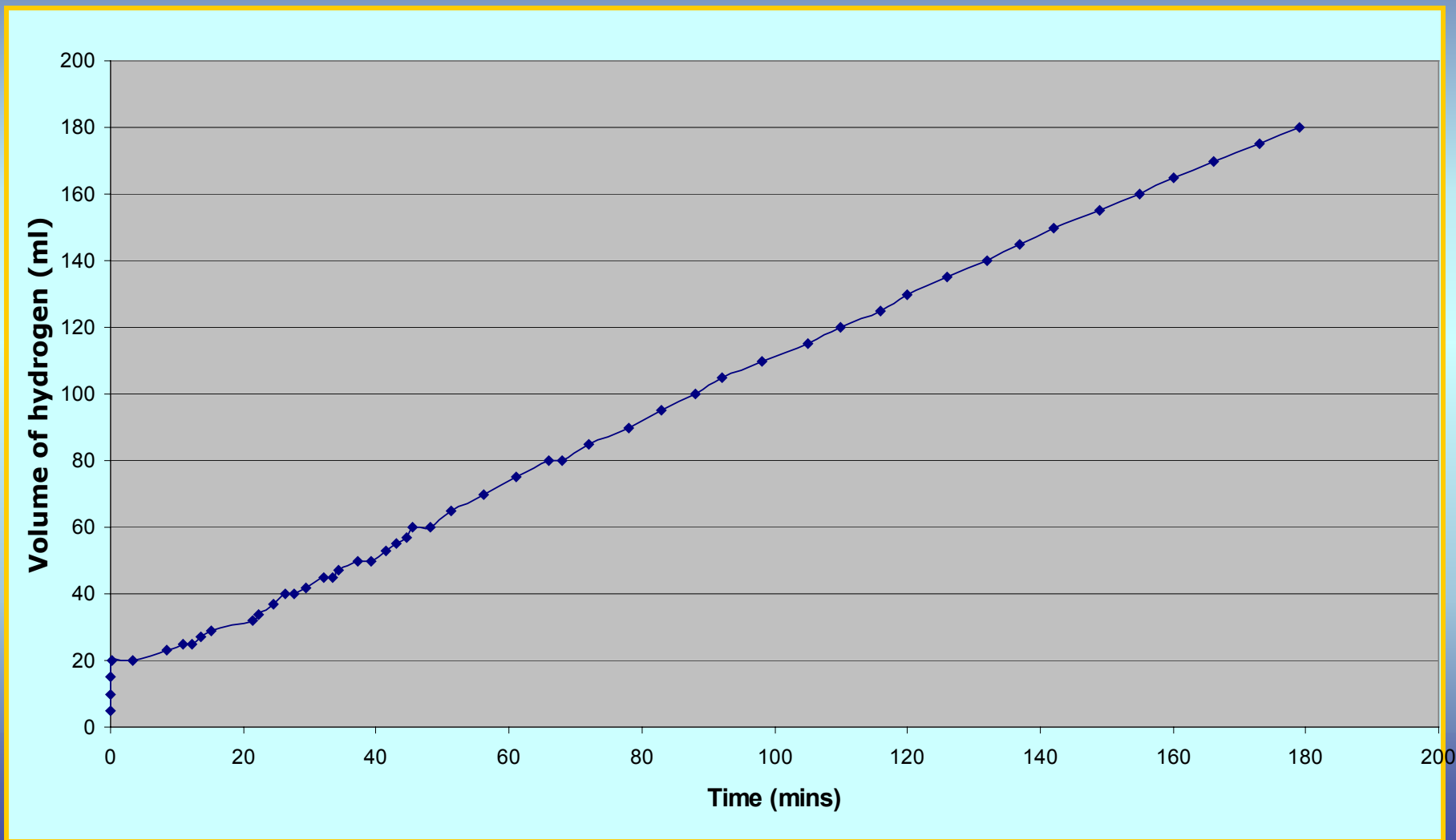
pH Effect on H₂ Evolution

- H₂ evolution from a borohydride solution thought to be driven by a bimolecular process involving borohydride ion, BH₄⁻, and solvated hydrogen ions, H⁺.

$$\text{Rate} = k [\text{H}^+][\text{BH}_4^-]$$

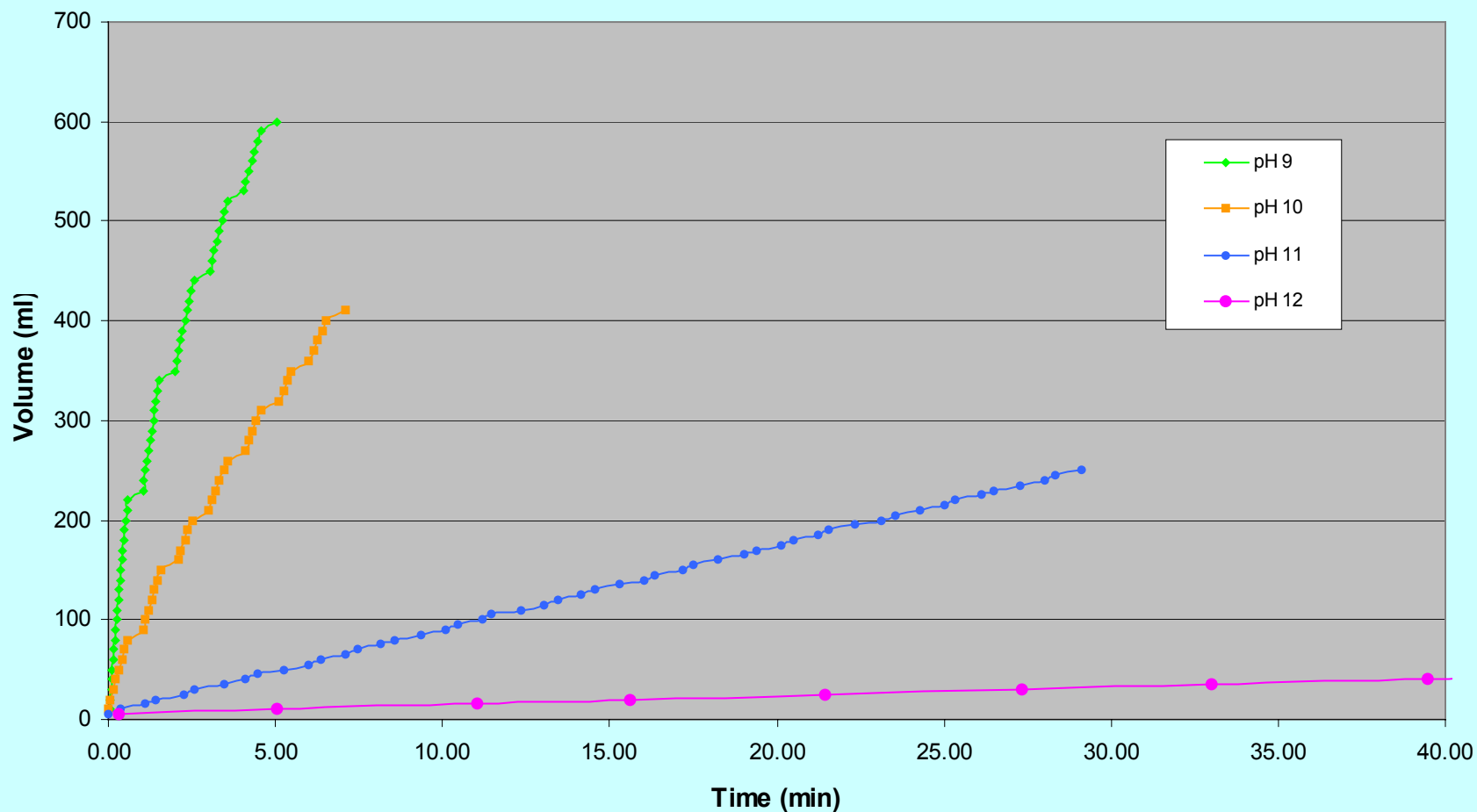
- Difficult to monitor the reactions with both pH and background borohydride concentration changing
- pH variation eliminated by use of buffered solutions.

Figure 2, H₂ evolution from phosphate-buffered borohydride solution at pH 11.



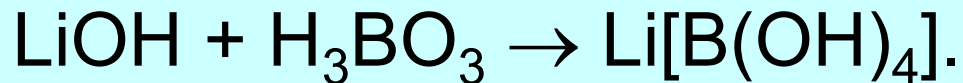
- As shown in Figure 2, by using phosphate buffer solutions, the H₂ evolution curves straightened out. A pH of 11 using 0.1 M NaBH₄ allowed for a steady H₂ output that could be reasonably observed with volumetric collection apparatus
- Despite ability of pigments to accelerate rate of H₂ evolution, this did not substantially change effect of pH. Figure 3 shows decade dependence on hydronium ion concentration, as for uncatalyzed case, except that absolute rate for each pH is higher.

Figure 3, pH dependence of H₂ evolution from borohydride solution using pyranthredione catalyst.



Borate Buffering Effect

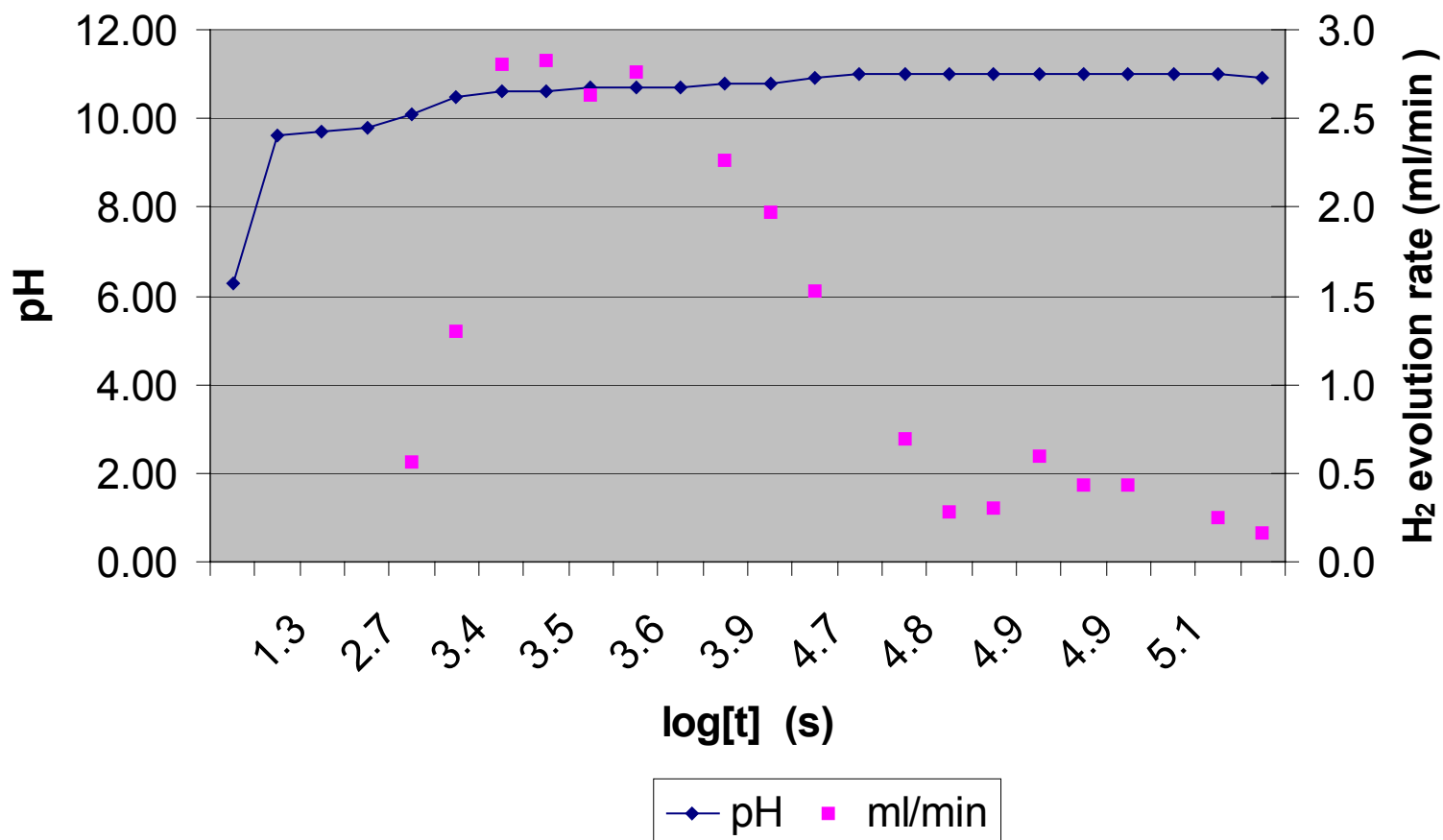
- LiOH by-product from decomposition reaction is responsible for pH-increasing effect.
- Boric acid is expected to react further with lithium hydroxide, however, to generate a hydrous metaborate salt:



Borate buffering effect (2)

In an uncatalyzed BH_4^- decomposition experiment, pH was monitored versus time, along with the incremental H_2 evolution rate. It is seen that as the experiment continued over a 2-day period, the pH eventually reached 11.0. Therefore, a system already set to this pH would maintain that value. Results are shown in Figure 4.

Figure 4. Time dependence of pH and H₂ evolution rate from a 0.1 M NaBH₄ solution.



Conclusion

- Rates of H₂ evolution from aqueous borohydride solution can be controlled by means of hydride concentration, pH, and the use of catalysts
- Developed new class of borohydride decomposition catalysts based on fused aromatic compounds
 - Aromatic catalysts should contain sufficient heteroatoms to lower its first excited electronic state to where it can be accessed by the borohydride.

Conclusion (2)

- Some of these catalysts, at least on a weight basis, are more active than the conventional inorganic metallic powder catalysts.
- Holding the pH of the solution constant will enable a constant rate of borohydride ion decomposition
- Borohydride decomposition in solution is a dynamic situation, where the LiOH produced may or may not interact with boric acid, depending on the pH. By operating the system near the maximum buffering pH, ~11, such fluctuation may be avoided.

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