HYDROGEN GAS EVOLUTION AND VENTILATION FROM BATTERY ROOMS-EXPERIMENTAL EFFORTS

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ABSTRACT

Hydrogen evolution is examined beginning with Tafel data and the Ideal Gas Law. Equations and methods of efficiently venting this gas are detailed. In many applications gas recombining battery product is housed in relatively small rooms with minimal control of ambient temperature and battery charge current. Improper control of these variables[i] and tardy replacement of the battery can result in inefficient gas recombination and the evolution of large volumes of hydrogen. Due to these undesired operating conditions potentially explosive mixtures of hydrogen in air develop and the battery room is no longer a safe environment. It is then imperative that one has a thorough understanding of the properties of hydrogen transport and its ventilation.

In this study the parameters necessary to provide efficient hydrogen ventilation are measured and defined as summarized in the following:

- Measurements of the H_2 diffusion coefficient are made and shown to be applications sensitive;
- The hydrogen concentration is a linearly related to the vent path as indicated by the classical diffusion equations;
- Hydrogen ventilation calculations and methods are presented for conditions of simple diffusion and forced air convection (fans);
- It is experimentally demonstrated that the friction and turbulence of air flow when using fans needs to be determined by direct measurement.

INTRODUCTION

The rate of hydrogen evolution from a lead-acid cell can be determined from a graph of the negative plate Tafel shown in figure 1.

The value of I_d, 100mA for the cell shown, is the maximum rate that oxygen can be recombined. Consequently one experiences the minimum rate of hydrogen evolution when below I_d, as indicated by the Tafel slope of zero.

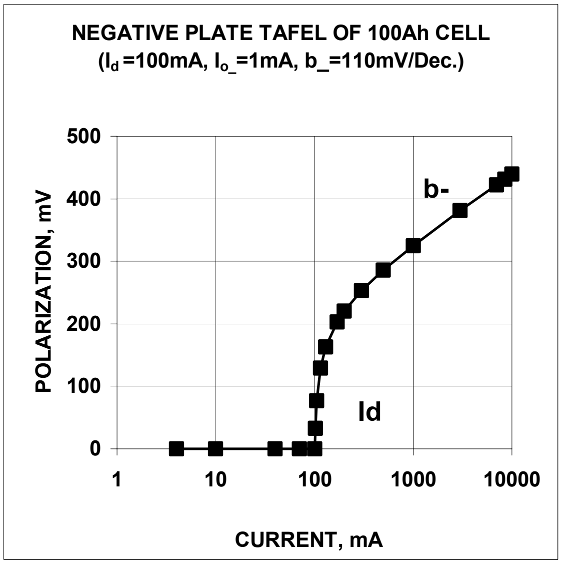

FIGURE 1

Above I_d the oxygen recombination rate decreases and hydrogen evolution accelerates.

To insure minimum hydrogen evolution in the suggested float voltage range one should be assured that the negative Tafel slope below I_d is less than 10 mV/Dec. of current. In this Tafel region it is suggested that Tafel graphs be employed to determine ventilation needs in lieu of collecting hydrogen.

At or below 100mA one can assume near 100% oxygen recombination and minimal hydrogen evolution. Ventilation required by the EPA for people occupied buildings will be adequate to keep the hydrogen content in air below its explosive limit, 4% by volume. Above I_d the rate of hydrogen gassing in the recommended float voltage range is calculated by subtracting 100mA from the charge current (100% Efficiency).

To convert current into the rate of hydrogen evolution (V) the following calculation is employed.

1. $V = 0.42*I*[1+ (T/273)]*N$

In ventilation calculations it is required that one know the weight of a particular volume of hydrogen. This conversion is made using the Ideal Gas Law,

2. Grams Hydrogen = $2PV/(82.06*T)$,

P=pressure, atmospheres
V=hydrogen volume, cc
T= absolute temperature, K
M=mass of hydrogen, grams

To probe into the intricacies of simple hydrogen diffusion one needs the following inputs,

- The diffusion coefficient of hydrogen gas, D (cm^2/sec.);
- The physical dimensions of the battery room vent, i.e. length, L (cm), and cross sectional area, A (cm^2);
- The maximum concentration of hydrogen, d_2 (grams/cm^3), allowed in the battery room. Most design for 1 to 2 % hydrogen in air by volume;
- Time, t (seconds.).

Equation 3 calculates the maximum weight of hydrogen, M (grams), allowed to evolve from the battery so as to maintain the desired steady state concentration of hydrogen, d_2.

3. $M = (A/L)* t*D (d_2-d_1)$

The concentration of hydrogen (d_1) in air is assumed = 0.

The diffusion coefficient of hydrogen in air is a function of temperature, pressure, and concentration gradient. The data in figure 2 shows the effect of temperature on the diffusion coefficient at one atmosphere.

The graph was developed[ii] from kinetic theory and agrees with experimental data to within 8 percent[iii]. From figure 2 it is seen that the diffusion coefficient for hydrogen in air at 25^0C is **0.77 cm^2/sec**.

The ventilation of hydrogen by forced air convection or air movement due to the use of a fan, where the fan capacity (F, cm^3/minute) is calculated from the following,

4. $F = Bx100/M$

M=decimal % of max. H_2 content allowed
B= battery H_2 evolution rate, cm^3/minute.

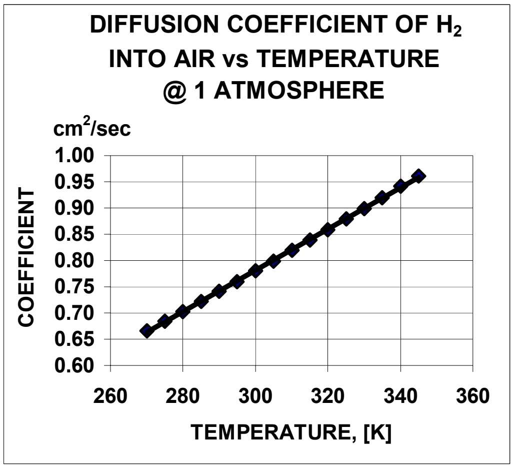

FIGURE 2

The fan equation is only valid when the air inlet area is sufficiently large to insure sufficient airflow. Air turbulence and friction flow due to the contents of the room can further act to prevent efficient ventilation. For each application these impediments may require actual room measurements.

In a review of the ventilation systems provided by battery cabinet manufacturers we have found either no provision for, or insufficient ventilation. **In this work the classical methods and equations used to design ventilation systems are tested in actual battery applications. From these efforts we expect to at least clarify the practices and processes needed to attain acceptable hydrogen ventilation.**

EXPERIMENTAL AND RESULTS

Simple Diffusion

In designing for the ventilation of hydrogen by natural diffusion or forced air convection a steady state concentration of hydrogen is maintained in the battery room not to exceed the lower explosive limit of 4% in air by volume. As should be evident from the above equations knowledge of the battery room volume is not necessary, a fact that is often disputed.

To perform the required experimentation a 76-liter sealed drum was used as the battery room. In figure 3 this battery enclosure and measurement devices are shown. The drum is 52 cm high by 48 cm in diameter. The vent opening was 36 cm above the H_2 inlet that was at the bottom of the drum. A fan was later added to replace the vent opening. The drum lid is sealed at the top by a compressed rubber gasket. The initial experimentation was performed with pure hydrogen (certification 99.99%); this was later followed with VRLA battery gassing.

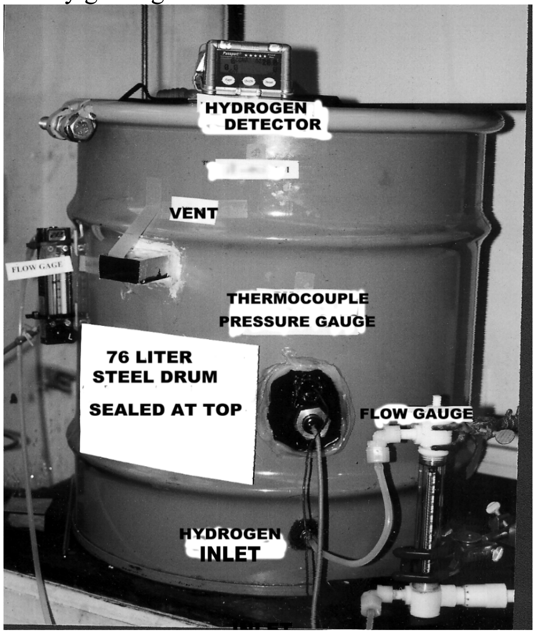

FIGURE 3

First, the above container was tested to determine its seal integrity. The radius of the hole responsible for a seal leak was then calculated using the Poiseuille's Law. Pressurizing the drum container with nitrogen and measuring the pressure drop with time accomplished this. Using the pressure loss, the leak rate was calculated and substituted in the equation of the above law to solve for the radius. The leak hole radius was found to be 0.15 mm; an opening which would not to be of consequence in the following experimentation.

The hydrogen detector used was manufactured by the Mine Safety Appliance Co. in Pittsburgh PA. It measures hydrogen concentrations in air to 2 % by volume. The detector as well as all of the measuring and monitoring devices were meticulously calibrated and maintained to insure data accuracy.

The first test run was to determine if there was a hydrogen concentration gradient in our test drum. This was accomplished at H_2 flow rates of 10 and 40 cm^3/minute with a vent diameter of 1.3 cm. The H_2 was introduced at the bottom and measurements were made at the bottom, center, and top of the test container. The largest concentration difference was 7%, with the concentration greatest at the top of the drum.

Experimentation began with evaluation of equation 3, which defines the parameters related to the natural diffusion of hydrogen. The rate of which is controlled by the difference in hydrogen concentration across a divider. In this study the divider between the outside world and the interior of the drum is the drum wall. The test parameters and results are shown in figure 4. For this static test the concentration of H_2 in the drum was raised to 1.85%. The H_2 was then allowed to diffuse naturally from the drum through a vent whose dimensions are listed in the figure.

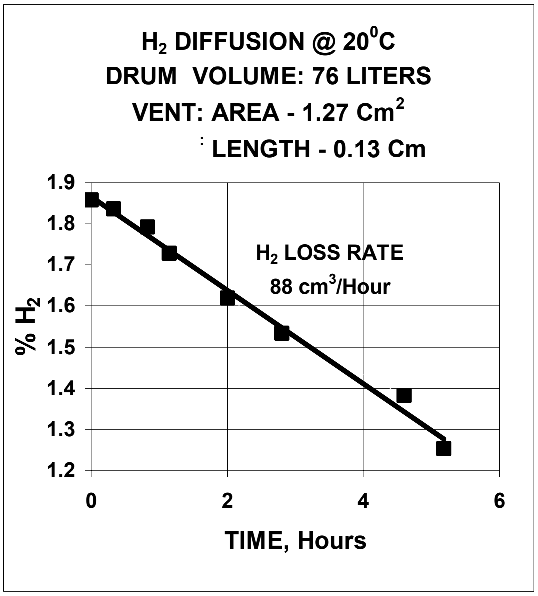

FIGURE 4

In figure 4 the percent hydrogen should decrease exponentially with time in the narrow concentration range explored this behavior was not evident. The physical dimensions of the vent and loss of H_2 in one hour (88 cm^3) were substituted in a re-arranged form of equation 1.

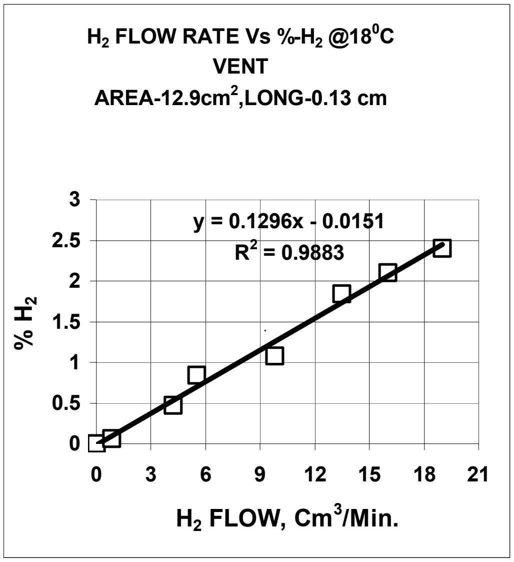

FIGURE 5

The value of the diffusion coefficient (D) was then solved for. The steady concentration (d_2) used in the calculation was the average percent hydrogen shown in the plot. This concentration was 1.58 % or $1.32*10^{-6}$ grams/cm^3 which are the units required for the calculation.

$D = m*L / (A* t*d_2)$

$D =(7.32*10^3)(0.13)/(1.27*3600*1.32*10^{-6})$

D = 0.16 cm^2/second @ 20^0 C

The value of the diffusion coefficient from the literature, figure 2, is **0.75 cm^2/second @ 20^0 C.** This value is about five times greater than our experimental findings and of course would impact on the ventilation design parameters.

To verify our initial test results a second dynamic method was employed to determine the steady state concentration (d_2) of hydrogen at various flow rates of H_2. The test parameters and results are in figure 5.

The relationship of the steady state H_2 concentration to H_2 flow rate is linear at any coordinate in the curve of figure 4 and can be used to find the diffusion coefficient. The calculated coefficient, from this data, was found it be **0.14 cm^2/second @ 20^0 C**. **These results then justify our concern with using the literature coefficient to engineer hydrogen ventilation methods.**

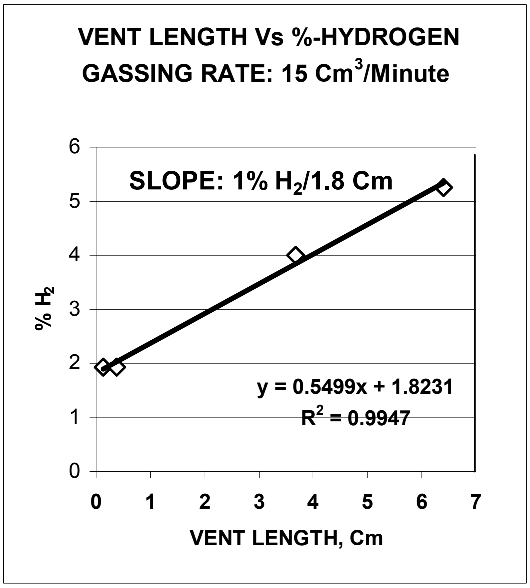

FIGURE 6

In the following test the effect of the vent length on the diffusion of hydrogen from the test drum was tested. In all test sequences the H_2 concentration in the drum, not the vent, was measured. Monitoring the vent environment yielded low concentrations of H_2. In figure 6 we develop the relation of the vent length to the steady state hydrogen concentration.

The data in figure 6 shows the steady state **H_2 concentration in the battery room to double when the vent length is likewise increased. This is in agreement with equation 3. Placing a 15 cm length of the vent inside the test drum did not change the above relationship.**

Several other areas of peripheral interest to anyone designing methods of ventilating hydrogen were investigated. They were the following,

1. The relationship of the battery hydrogen evolution rate to the battery Tafel plot;
2. Hydrogen gassing during the charge/ discharge cycle.

The steady state hydrogen concentration relationship to Tafel was determined for a new gel 12V battery. This battery was chosen because of its expected high H_2 evolution rate. The battery was placed in our test drum that had a vent diameter of 0.7 cm and a length of 0.030 cm. As the battery voltage was varied, the current and steady state hydrogen concentration were measured. Figure 7 shows those measurements (X). As expected a Tafel slope shift to higher values was followed by an increase in hydrogen concentration (or evolution rate), indicating a decrease in gas recombination efficiency. For purposes of the next calculation it is important to note that the Tafel slope between 2.25 and 2.30 V is approximately 80mV/Dec. of current. This slope value indicates the oxygen recombination efficiency is high.

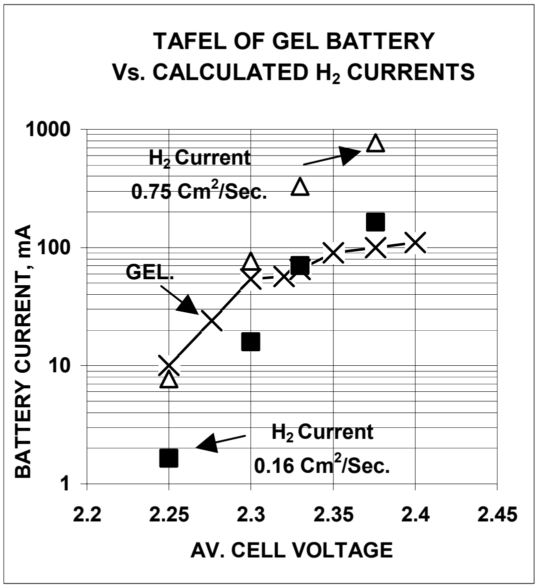

FIGURE 7

Also, in this figure are the results of calculations made to determine the current going to H_2 evolution. This was accomplished employing the diffusion coefficient we found to be 0.16 cm^2/sec. and the literature coefficient of 0.75 cm^2/sec., both @ 20^0 C. To accomplish this we substitute a steady state H_2 concentration (d_2) from figure 7 into equation 3, the above vent dimensions, and the appropriate diffusion coefficient. We then solve for the weight of hydrogen (M) and convert that weight into a battery hydrogen evolution current.

The data points for these calculations are in the figure. Those for the literature coefficient (triangle) indicate that the gel cell does not recombine oxygen at 2.25 to 2.30 V, or any voltage. This is evidenced by the H_2 current being the same as the battery current (x-axis).

Our diffusion coefficient calculations (squares) for the same voltage range shows the current is less than the cell charge current. This is similar to the Tafel plot and indicates oxygen recombination is occurring. The calculated recombination efficiency, for our coefficient, at 2.29 V is 66%, and 84% at 2.25 V. The cell voltage at which the oxygen recombination falls to zero is when the cell current equals the H_2 evolution current. In figure 7 this is shown to be approximately 2.33 volts.

The battery Tafel slope at the lower voltage range is an indication that oxygen recombination on the negative plate is in effect. **The above calculation using our coefficient is in agreement with the Tafel slope finding, and reveals an oxygen recombination efficiency for this reaction of 66 to 84% within the 2.25 -2.30 volt range.** On the other hand, the calculation using the literature coefficient indicates there is no recombination in the low voltage range, which is in conflict with the Tafel slope. The currents for the voltages above the oxygen reduction region require additional examination, this especially for the literature value calculations.

The agreement between the Tafel slope and the calculations based on our diffusion coefficient for hydrogen is additional proof that the diffusion coefficient we find is valid. From the above it is apparent that one needs to know the cell Tafel characteristics and recombination efficiencies at the various charge voltages to engineer accurate ventilation. This information is usually not available, and it is assumed, incorrectly, that all of the charge current is used to evolve hydrogen.

Employing the above test arrangement the battery was discharged at the 3-hour rate. At the end of the discharge to 1.75 V/Cell, the H_2 concentration was 0.13 %. At the end of recharge, at 2.30 V/Cell and a 10 ampere-limiting current, the maximum H_2 concentration was 0.11 %. **This data shows that VRLA battery strings on discharge and recharge, during normal operation, produce volumes of H_2 that can be readily ventilated.**

Forced Air Convection (Fans)

The fan equation 4 shows that the required fan capacity is only dependent on the rate of hydrogen gassing. In practice however, one has to be concerned with the room contents. The occupants of the room can influence the degree of air turbulence and friction and slow the movement of hydrogen. Because of this turbulence it may be necessary to provide excess fan capacity to insure adequate hydrogen removal. Ideally, it is wise to test monitor the hydrogen content of the actual room to ensure there is adequate ventilation. This test run should be at worst-case hydrogen evolution.

In our efforts to accomplish such a measurement, we employed a fan capacity of 3 CFM (ft^3/minute) of air. Although it was the smallest fan available, its rate of flow was still too great for our experimental design. To lower the fan speed its operating voltage was decreased. The fan capacity for each D.C. voltage was calculated by measuring the velocity of the exiting air and multiplying it by the area of the fan cross section (Bernouilli's theorem).

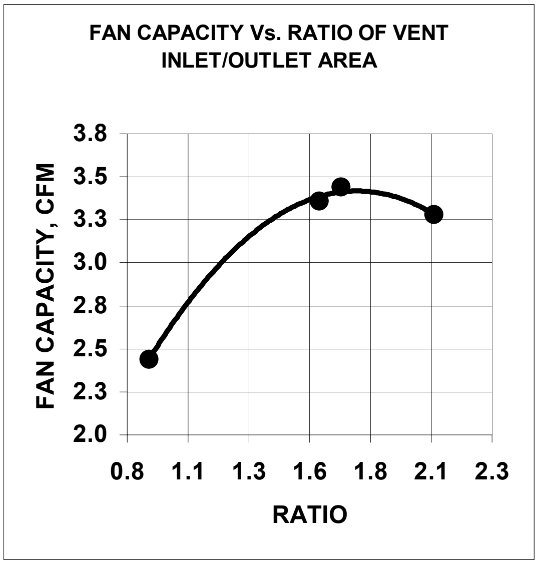

FIGURE 8

It is also necessary to insure that the air intake vent area is large enough so as to not starve the fan, and slow its speed. It was determined (figure 8) that the intake vent area must be approximately 1.5 times that of the fan outlet area if the fan speed is to be maintained. The above information was used to determine the necessary fan capacity at two H_2 evolution rates.

The following effort involved evaluating the relationship between the H_2 evolution rate and the fan capacity. This included the influence of air turbulence on the equation as well. To cause air turbulence 15% of the in the drum void volume was occupied by a battery placed above the hydrogen inlet.

FIGURE 9

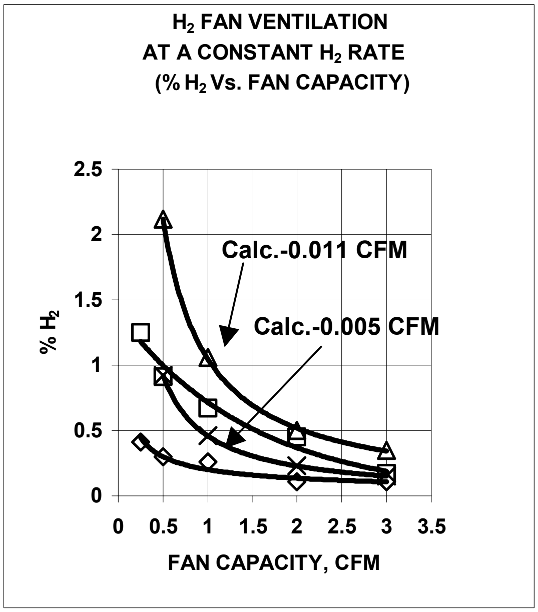

Figure 9 graphs the calculated fan capacity (equation 4) for H_2 evolution rates of 0.005 and 0.011CFM. Beneath each calculated curve is the experimental data curve for the same H_2 evolution rates.

This figure shows good agreement between the calculated and experimentally determined fan capacities between 2 to 3 CFM. At slower fan speeds the curves deviate. **This data shows that at relatively slow fan speeds and high H_2 evolution rates, large H_2 concentration gradients can form.** Although the percentages of H_2 in figure 8 are below 2%, measurements found pockets of H_2 that were above that percentage. The equation 4 calculations show higher steady state H_2 concentrations than the turbid air flow experimental data. This was unexpected and perhaps the result of the large concentration gradient. We did not readily detect this gradient because our measurements where made at the same location in the drum by experimentally necessity.

CONCLUSIONS

The author understands that the result of this work is in contradiction with classical methods pertaining to hydrogen diffusion and the reported hydrogen diffusion coefficient[iv]. Specifically we find,

1. The diffusion coefficient to be 0.16 not 0.75 cm^2/sec.;
2. For each doubling of the vent length, the steady state concentration of hydrogen increased two fold as predicted by equation 3.

The lower diffusion coefficient will require a substantial increase the amount of ventilation necessary and the practicality of employing natural diffusion. Most importantly, the safety of the battery room or enclosure must not be comprised by application of an incorrect H_2 diffusion coefficient. The matter of safety is of further concern since some designers of battery room ventilation methods employ a coefficient well in excess of the literature value[v]. In addition some, fortunately fewer each year, still are not aware that lead-acid batteries evolve hydrogen.

As to the difference between the coefficients, we have attempted to retrieve the original works of Obermayer. His coefficient for hydrogen is quoted in reference iii. A review of his experimentation might explain this conflict, but we have not been able to find a reference to his work.

The coefficient reported on in this work has been determined by several methods, which include:

1. Measuring H_2 concentration change with time;
2. Measuring the H_2 steady state concentration;
3. Comparing actual battery test results to calculations employing our coefficient.

The H_2 diffusion coefficient obtained from each of these methods is consistent with the value we report, which is approximately one-fifth of the literature value. This variation will result in substantial differences in the calculated vent size necessary to maintain acceptable H_2 concentration limits.

The methods employed to remove hydrogen from battery rooms should be based on worst-case conditions of hydrogen evolution and temperature. In these worst-case calculations it is normally determined that a fan is required. **Employing only simple diffusion to exhaust hydrogen should be reserved for the most benign battery application and H_2 evolution rates.**

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[i] F. Vaccaro, R. Landwehrle, INTELEC'1992, Paper 3-3.

[ii] J.C. Slattery and R.B. Bird, *A.I. Ch.E. Journal*, **4**, 137-142(1958)

[iii] R.C. Reid and T.K. Sherwood, *The Properties of Gases and Liquids,* McGraw-Hill, New York (1958), pp. 267-276.

[iv] CRC, Handbook of Chem. & Physics, 65thEd., pp. F-45.

[v] F. Vaccaro Informal Conversations with Cabinet Designers, 1998-2000.