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Steady state pressures in vials sealed with butyl rubber stoppers

1. Expressions for pressure development

Bengtsson et al. (2013) describe a series of experiments where molecular hydrogen gas is generated in glass vials sealed with butyl rubber stoppers. In several experiments there are indications that the measured pressure levels off after typically 3 months. In this Memo, it is demonstrated that this behaviour of the pressure development is consistent with a constant gas generation rate being balanced by out diffusion through the rubber stoppers. The case with an initial hydrogen gas pressure and no gas generation is also discussed.

Butyl rubber in equilibrium with a gas phase has a solubility, S , of a particular gas species according to

$$C = pS \tag{1}$$

where C is the concentration of the species in the rubber and p is the partial pressure of the gas in question. The linear relationship is valid for gaseous species that do not dissociate in the solid material in question. Molecular hydrogen does not dissociate in butyl rubber (George and Thomas 2001), meaning that the relationship is applicable in this case. Furthermore, the pressures under consideration are sufficiently low for the ideal gas law to be applicable. (For non-ideal conditions, the gas pressure in Equation (1) should be replaced by the gas fugacity.)

Gas is transported by diffusion in butyl rubber. Consider a butyl rubber stopper of cross sectional area A_{Rubber} and length d_{Rubber} , and with zero initial gas concentration. The inner surface is exposed to a constant pressure p and hence held at a constant concentration $p \cdot S$ from time $t = 0$ and the outside is held at zero pressure/concentration. After an initial transient phase, a constant transport rate through the stopper is established and given, according to Fick's first law, by

$$\frac{dn}{dt} = p \frac{SA_{Rubber}D}{d_{Rubber}} \tag{2}$$

where D is the diffusivity of the gas in butyl rubber. Equation (2) is valid if the diffusing species does not interact with the material in which it diffuses. Hydrogen does not interact with butyl rubber under the experimental conditions considered here (George and Thomas 2001). The characteristic time, $\tau_{Diffusion}$, to reach this constant rate is determined by the diffusivity and the length of the stopper, d_{Rubber} , as (Crank 1975)

$$\tau_{Diffusion} = \frac{d_{Rubber}^2}{4D} \tag{3}$$

In the following, it is assumed that this time constant is small compared to those of other processes governing the development of the system, an assumption that is justified later. The transport through the stopper is thus assumed to be governed by Equation (2).

If gas is generated on the inside at a rate G , then the overall rate of change of matter in the gas phase is

$$\frac{dn}{dt} = G - p \frac{SA_{Rubber} D}{d_{Rubber}} \quad (4)$$

Expressed in terms of pressure, Equation (4) becomes

$$\frac{dp}{dt} = \frac{GRT}{V_{Gas}} - p \frac{SA_{Rubber} DRT}{d_{Rubber} V_{Gas}} \quad (5)$$

where R is the gas law constant, T is absolute temperature and V_{Gas} is the volume of the gas phase.

This is a first order ordinary differential equation of the form

$$\frac{dp}{dt} = a - bp \quad (6)$$

For the initial condition $p(0) = 0$, the solution to Equation (6) is

$$p = \frac{a}{b} [1 - \exp(-bt)] \quad (7)$$

or

$$p = \frac{Gd_{Rubber}}{SA_{Rubber} D} \left[1 - \exp\left(-\frac{SA_{Rubber} DRT}{d_{Rubber} V_{Gas}} t\right) \right] \quad (8)$$

As t tends to infinity, a steady state pressure, p_{SS} , is established where

$$p_{SS} = \frac{Gd_{Rubber}}{SA_{Rubber} D} \quad (9)$$

This pressure is thus solely determined by the gas generation rate and the properties of the stoppers. The characteristic time associated with the establishing of the steady state, τ_{SS} , is obtained directly from the exponential term in Equation (8) as

$$\tau_{SS} = \frac{d_{Rubber} V_{Gas}}{SA_{Rubber} DRT} \quad (10)$$

At time τ_{SS} , the pressure has increased to 63% of its final value p_{SS} according to Equations (8), (9) and (10). This time constant is independent of G , i.e. the time required to establish the steady state is independent of the gas generation rate. Rather, it is determined by the properties of the stoppers and of the gas phase.

Furthermore, the rate of pressure increase, when the pressure is low and the out diffusion is insignificant, is obtained by setting $p = 0$ in Equation (5) as

$$\frac{dp}{dt}_{Initial} = \frac{GRT}{V_{Gas}} \quad (11)$$

This rate is obviously dependent on the gas generation rate, but independent of any property of the stopper.

2. Application to conditions in Bengtsson et al. (2013)

At 25 °C, Brandrup et al. (1999) report the following for S and D of molecular hydrogen in poly(isobutene-*co*-isoprene) 98/2 (butyl rubber):

$$S = 3.55 \cdot 10^{-7} \text{ cc(STP)/(cm}^3 \cdot \text{Pa)}$$

$$D = 1.52 \cdot 10^{-6} \text{ cm}^2/\text{s} = 1.52 \cdot 10^{-10} \text{ m}^2/\text{s}$$

S is thus given as the amount of gas, expressed as the volume it occupies at STP, i.e. at 273 K and 1 atm, dissolved per unit volume of butyl rubber (in cm^3) and per unit pressure of the gas phase in contact with the stopper (in Pa). Converting to a molar concentration in the stopper, one gets

$$S = 3.55 \cdot 10^{-7} \text{ cc(STP)/(cm}^3 \cdot \text{Pa)} = 3.55 \cdot 10^{-7} \text{ cc} \cdot 1 \text{ atm} / (82.057 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \cdot 273.15 \text{ K}) / (\text{cm}^3 \cdot \text{Pa}) \approx 1.584 \cdot 10^{-11} \text{ mol}/(\text{cm}^3 \cdot \text{Pa}) = 1.584 \cdot 10^{-5} \text{ mol}/(\text{m}^3 \cdot \text{Pa})$$

According to Brandrup et al. (1999), S and D increase with temperature as

$$S = S_0 \exp\left(-\frac{2.5 \text{ kJ/mole}}{RT}\right) \quad (12)$$

and

$$D = D_0 \exp\left(-\frac{33.9 \text{ kJ/mole}}{RT}\right) \quad (13)$$

The temperature range in which these expressions are reported in Brandrup et al. (1999) is 25-50 °C. Assuming that the range can be extended to 70 °C, this means that, at 70 °C, the product $S \cdot D$ will increase by a factor $f_{70/25}$ compared to data for 25 °C where

$$f_{70/25} = \exp\left(\frac{(33.9 + 2.5) \cdot 10^3}{8.314} \frac{343 - 298}{298 \cdot 343}\right) \approx 6.87$$

Using these values and

$$d_{Rubber} = 0.014 \text{ m}$$

$$A_{Rubber} = \pi \cdot 0.007^2 \text{ m}^2 \approx 1.539 \cdot 10^{-4} \text{ m}^2$$

$$V_{Gas} = 5 \text{ mL} = 5 \cdot 10^{-6} \text{ m}^3$$

$$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$$

$$T = 70 \text{ }^\circ\text{C} = 343 \text{ K}$$

one obtains with Equation (10)

$$\tau_{SS} \approx \frac{0.014 \cdot 5 \cdot 10^{-6}}{1.584 \cdot 10^{-5} \cdot 1.539 \cdot 10^{-4} \cdot 1.52 \cdot 10^{-10} \cdot 6.87 \cdot 8.314 \cdot 343} \approx 9.64 \cdot 10^6 \text{ s} \approx 112 \text{ days}$$

This is in agreement with the times at which the pressure is observed to level off in many of the experiments reported in Bengtsson et al. (2013, Section 2.2).

It is hence concluded that the observed development of the pressure in the vials in many of the experiments reported in Bengtsson et al. (2013) may well be due to a balance between a continuing, relatively constant rate of production of hydrogen in the vials and an outward diffusion of hydrogen through the rubber stoppers.

3. Justification for assuming steady state diffusion in the stoppers

The assumption that the diffusion through the stoppers is approximated as being in steady state and hence described by Equation (2) is justified if the time constant for diffusion is much smaller than that to reach steady state, i.e. if $\tau_{Diffusion} \ll \tau_{SS}$. Combining Equations (3) and (10), this condition can be expressed as

$$S \ll \frac{4V_{Gas}}{d_{Rubber} A_{Rubber} RT} = \frac{4V_{Gas}}{V_{Rubber} RT} \quad (14)$$

This expression is the most direct way of evaluating the condition for steady state and it also demonstrates that the condition is independent of the diffusivity. For the understanding of the system behaviour it is though also interesting to calculate both τ_{SS} and $\tau_{Diffusion}$ explicitly. From the data above, $\tau_{Diffusion}$ is obtained as

$$\tau_{Diffusion} \approx \frac{0.014^2}{4 \cdot 1.52 \cdot 10^{-10} \cdot 6.02} \approx 5.4 \cdot 10^4 \text{ s} \approx 0.62 \text{ days}$$

The factor 6.02 is here obtained from Equation (13) as the increase in diffusivity in going from 25 °C to 70 °C. The calculated value of 0.62 days is much smaller than that of τ_{SS} (112 days, see above) and the steady state assumption is thus justified from this point of view.

It is also of interest to determine the fraction of hydrogen in the stoppers when steady state is established. If the pressure in the gas phase inside the vials is p , then this fraction is readily obtained from the solubility, S , and the volumes of the gas phase and the stoppers. At 25 °C and a H_2 pressure of p , a stopper contains $1.584 \cdot 10^{-5} \cdot p \cdot V_{Rubber}/2$ moles, while the gas phase in the vials contains $p \cdot V_{Gas}/(R \cdot 298)$ moles. Evaluating the expressions shows that less than one percent of the hydrogen is found in the stoppers in this case. Evaluating at 70 °C yields a similar result.

Hence steady state is established on a short time scale compared to τ_{SS} and the amount of hydrogen in the stoppers is small compared to that in the gas phase at steady state.

4. The case with an initial pressure and no gas generation

The pressure development for a case where the vial is initially filled with gas at partial pressure p_0 , and where there is no gas generation in the vial is readily obtained by solving Equation (5) for the case $G = 0$ and $p(0) = p_0$. The solution is

$$p = p_0 \exp\left(-\frac{t}{\tau_{SS}}\right) \quad (15)$$

This means that the pressure is expected to have dropped to roughly half the initial value at $t = \ln(2) \cdot \tau_{SS} \approx 78$ days at 70 °C.

Bengtsson et al. (2013, Section A1.3.2) have performed several tests of such cases and demonstrate that the results are compatible with Equation (15), using butyl rubber data from the same source as in this Memo. This further corroborates the interpretation of the levelling off of pressures observed in the experiments with a gas source in Bengtsson et al. (2013) as being a balance between gas generation and out diffusion.

5. Conclusions

It has been demonstrated that a constant hydrogen gas production rate in the experiments described in Bengtsson et al. (2013) is expected to lead to a steady state partial pressure of hydrogen in the gas phase in the vials as the production is balanced by out diffusion through the rubber stoppers. The time required to establish the steady state is estimated to be around 100 days. The observed levelling off of the pressure is thus compatible with a continuing gas production in the vials.

It has also been demonstrated that a test tube with only water and a gas phase will lose half its initial partial pressure of hydrogen gas through the stoppers in about 80 days, if there is no hydrogen in the external gas phase and if there is no hydrogen production in the vials.

It is also noted that the diffusion properties of the stoppers could be one of several sources of variability yielding the observed variability in the results in Bengtsson et al. (2013).

Longer exposure times than those in Bengtsson et al. (2013) could shed additional light on the establishment of steady state pressures in this system. Such experiments are underway.

Finally, it is noted that hydrogen potentially present in the gas phase outside the vials would affect the pressure development in the internal gas phase.

References

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