# The Fizz Keeper, a Case Study in Chemical Education, Equilibrium, and Kinetics

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Teachers of chemistry know that chemistry is both important and interesting. It is applicable to many situations encountered in every day life. We look for cases where there is clear evidence of chemical reactions occurring in situations well known to students. One excellent example is carbonated beverages. These are prepared and rendered more acidic by exposure to carbon dioxide gas at high pressures. We can describe the process by which they lose carbonation by the simple process, eq 1:

$$CO_2(aq) = CO_2(g) \qquad (1)$$
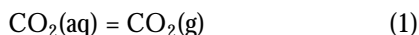
which has an equilibrium constant expression of the form:

$$K = P_{CO_2}/[CO_2]$$

The Fizz Keeper

This interesting chemistry was thoroughly discussed on the ChemEd-L list on the World Wide Web in connection with the Fizz Keeper, a simple plastic screw cap and pump shown in Figure 1. The discussion was initiated by Philip Reedy Jr. (*1*), who wrote:

> A colleague and I have been discussing a device known as the Fizz Keeper. It is a pump which can be screwed onto the top of plastic beverage bottles and is used to repressurize the bottles once they have been opened. The product claims that the increased pressure will maintain the carbonation in the beverage and keep it from going flat as quickly.

> It is my feeling that increasing the air pressure above the liquid will not affect the position of the equilibrium between gaseous CO_2 and dissolved CO_2, that the amount of each gas dissolved in the beverage depends on the partial pressure of that particular gas (Henry's law).

> I would appreciate any thoughts you might have regarding the Fizz Keeper and why you believe it will or will not work as claimed.

Equilibria

The Fizz Keeper pumps air, mostly N_2 and O_2, into the resealed bottle. Since neither of these gases is involved in reaction 1, they do not appear in the expression for the equilibrium constant.

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Figure 1. The Fizz Keeper.

The proper approach to disagreement in science is an appeal to experiment. If one watches carefully while using a Fizz Keeper, bubbles in the liquid can be seen to disappear as the pressure is increased. The pressure increase will reduce the size of any bubbles and increase the partial pressure of CO_2 in the bubble. This will shift the local equilibrium toward more dissolved carbon dioxide, and a bubble of CO_2 and H_2O gas should redissolve completely. Even in the head space there can be regions in which the partial pressure of CO_2 is temporarily increased, but adding another gas to a well-mixed gas space does not increase the partial pressure of the gases already present (primarily CO_2 in this case).

A resealed and repressurized bottle of a carbonated beverage will not be at equilibrium. The partial pressure of CO_2 in the head space will be less than atmospheric pressure, much lower than the partial pressure for equilibrium with the liquid phase. The amount of CO_2 in the head space at equilibrium will be given by the gas law, $n_i = P_i V/RT$. Adding O_2 and N_2 will not change the equilibrium value of P_i or V appreciably, so eventually the same amount of CO_2 will be lost from the liquid with or without the Fizz Keeper. In both cases the pressure will rise as the partial pressure of CO_2 increases from less than one atmosphere to the higher equilibrium value.

The rate of this pressure increase is measurable, and it will be affected by the presence of air. A complete consideration of the Fizz Keeper technology must include kinetics as well as equilibria.

Kinetics

Leaving the experimental study of the rates of approach to equilibrium as a laboratory problem for students, let us consider the kinetics from a theoretical viewpoint. Reaction 1 does not involve a chemical change, and equilibrium should be

rapidly established in a boundary layer. The rate-determining steps are diffusion or mixing in both the liquid and gas phases. Added O_2 and N_2 will remain primarily in the gas phase and will have negligible effects on mixing and diffusion within the liquid phase. They do affect the rate at which an equilibrium uniform composition is reached in the gas phase.

If the gas is predominantly CO_2, the pressure will rise or fall uniformly by gas flow, a fast process that will not limit the rate of approach to the new equilibrium. But diffusion in a gas primarily composed of other molecules is slow[1] for distances of centimeters or meters. The average distance moved by diffusion is

$$x = (2 D t)^{1/2}$$

where D is the diffusion coefficient in $cm^2\ s^{-1}$ and t is time in seconds. The diffusion coefficient for diffusion of CO_2 into air at one atmosphere pressure is 0.139 (2). Thus 10 hours is required for an average displacement of one meter, $t = 100^2/(2 \times 0.139) = 36,000$ s. The diffusion coefficient of gases is proportional to the mean free path and is thus inversely proportional to pressure. Estimating values of 3 atm and 10 cm for the Fizz Keeper diffusion problem gives $D = 0.046\ cm^2\ s^{-1}$ and $t = 1080$ s. Adding air to a pressure near 3 atm will measurably slow the rate of approach to equilibrium by diffusion in the gas phase. However, essentially the same equilibrium will eventually be reached, and the Fizz Keeper should be ineffective if the resealed bottle is to be stored for several days.

One simple and easy way to shift the equilibrium so that less carbonation is lost on storage of resealed pop is to reduce the gas volume. Thus the suggestion made on the ChemEd-L list of pouring the leftover pop into a smaller container, one that it nearly fills, should be much more effective than use of the Fizz Keeper device, provided one is very careful in pouring so as not to lose even more CO_2.

Stirring in either the liquid or gas will increase the rate of approach to equilibrium. The Fizz Keeper should not be expected to work unless the bottle is stationary. Students can also check this point experimentally.

At the high acidity of most carbonated beverages, the principal carbon species present is $CO_2(aq)$, and the situation is well described by reaction 1 alone. However, CO_2 is an acid anhydride, and carbonic acid and its ions are also present. The calculated equilibrium concentrations in Table 1 show that the concentrations of $H_2CO_3(aq)$ and of ions are small

and can be neglected to a first approximation. A discussion of the situation in a neutral liquid is deferred to the appendix.

Summary

The loss of CO_2 from carbonated beverages provides an interesting case of the combination of equilibrium and kinetic principles. Adding air with a pump like the Fizz Keeper has negligible effect on the various equilibria present, but will slow diffusion in the gas space of a resealed bottle, decreasing the rate at which equilibrium is reached. This rate effect can be observed experimentally (for instance, with a pressure sensor) or predicted by simple calculations as shown here.

Note

1. When we show that ammonia can be smelled by students in the back of a room, we are demonstrating *eddy diffusion*, not diffusion itself.

Literature Cited

1. Reedy, P. Archives for the ChemEd-L list for February 1997. URL *http://www.optc.com/chemed-l-thread/*.
2. *Handbook of Chemistry and Physics*, 49th ed.; Weast, R. C., Ed.; Chemical Rubber Company: Cleveland, OH, 1968; p F 47.

Appendix. Additional Chemical Steps

In nearly neutral solutions, as in blood, the concentration of bicarbonate ions is appreciable. In this case additional chemical reactions are required for the loss of HCO_3^-:

$$H^+(aq) + HCO_3^-(aq) = H_2CO_3(aq) \tag{2}$$
$$H_2CO_3(aq) = CO_2(aq) + H_2O(l) \tag{3}$$
$$CO_2(aq) = CO_2(g) \tag{1}$$
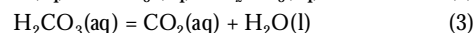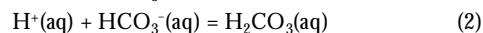
Simple acid–base reactions like step 2 are incredibly fast. Steps 3 and 1 are slower, rate-determining steps in this case.

The half-lives in step 3 are on the order of minutes. The first-order rate constant for reaction 3 is reported (A1) to be 8 s^{-1} at 13–14 °C. Combining this with the equilibrium constants $K_3 = k_3/k_{-3} = 1100$ (A1) and the first ionization constant for carbonic acid (A2):

$$K_a = 3.6 \times 10^{-7} = 1/(K_2 K_3) = [H^+][HCO_3^-]/[CO_2(aq)]$$

gives $K_2 k_3 = 20,000\ s^{-1}$ (or 2×10^4 L $mol^{-1}\ s^{-1}$ if one uses units for equilibrium constants, a useful convention for introductory chemistry). From this one can calculate a half-life for the bicarbonate ion of $0.693/(2.0 \times 10^{-3}) = 340$ s at a pH of 7.

In step 3 the coordination number of carbon changes from 3 to 2, and this is slow enough to give measurable rates of reaction. In fact the slowness of this step would be a problem for mammals if they did not have an effective enzyme present in their blood to catalyze it. Even increasing the surface area (as in a lung) or by shaking a bottle of pop does not immediately reduce the concentration of HCO_3^- ions to the new equilibrium value in the absence of a catalyst. However, we all know that shaking does increase the rate at which CO_2 comes out of solution, so diffusion within the liquid phase is also one of the rate-determining steps in this system.

References

A1. Saal, R. N. J. *Recl. Trav. Chim. Pays-Bas* **1928**, *47*, 264–285.
A2. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties*; *J. Phys. Chem. Ref. Data* **1982**, *11*(Suppl. 2).

Table 1. Calculated Equilibrium Concentrations in Pure Water at 298.15 K and 3.0 atm CO_2

Species	Conc/ mol L^{-1}
$CO_2(g)$	0.123
$CO_2(aq)$	0.103
$H_2CO_3(aq)$	0.00009
$H^+(aq)$	0.00021
$HCO_3^-(aq)$	0.00021