Spontaneous “Distillation.” Approaching Thermodynamic Equilibrium, A Marathon Experiment in Physical Chemistry

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Abstract: If the left side of a sealed tube (shaped like an inverted U) is filled with chloroform, after many months, the chloroform passes spontaneously to the right side of the vessel in accord with the minimum energy principle. A similar experiment with a half-filled disposable lighter can be performed successfully in a much shorter period (6–8 days). The rate of the process (spontaneous transfer of a substance from one side of the vessel to the other side) decays with time. Curve fitting reveals the existence of two independent exponential-decay processes. An explanation of the possible mechanisms for the transfer of the substance is offered in this paper.

Introduction

Marathon experiments (long-period experiments) [1] are experiments that may last from a couple of days to many years (the term supermarathon experiment seems to be appropriate for the latter). There are a few well-known examples of marathon experiments, for example, those demonstrating rusting of iron [2–3], osmosis [4], and diffusion [5]. These experiments and a number of their modifications are well known, believed to be perfectly understood (on a microscopic level), and are correspondingly well-explained in the literature.

The experiments offered in this paper are also part of the class of marathon experiments; however, to the best of our knowledge, they are not known or, at least, not mentioned in the literature. For a couple of years, the authors wondered whether such experiments could be performed at all. The brief discussion below is intended to give some basic details about the experiments.

Let us consider a sealed tube (an inverted U tube with a side arm), the left side of which is filled with chloroform (CCl_4 or any other low boiling nonflammable liquid may safely be used) as depicted in Figure 1a. Considering the vessel as the system of interest, it is intuitively clear (and could also be rigorously proved) that this is not an equilibrium state. The state depicted in Figure 1b, on the other hand, is an equilibrium state (An equilibrium state is, of course, characterized by a minimum of the Gibbs energy function of the system). Therefore, from a purely phenomenological thermodynamic point of view, it follows that there will be a tendency for transition of the system from the initial (Figure 1a) to the final (Figure 1b) state.

There is no doubt that such a transition (process) is feasible. The important question is “can it really be observed?” One thing that thermodynamics does not tell us is the time period required for the experiment (process) and this period is of vital importance. If, for example, many decades are needed for 1% of the chloroform to pass from the left-hand to the right-hand side of the vessel, the experiment is obviously of no use as a demonstration (not even as a supermarathon one). If, on the other hand, the process is practically complete in a few days, than it is an almost ideal and novel marathon experiment showing spontaneous changes in a closed system.

With this goal in mind and curious about the possible result, we decided to try the experiment in order to get some insight about the rate of the spontaneous process. The term spontaneous “distillation” was used in the title of this article. Of course, it is not really a distillation, for the system as a whole is in thermal equilibrium. The term mass transfer will be used later on.

The Vessel, Experimental Setup, and Measurements

The vessel is built from a graduated glass tube (a piece of broken burette). The height of the vessel is between 10 and 30 cm (we recommend a higher vessel for a faster rate of the process). The side-arm tube should be made from glass of the same quality as the burette. It is perhaps convenient to pass this part of the job to a glassblower (although those who are experienced can make the vessel themselves).

The left side of the vessel is almost filled with chloroform (use a syringe with an appropriate needle). Using a burner, carefully seal the side-arm tube (hold the right side of the vessel and turn its upper part slightly to the left to avoid flow of the liquid to the right). Hang the vessel over a nail of suitable size (3–5 cm) in a room with more or less constant temperature. Calculate the equilibrium level of the liquid (in an ideal case, it should be half of the initial height). This equilibrium height is taken as reference (zero height). During a long period (several months to several years), take readings of the chloroform level in the left side of the vessel.

Alternatively, a half-filled gas lighter (providing it is made of transparent plastic) may be used (Figure 2). Tilting the lighter in a horizontal position brings all the liquid (butane) into one of the compartments. A piece of graduated paper is fastened on the back of the lighter so that the liquid butane level can be read precisely. Calculate (or read experimentally) the equilibrium level (zero height) and use it as a reference. Read the butane level. The first three readings should be taken

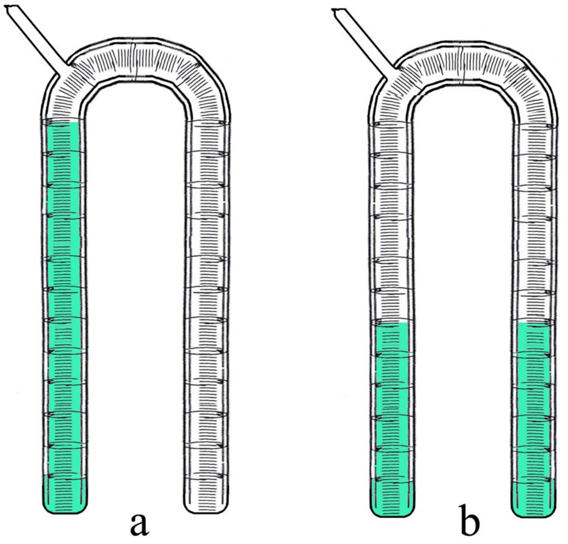

Figure 1. Initial (a) and equilibrium (b) state of the $CHCl_3$ liquid in the sealed inverted U tube (color is added for presentation purposes only).

Figure 2. The half-filled disposable lighter used in the second part of the experiment demonstrating spontaneous distillation.

every 10 min; increase the time interval between successive readings until you read the level once a day. Take the readings until the difference of the levels in the left and right compartments of the lighter is 1–2 mm (this usually takes about one week).

Theoretical Considerations

We start with the definition of the law of linearity [6]: the rate at which a given thermodynamic system approaches equilibrium is proportional to the thermodynamic driving force, which can always be shown as a gradient of some potential.

The driving force in our case is the height difference, $\Delta H = |H_L - H_R|$, between the levels of the liquid in the left-hand and right-hand tubes (or, corrected for zero height, the effective driving force is $h = \Delta H/2$); that is, the system tends to reach gravitational equilibrium. It is obvious that, providing the process of transfer of liquid occurs, the center of mass of the liquid in the system will move downward with time, thus lowering the gravitational potential energy (it is this energy that is equal to the effective part of the Gibbs free energy of the system). Assuming a single mechanism responsible for the change, one could write the law of linearity as:

$$dh/dt = -kh \qquad (1)$$

where t is the time and k is a constant characteristic of a given vessel. The minus sign, being written explicitly, ensures that k is always positive. By integration one obtains

$$h = h_o \exp(-kt) \qquad (2)$$

where h_o is one half of the initial difference between the levels of the liquid in the left-hand, H_{L_o}, and right-hand, H_{R_o}, sides of the vessel. Usually $H_{R_o} = 0$, in which case $h_o = H_{L_o}/2$. Note that this form of eq 2 is equivalent to the basic equation of radioactive decay.

What is the possible mechanism responsible for the transfer of substance? One possibility is that the mass transfer (an approach to equilibrium) is accomplished via the gas phase, and this indeed is analogous to distillation. Another possibility is that the liquid crawls up the wall between the two sides of the tube and then flows into the other (initially empty) part of the vessel (or disposable lighter). This mechanism (resembling tunneling through the potential energy barrier) is similar to the one known to occur in liquid helium II, which is the first known quantum liquid [7]. Of course, this is only an analogy, for liquid butane is definitely not a quantum liquid.

If any one of these two mechanisms is operative, the change of the level of the liquid with time may be described by eq 2. If, on the other hand, both mechanisms are effective, a more general equation may be written

$$h = A_1 \exp(-k_1t) + A_2 \exp(-k_2t) \qquad (2)$$

where the meaning of h and t is the same as in the above equations, k_1 and k_2 are the constants related to the two independent processes, and A_1 and A_2 are the amplitudes of the two processes. Based on purely physical reasoning, it is obvious that $A_1 + A_2 = h_o$, and also $A_1, A_2 > 0$.

We turn now to the experimental results and our attempts at their interpretation.

Results and Discussion

A vessel with a height of approximately 30 cm was used in the first variant of the experiment. The left side was filled with chloroform to the height of exactly 25 cm (meaning the zero height is 12.5 cm). Then it was sealed and was hung over a nail on a wall, in a room with more or less constant temperature [8]. It should be noted here that the initial chloroform level was about 3 cm lower than the barrier height.

About two months after the experiment was set up, it was obvious that a transfer of liquid from the left to the right tube had occurred. Readings of the $CHCl_3$ level were taken for

Table 1. Change in the Level of Chloroform in the Left Side of the Vessel with Time (Level Corrected for Zero Height)

t (days)	*h* (cm)
0	12.5
197	11.5
320	11.2
419	11.0
483	10.7
544	10.5
640	10.3
726	10.1
853	9.9
1005	9.5
1105	9.3

Table 2. Change in the Level (Height difference) of Butane in a Half-Filled Disposable Lighter (Level Corrected for Zero Height)

t (hours)	*h* (cm)
0.0	2.0
0.08	1.8
0.17	1.7
0.30	1.6
0.40	1.5
0.57	1.4
0.80	1.3
3.17	1.2
4.67	1.1
6.75	1.0
23.25	0.6
47.25	0.4
72.80	0.3
96.00	0.2
168.00	0.1

more than three years! The results (corrected for the zero height) are given in Table 1.

These data pairs were curve-fitted using a simple two-parameter exponential function of the form: $h = A \cdot \exp(-kt)$. The least-squares refinement gave the following results (the standard deviations given in parenthesis refer to the least significant digit):

$$A = 12.21(8) \text{ cm}$$

$$k = 0.0002545(106) \text{ d}^{-1}$$

$$R^2 = 0.9847$$

The correlation is highly significant (on the basis of statistical criteria). Note also that $A \approx 12.2$ cm, which is close to the theoretical value for h_o (12.5 cm). In this particular case, it seems safe to assume that a single mechanism is operative; however, on the basis of only one experiment, no definite answer about the nature of the mechanism of spontaneous mass transfer can be given (i.e., whether it occurs due to a distillation-like process or due to up-barrier crawling).

For a deeper understanding of the processes in question, a simpler and faster experiment with a half-filled, transparent, disposable butane gas lighter was performed (in this case, the butane level in the left-hand compartment of the lighter was only about 1 mm lower than the barrier height). The experiment was performed several times. The results of one representative experiment are given in Table 2 [9].

These data pairs were also fitted by a two-parameter exponential function. The results were

$$A = 1.356(113) \text{ cm}$$

$$k = 0.01780(145) \text{ h}^{-1}$$

$$R^2 = 0.9203$$

The results of the fit are much worse than in the previous case, suggesting that a single decay process may not be sufficient for a quantitative explanation of the phenomenon. This impression is even stronger when one looks at the data plot (cf. Figure 3).

We considered all of this a strong indication that both (competitive) exponential-decay processes (distillation-like and crawling) are operative in this case. This behavior strongly resembles the activity decay of a sample consisting of two generically independent radioactive nuclides [10]. In order to perform a proper statistical treatment, the following procedure was carried out: the last four data points (those taken several days after the initial moment) were analyzed statistically. This treatment gives the first-guess value for k_1 (regarding the slow exponential-decay process). The difference between actual and fitted (with the first-guess function) data was again fitted by a simple exponential function, giving the first-guess value for k_2 (for the fast decay process). Finally, a multiple nonlinear regression is performed, in which the h_{actual} data are fitted as

$$h_{\text{actual}} = A_1 \exp(-k_1^* t_{\text{actual}}) + A_2 \exp(-k_2^* t_{\text{actual}}) \qquad (2a)$$

(the asterisk denotes first guess values, obtained as explained above). In order to obtain results for this nonlinear regression (which is far from trivial), the following trick was used: h_{actual} was fitted as a bilinear function of $\exp(-k_1^* t_{\text{actual}})$ and $\exp(-k_2^* t_{\text{actual}})$ using multiple linear regression. As a next step, k_1 was varied (keeping k_2 constant) until a highest value of R^2 (the adjusted coefficient of determination) was obtained. Now, this (iterated, or improved) value of k_1 was kept constant while varying k_2. Then k_1 was iterated again, until finally there was no change in the R^2 statistics (self-consistency reached). The following results were obtained:

$$k_1 = 0.0223 \text{ h}^{-1}$$

$$k_2 = 2.310 \text{ h}^{-1}$$

$$A_1 = 1.203(26) \text{ cm}$$

$$A_2 = 0.766(49) \text{ cm}$$

$$R^2 = 0.9983$$

The value of the R^2 statistics is exceptionally high giving excellent fit (cf. Figure 4). Also, the sum of the amplitudes is 1.969 cm, within one standard deviation of the theoretical value of 2.00 cm.

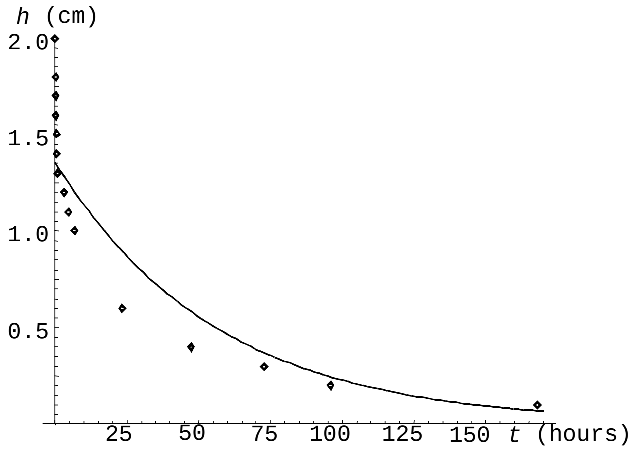

Figure 3. Data plot and best-fit function, assuming single processes (most probably distillation) are responsible for the spontaneous distillation in the disposable lighter.

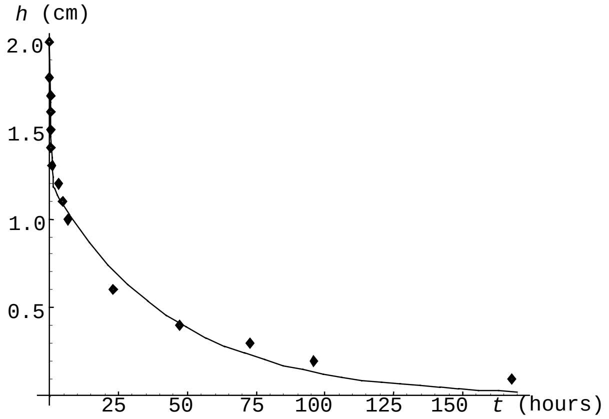

Figure 4. Data plot and best-fit function, assuming that two independent processes (distillation and crawling) are effective for the spontaneous distillation in the disposable lighter.

The principal difference between this experiment (liquefied butane in a lighter) and the previous one (chloroform in an inverted U tube) is in the barrier height. It is an order of magnitude lower in the butane-in-lighter experiment. The only logical explanation is that the fast decay process is due to up-barrier crawling of the liquid butane (and this is observed only when the barrier is a very shallow one), and the slow decay process is due to a distillation-like process (which does not depend on the barrier height, but rather on the level difference of the liquid in the left-hand and right-hand compartments).

Further experiments (with various vessels, different liquids, and at different temperatures) are currently in progress.

Conclusion

This is an original and very interesting experiment (the result is, perhaps, unexpected for some readers). We feel that it could be further improved using fluorinated hydrocarbons in a sealed glass vessel (expecting that this system would approach equilibrium much faster than when chloroform is used). If this improvement proves to be really efficient (if the whole process practically ends within one month or so), then this would be an excellent demonstration of a spontaneous process in a closed physical system. In any case, the cheap alternative with a half-filled disposable lighter will always work, although it may not look as attractive.

Safety Tips. Wear safety goggles while sealing the vessel. Halogenated hydrocarbons are toxic substances, and some of them are suspected to cause cancer. Avoid spilling and swallowing the liquid, or inhaling the vapor. For safety reasons, the sealing of the side-arm tube should be done in a hood.

References and Notes

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8. Actually, as described (hanging the tube over a nail on a wall) the experiment is not performed under isothermal conditions. The temperature variation during one year in the room where the tube was placed was about 5 K, and this certainly has an influence on the basic process (mass transfer). Temperature variations induce vapor pressure fluctuations. When the vapor pressure falls (due to a decrease in temperature) part of the vapor condenses and this condensation occurs in both the left and right sides of the vessel (with a probability proportional to the available glass surface). In this way, the liquid may be thought of as being "pumped" from the left to the right side of the vessel. With large temperature variations, this mechanism (a very slow distillation) may become very important. A parallel (still running) experiment with a lower barrier was started in the summer of 2000. The extent of mass transfer was comparable to that in the present experiment, although the temperature variations were smaller. This suggests that the slow distillation mechanism is probably not the dominant one under the conditions of the experiment. Of course, it is desirable to study this process under true isothermal conditions (this we could not do because we do not have a reliable and precise thermostat).
9. The temperature variations in this experiment are, naturally, much less (about 1 K), due to the appreciably shorter time period required for completion. This strongly suggests that slow distillation (induced by temperature variations) is only of secondary importance.
10. Friedlander, G.; Kennedy, J. W. *Nuclear and Radiochemistry* (Revised Version of *Introduction to Radiochemistry*); Wiley & Sons: New York, 1956, Chapter V.