



Thermodynamic Computer Simulations An Educational Java-Script

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Introduction

Entropy is often introduced to the student using abstract notions such as *disorder* or *information density*. Although these interpretations of the entity entropy proved to be very powerful in scientific research, the standard chemistry student with little interest in maths or physics has difficulties to apply these ideas to everyday lab problems.

Entropy has this unique property to produce itself from its own flow. Of course, it is possible to demonstrate this effect in a standard lab experiment. As the entropy production caused by the entropy flow is small, it is necessary to use thermal insulators to prevent artefacts from external entropy sources. Those insulators are not necessary in a simulation. The simulation highlights the original simplicity of the thermodynamic experiment and this principal benefit of a simulation should be exploited more often in chemistry courses.

The Experiment

It is possible to measure entropy directly with an ice-water calorimeter (on the right side of the figure 1). As entropy flows into the ice-water calorimeter, some ice melts. Ice has a lower density than water and the transformation from ice to water is therefore accompanied by a volume reduction of the ice-water mixture. Consequently, the water level in the calorimeter decreases ($\Delta h < 0$).

$$\Delta h = \frac{\Delta S}{\pi r^2 S_m} \cdot \frac{\rho_{\text{ice}} - \rho_{\text{water}}}{\rho_{\text{water}} \cdot \rho_{\text{ice}}} = \frac{-\Delta S}{r^2} \cdot 23.286 \frac{\text{K mm}^3}{\text{J}} \quad (1)$$

ΔS is the amount of entropy flown into the calorimeter, S_m the entropy change of melting, ρ the density of water or ice and r the capillary radius. Equation (1) shows very well that the resolution of any entropy measurement is solely determined by the capillary radius r .

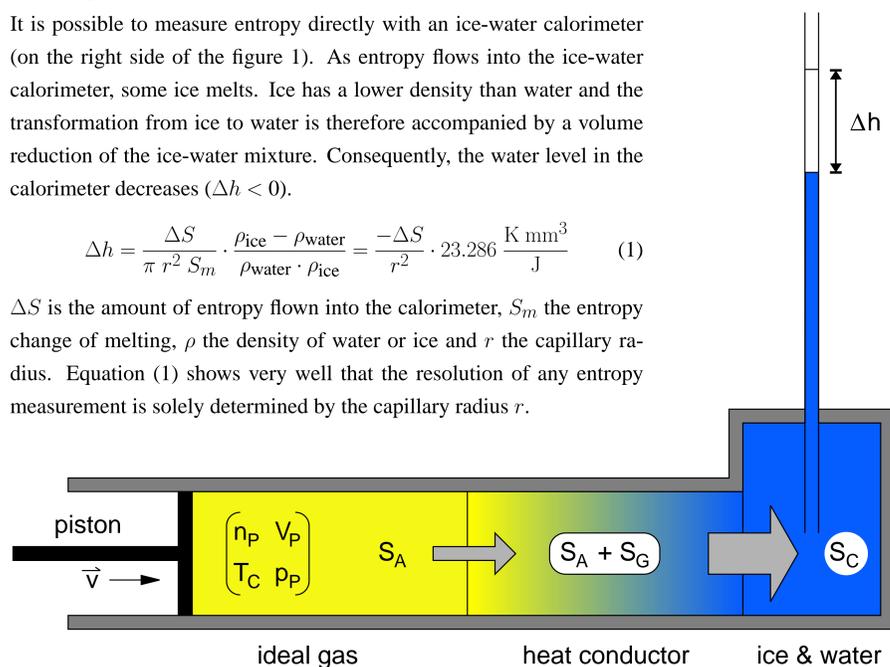


Figure 1 The simulated experiment.

The entropy source in the experiment is an ideal gas (n_P, V_P, p_P) confined in a piston. The gas has the temperature of the calorimeter ($T_C = 273.15 \text{ K}$) and as the plunger moves down the piston with the velocity \vec{v} , the gas heats up ($T > T_C$). The entropy S_A leaking from the piston can be computed from the work dW done on the ideal gas

$$dW = -p_P \cdot dV_P = -T \cdot dS_A + c_V \cdot dT \quad \Rightarrow \quad dS_A = \frac{p_P \cdot dV_P + c_V \cdot dT}{T} \quad (2)$$

c_V is the heat capacity of the gas. $-T \cdot dS_A$ is equal to the amount of energy leaving the piston with dS_A and $c_V \cdot dT$ is equal to the energy used to heat up the gas. As indicated in Figure 1, the size of dS_A is controlled by the choice of the heat conductor. As dS_A flows along the temperature gradient, entropy dS_G is generated. The size of dS_G can be calculated from a simple energetic argument. The energy entering the heat conductor with dS_A is equal to $T \cdot dS_A$ whereas the energy leaving the conductor at the calorimeter is equal to $T_C \cdot dS_A$. The energy difference $(T - T_C) \cdot dS_A$ is used to generate dS_G and hence we obtain for dS_G entering the calorimeter

$$dS_G = \frac{(T - T_C) \cdot dS_A}{T_C} \quad (3)$$

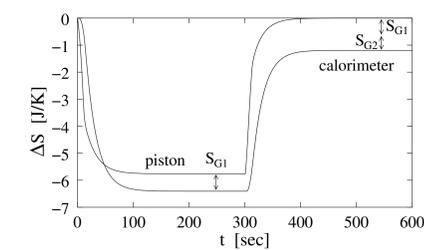
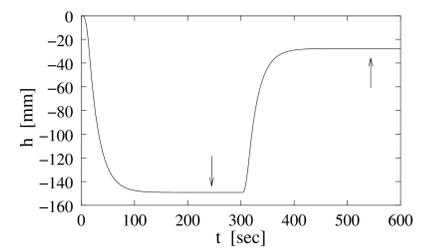
The change in the capillary level Δh is therefore determined by the sum of both entropies dS_A and dS_G and it is impossible to distinguish them. Now, the plunger is brought back into its original position and the system is allowed to equilibrate again ($T = T_C$). At the end of the experiment the gas in the piston is in the same state as at the beginning and the entropy S_A , which was forced out of the gas on compression, returned from the calorimeter into the gas on expansion. The only difference between the start and the end of the experiment is the level of the calorimeter capillary. The capillary level is lower at the end of the experiment than at the beginning. This decrease is solely caused by the newly generated entropy S_G as S_A was moved back and forth between the calorimeter and the piston.

Computational Set Up

The user can select the ideal gas in the piston by its heat capacity c_V , its initial pressure p_P and its amount n_P , whereas the remaining gas data are computed by the program from the gas law. The selection of the heat conductor is much simpler: 11 materials ranging from *diamond* to *styrofoam* are stored in an internal database. It is possible to choose the velocities of compression \vec{v}_1 and expansion \vec{v}_2 independently from each other and the extent of compression is described by a factor $V_{\text{fac}} = V_P/V_{\text{min}}$.

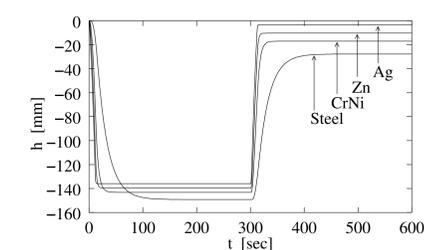
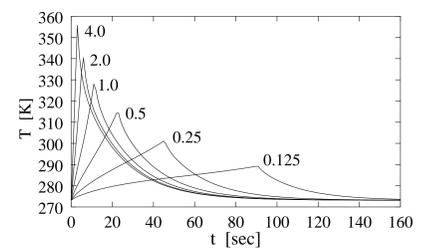
Possible Computer Experiments

The figure display the result of a typical computer experiment with our teaching applet. The ideal gas ($c_V = 1.5 R$, $n_P = 1 \text{ mol}$, $T_C = 273.15 \text{ K}$) is compressed and expanded with a velocity of $|\vec{v}| = 1 \text{ l/s}$ and each phase of the experiment was simulated for 300 seconds. Steel was chosen as heat conductor and thermal equilibrium was reached for the first time after 240 seconds (marked with an arrow). As predicted by theory, the water level in the capillary does not reach its original value. The student may try to vary the experiment in order to minimize this effect. But, the gauge reading will never return to its initial value.



This figure provides an explanation for the residual entropy in the ice-water calorimeter by plotting the entropy change $\Delta S = \int dS$ in the piston and in the calorimeter. The sign of ΔS for the calorimeter has been inverted to simplify the comparison of both graphs. Whereas the entropy change in the piston is caused by S_A , the change in the calorimeter is caused by S_A and S_G . The difference between both curves ($t < 300 \text{ sec}$) is equal to S_G . The index "G1" indicates, that this part of S was produced during the compression. As the gas expands again, entropy flows from the calorimeter into the gas. And again, entropy is generated – this time called S_G2 . This *extra*-entropy flows also into the gas and it is therefore not necessary to remove S_A completely from the calorimeter.

The Figure on the right side shows the gas temperature as a function of the plunger velocity \vec{v}_1 ($0.125 \text{ l/s} \leq \vec{v}_1 \leq 4 \text{ l/s}$) and time t . The *adiabatic* temperature of 476.22 K was not reached in the simulation; even at very high velocities. This observation can be explained with the heat conducting steel bottom of the piston. As the gas heats up in the piston, the tendency of entropy to leave the piston via heat conduction also increases. Since a process is labelled as *adiabatic* for $dS = 0$, it is impossible to observe a purely *adiabatic* process in the simulation. On the other side, the label *isothermal* is used for a process with $dT = 0$. Because S_A needs some time to leave the piston by heat conduction, the gas will always heat up on compression, even if the gas is compressed very slowly. Further, such a temperature increase is absolutely unavoidable, since entropy needs the temperature gradient to move.



The influence of the chosen heat conductor on the capillary reading is shown in the figure on the left side. Steel, the worst heat conductor in the series, causes the strongest effect. This result can be explained easily using equation (3), as the entropy production S_G increases with the gas temperature T in the piston, and the worst heat conductor with the smallest entropy leakage creates the highest temperature rise on gas compression. It is therefore possible to observe a nearly reversible result ($\Delta h \approx 0$), if a good heat conductor (eg. silver) is used for the simulation. The simulation can therefore be used to demonstrate *isothermal* (good heat conductor, low plunger velocity) and *adiabatic* (high plunger velocities, bad heat conductor) behavior as the limiting cases of the same experiment.

Applet Distribution

The simulation program has been transformed into a platform independent Java-Applet. The applet and additional material is freely available for teaching purposes at

<http://www.job-stiftung.de/ECCC9>

Questions concerning the program should be sent to

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Timm.Lankau@Job-Stiftung.de	simulation algorithm
Georg.Job@gmx.de	general concept

Although the program is offered to the public for free, we would be happy to get a short e-mail, if and how you use the Applet for teaching.