Notes on the First Law of Thermodynamics Chemistry CHEM 213W

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1. Zeroth Law of Thermodynamics

If two bodies at equilibrium are brought into thermal (i.e., no mechanical, electrical, magnetic, gravitational, etc., work is performed) and nothing happens, then they are at the same temperature.

Given this, we can always measure the temperature of any system by bringing it into thermal contact with some standard thermometer. As we shall see, a very convenient choice is the ideal-gas thermometer. Here a manometer is used to measure the pressure of a fixed amount of gas in a fixed volume and the relation

\[ V = \frac{NRT}{P} \]

is used to calculate the temperature. Needless to say, other temperature standards can (and are) used.

2. Some Definitions

**Intensive**

Doesn’t depend on the size of the system; e.g., P, T, partial molar quantities.

**Extensive**

The opposite of intensive; e.g., mass, volume, energy (but not energy per unit volume or mass), heat capacities (but not specific heats).

**System**

The part of the universe under investigation. Systems can be:

a) Isolated: no interaction of any kind with surroundings. Note that real systems cannot be truly isolated, but can be approximately so on the time-scale of relevance.

b) Closed: energy can be exchanged with surroundings, but matter cannot.

c) Open: matter and energy can be exchanged.

**Surroundings**

The part of the universe not under investigation.

**Boundary**

What divides the system from the surroundings (and controls whether the system is open, closed, or isolated).

**State**

A system’s state is specified when all measurable properties have definite values to the accuracy of the experiment.

**State Variables**

A set of measurable quantities, which when known, completely specify the state of the system. In classical or quantum mechanics there are on
the order of $10^{23}$ state variables; however, in thermodynamics, experience tells us that the **macroscopic** state of the system is specified after a small set of measurements are made (e.g., $T$, $P$, $V$, $x_1, \ldots, x_r$).

**Process**

Something whereby the state of a system is changed. A process has two parts:

a) Initial and final states (i.e., where the system starts and ends).

b) Path. The path describes how the change was effected. In order to specify the path, intermediate changes in the system, surroundings and boundary must be specified. This is clearly something which we would like to avoid in many cases.

**Reversible**

A process is said to be reversible if it is possible to return **both** the system and the surroundings to their original state. If not, it is irreversible (even if the system can be returned to the original state).

**State Function**

A property of the system which only depends on the current state of the system. Hence, changes in state functions do not depend on the path taken. State functions play a key role in thermodynamics and allow macroscopic properties of matter to be studied in a rigorous, systematic manner. Examples of state functions are: energy, entropy (to be introduced later), $P$, $V$, $T$, etc. A one-component ideal gas has a pressure, $P(T,N,V)$, given by $PV=NRT$ no matter what--how the $T$, $V$, or $N$ attained their current values is irrelevant.
3. Euler’s Theorem, Partial Molar Quantities, and the Gibbs-Duhem Relations

Next consider any extensive quantity in a mixture containing $r$ components; i.e., $A(T, P, N_1, \cdots, N_r)$. Real examples could be the energy, volume, mass, heat capacity, etc. Consider the small change in $A$ associated with changes in its arguments, namely

$$dA = \left( \frac{\partial A}{\partial T} \right)_{P,N_1,\cdots,N_r} dT + \left( \frac{\partial A}{\partial P} \right)_{T,N_1,\cdots,N_r} dP$$

$$+ \left( \frac{\partial A}{\partial N_1} \right)_{T,P,N_2,\cdots,N_r} dN_1 + \cdots + \left( \frac{\partial A}{\partial N_r} \right)_{T,P,N_1,\cdots,N_{r-1}} dN_r,$$

(1)

Now, by assumption, $A$ is extensive; hence,

$$A(T, P, \lambda N_1, \cdots, \lambda N_r) = \lambda A(T, P, N_1, \cdots, N_r).$$

(2)

If we differentiate both sides of this equation with respect to $\lambda$ and evaluate the answer at $\lambda = 1$ it follows that

$$A(T, P, N_1, \cdots, N_r) = \left( \frac{\partial A}{\partial N_1} \right)_{T,P,N_2,\cdots,N_r} N_1 + \cdots + \left( \frac{\partial A}{\partial N_r} \right)_{T,P,N_1,\cdots,N_{r-1}} N_r$$

$$\equiv \sum_{i=1}^r \bar{A}_i N_i,$$

(3)

(4)

where

$$\bar{A}_i \equiv \left( \frac{\partial A}{\partial N_i} \right)_{T,P,N_{j\neq i}}$$

(5)

is called a partial molar quantity. Note that the partial molar quantities are intensive. In obtaining Eq. (3) you may use Eq. (1) for $dT = dP = 0$ and $d(\lambda N_i) = N_i d\lambda$ for $i = 1, \cdots, r$. Also note that Eq. (3) is a special case of Euler’s theorem for homogeneous functions in calculus.

Equations (3) or (4) allow us to explicitly express the nontrivial features of an extensive quantity in terms of intensive ones, thereby reducing the number of dependencies we must worry about. It also turns out that the partial molar quantities (or more specifically changes in them) are not all independent. To see this, we calculate $dA$ from Eq. (4):

$$dA = \sum_{i=1}^r \bar{A}_i dN_i + N_i d\bar{A}_i,$$

(6)

where we have used the calculus result $d(xy) = xdy + ydx$. Of course, $dA$ could have been computed from Eq. (1); i.e.,

$$dA = \left( \frac{\partial A}{\partial T} \right)_{P,N_1,\cdots,N_r} dT + \left( \frac{\partial A}{\partial P} \right)_{T,N_1,\cdots,N_r} dP + \sum_{i=1}^r \bar{A}_i dN_i,$$

(7)

where we have rewritten the derivatives with respect to the numbers of moles in terms of the partial molar quantities, cf. Eq. (5). By equating the right hand sides of Eqs. (6) and (7) it follows that
\[
\left( \frac{\partial A}{\partial T} \right)_{P,N_1,\ldots,N_r} \, dT + \left( \frac{\partial A}{\partial P} \right)_{T,N_1,\ldots,N_r} \, dP - \sum_{i=1}^{r} N_i \, d\bar{A}_i = 0
\]  

(8)

and hence, the changes in the partial molar quantities and other derivatives are not all independent. Equation (8) is known as a Gibbs-Duhem relation and can be used to relate seemingly disparate thermodynamic derivatives.

As an exercise, what are the partial molar volumes for an ideal gas mixture obeying Dalton’s law of partial pressures? Do they obey the Gibbs-Duhem relation?

4. Work and Heat in Thermodynamics

Two central concepts in thermodynamics are work and heat. You probably have seen examples of the former in your freshman physics class, and the latter is something you experience in daily life. In thermodynamics, both have very precise definitions.

Work: anything which crosses the boundary of the system and is completely convertible into the lifting of a weight in the surroundings.

Note that work only appears at the boundary of a system, during a change of state, is extensive, and is manifested by an effect in the surroundings. From mechanics, we know that

\[
dW = F \, dx = mg \, dx,
\]

where dW is the incremental work done by the system, F is the force, and dx is the distance traversed. The second equality is for moving a mass m a distance dx in a gravitational field (g is the gravitational acceleration constant). Consider the following apparatus:

The inside of the piston is filled with some gas at pressure P and is maintained at constant temperature T. Instead of characterizing the work done in terms of the mass, it is more convenient to introduce the pressure exerted on the top of the piston (i.e., force per unit area, A)

\[
P_{op} \equiv \frac{F}{A} = \frac{mg}{A}.
\]

Note that \(P_{op}\) need not equal P.

Thus

\[
dW = P_{op} A dx = P_{op} dV
\]

where dV is the incremental change in the volume of the system. The work involved in these sorts of processes is known as pressure-volume work.

Note that the work done is not a state function—it depends on the pressure exerted on the piston (the path) and is not simply a function of the state of the gas in the piston. To stress this fact, the notation \(\delta W\) will be used for infinitesimal changes in quantities which depend on the path.

For an process whereby the gas is expanded against some pressure, \(dV > 0\), and hence, \(\delta W > 0\). Conversely, in a compression process, \(\delta W < 0\), i.e., negative work is done by the system. The surroundings do positive work on the system.
This diagram shows a process for the isothermal expansion of a gas (in this case an ideal gas). The solid curve gives the pressure of the gas (i.e., its equation of state). The dotted curve gives the opposing pressure actually used in the expansion. Note that the latter lies completely below the former. If at any point this were not the case, then the expansion would not proceed spontaneously (i.e., the opposing pressure would be too large and the gas would contract).

The total work done by the system is just the area under the dotted curve:

\[ W = \int_{V_{\text{initial}}}^{V_{\text{final}}} P_{\text{op}}(V) dV \leq \int_{V_{\text{initial}}}^{V_{\text{final}}} P(V) dV \equiv W_{\text{rev}}. \]

If the gas inside the piston is ideal, then the ideal-gas equation of state is valid and

\[ W_{\text{rev}} = \int_{V_{\text{initial}}}^{V_{\text{final}}} \frac{NRT}{V} dV = NRT \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right). \]

Note that the maximum work you can get out of a spontaneous expansion is obtained when the opposing pressure is infinitesimally less than the pressure being exerted by the gas in the piston. In this case, \( W = W_R \). Unfortunately, the rate of such an expansion would be zero, as would be the power delivered by the system. On the other hand, it is easy to show that the path given by \( P_{\text{op}} = P \) is the only reversible one for the isothermal expansion of an ideal gas.

Consider the following apparatus (from L. K. Nash, *Elements of Chemical Thermodynamics*, Addison-Wesley, 1970):

The spring is assumed to obey Hooke’s law (i.e., the force is proportional to the elongation). A
series of experiments are performed whereby weights are moved to pan from platforms at various heights in the surroundings. In doing so, the system (the spring and pan) move from state I to II. How much work is performed in each of the cases (a)–(c) (assume that there is a total 1cm elongation of the spring and ignore the mass of the pan and spring)?

In order to reverse the process (i.e., the expansion of the spring) the weights are moved back to the adjacent platforms. However, it is easy to see that while the spring will be fully compressed at the end of the experiment, the surroundings will not be restored to their initial state; specifically, in the best case, the topmost weight will be transferred to the lowest platform, no matter how many platforms are used. Clearly the biggest change in the surroundings will happen in case (a) and the smallest in (c). Moreover, the smaller the individual weights we use, the more reversible the process becomes (i.e., the change to the surroundings decreases). The process is reversible in the limit where the applied force (the weight) is only infinitesimally more than the force exerted by the spring.

This argument can easily be extended to our discussion of pressure-volume work or to other kinds of work. Hence, the maximum work in a P-V expansion is obtained for a reversible path.

Another key quantity in thermodynamics is heat.

Heat: Anything which flows across the boundary of a system by virtue of a temperature difference between the system and the surroundings.

Heat is quantified by measuring the temperature rise (or fall) in a standard material (e.g., a calorie corresponds to the amount of heat required to raise the temperature of 1 g of water 1 °C). Like work, heat appears only at the boundary of a system, during a change of state, is extensive, and is manifested by an effect in the surroundings. It is also not a state function since it depends on the nature of the thermal contact allowed at the boundary of the system.

In a classic set of experiments in the 19th century, J. P. Joule showed that the same changes in the state of a system could be achieved by either adding work or heat to the system. One of his devices is shown below.

As the weight falls, the paddles turn and heat up the liquid in the container by friction (viscous heating). The same temperature rise can be achieved by directly heating the container using a known amount of heat.

The amounts of heat and work were definite and Joule concluded that work and heat were simply two different ways in which energy could be added to a system. Specifically, Joule showed that

\[ 1 \text{ calorie} = 4.184 \text{ kg m}^2/\text{sec}^2. \]

We are now ready to state the first law of thermodynamics. Before doing so, it is illustrative to consider energy in classical mechanics.
5. Energy in Classical Mechanics

You probably have heard the statement that "energy is conserved." What does this mean exactly? Consider a system comprised of N point particles of mass \( m \), at positions \( \mathbf{r}_1, \ldots, \mathbf{r}_N \), and moving with velocities \( \mathbf{v}_1, \ldots, \mathbf{v}_N \). The system is not subjected to any external forces. In addition, assume that Newton’s laws of motion are valid and that the particles interact via pairwise additive forces which are derivable from a potential; i.e., the force particle i exerts on j, \( \mathbf{F}_{i,j} \), is given by

\[
\mathbf{F}_{i,j} = -\frac{\partial u_{i,j}}{\partial \mathbf{r}_j}.
\]

Consider the energy function, \( E \), defined as

\[
E = \sum_{i=1}^{N} \frac{m}{2} \mathbf{v}_i^2 + \frac{1}{2} \sum_{i \neq j}^{N} \sum_{j=1}^{N} u_{i,j}.
\]

How does \( E \) change as the particles move around under the action of Newton’s Laws?

\[
\frac{dE}{dt} = \sum_{i=1}^{N} m \mathbf{v}_i \cdot \mathbf{F}_i - \frac{1}{2} \sum_{i \neq j}^{N} \sum_{j=1}^{N} \mathbf{F}_{i,j} \cdot (\mathbf{v}_i - \mathbf{v}_j),
\]

where \( \mathbf{F}_i \equiv \sum_{j \neq i} \mathbf{F}_{i,j} \) is the total force acting on the \( i \)'th particle. Using this definition of \( \mathbf{F}_i \) in our expression for the rate of change of \( E \) gives:

\[
\frac{dE}{dt} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{F}_{i,j} + \mathbf{F}_{j,i}) \cdot (\mathbf{v}_i + \mathbf{v}_j)
\]

\[
= \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{F}_{i,j} + \mathbf{F}_{j,i}) \cdot \mathbf{v}_i
\]

where the dummy summation indices, \( i \) and \( j \), were exchanged for the terms in \( \mathbf{v}_j \) in obtaining the last equality. Newton’s third law states that \( \mathbf{F}_{i,j} = -\mathbf{F}_{j,i} \); i.e., the force i exerts on j is equal and opposite to that j exerts on i. Using this in our last expression immediately shows that

\[
\frac{dE}{dt} = 0.
\]

In other words, the energy of our classical system of particles doesn’t change in time or is conserved. The same is true under the laws of quantum mechanics. What happens if, in addition to the forces acting between the particles, the particles are subjected to an external forces?

The first law of thermodynamics also has something to say about changes in energy, although not in precisely the same way as in classical or quantum mechanics

6. The First Law of Thermodynamics:

In any cyclic process (i.e., one where the system returns to its initial state) the net heat absorbed by the system is equal to the work produced by the system.

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Suppose this were not the case. Then you could presumably find a process which produced more work than it absorbed heat. This extra work could be used to run a generator, which in turn could be used to produce more heat, which could run more of process, producing even more excess work, and so on. The energy crisis, electric bills, etc. would be things of the past. Unfortunately, no such device has ever been built and the first law still stands.

In mathematical terms, the first law implies that there is a state function, called the internal energy of the system, defined up to an arbitrary additive constant through its differential

\[ dE \equiv \dot{\tau} Q - \dot{\tau} W, \]

where \( \dot{\tau} W \) is the work done by the system (the negative of the work done on the system). For a finite change of state, the change in the internal energy, \( \Delta E \), is given by

\[ \Delta E = \int_{\text{initial state}}^{\text{final state}} \dot{\tau} Q - \dot{\tau} W. \]

The first law states that

\[ \int dE = \int \dot{\tau} Q - \int \dot{\tau} W = 0. \]

The first law implies that the energy change computed along different paths must give the same answer. If not, two such paths could be used to build the energy-creating device discussed above (i.e., by reversing one of the paths).