

Sept. 11 2002: Lecture 4:

## State Variables and Functions

### Last Time

#### Microscopic Variables versus Macroscopic Variables

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#### Extensive versus Intensive Variable

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#### Canonical Conjugates

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#### Derived Quantities or Densities

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#### Zeroeth Law of Thermodynamics: Temperature

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## State Functions

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A state function is a relationship between thermodynamic quantities—what it means is that if you have  $N$  thermodynamic variables that describe the system that you are interested in and you have a state function, then you can specify  $N - 1$  of the variables and the other is determined by the state function.

A state function is a model for a material or a system.

Note that the definition of a state function implies a dependence between some variable and the *current* value of the other thermodynamic values—in other words, it doesn't matter *how* the system arrived at a certain state. State functions cannot depend on the any of the prior processes—state functions are history-independent.

Question: Can you write an equation that describes how far the lecturer is located from the corner of the room?

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Question: Is the distance of the lecturer from the corner of the room a state function? What are the variables?

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Question: Can you write a differential expression for this distance in terms of its variables?

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Question: What assumptions have been made in writing down the model for distance?

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Question: Imagine that you have closed your eyes for a few seconds and the lecturer walks to a new location in the room, can you write an equation expressing how far he has walked?

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Question: Is the 'distance the lecturer has walked' a state function?

Question: If the 'distance the lecturer has walked' is not a state function, is there any modification to the phrase that would make it a state function?

### Some Example State Functions

Pressure could be a state function of the variables,  $N$  the number of atoms present,  $V$  the volume of the container, and  $T$  the temperature:

$$P = f(N, V, T) \quad (4-1)$$

This says that we can pick any of the three and the fourth is determined by equilibrium properties of the material.

Note that the word pressure plays two roles here! One role is as a thermodynamic variable that could be measured and the other is the name of some function. Another way to think of this is that for *an arbitrary system*, there is no reason to expect that there might be a function called pressure that relates to only  $N$ ,  $V$ , and  $T$  but there is nothing preventing us from measuring the pressure anyways. However, if we are considering an ideal gas model for our system, then there is a function  $P = P(N, V, T)$  which tells us that we need not bother to measure  $P$  if we know  $N$ ,  $V$ , and  $T$ —or we can use our knowledge of  $P(N, V, T)$  for an ideal gas to construct a pressure gauge.

Another state function is total number of molecules or atoms:

$$N^{\text{total}} = q(N_1, N_2, N_3, \dots, N_C) \quad (N^{\text{total}} = \sum_{i=1}^C N_i) \quad (4-2)$$

Total mass:

$$M = g(N_1, N_2, N_3, \dots, N_C) \quad (M = \sum_{i=1}^C N_i MW_i) \quad (4-3)$$


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## Derived Variables

Last time we introduced two different kinds of thermodynamic variables: Extensive and Intensive

Intensive variables can be specified point by point; i.e.

$P(x, y, z)$	Pressure
$T(x, y, z)$	Temperature
$\vec{E}(x, y, z)$	Electric Field
$\phi(x, y, z)$	Electrostatic Potential ( $\nabla\phi = -\vec{E}$ )
$\vec{H}(x, y, z)$	Magnetic Field

They do not depend on the size of the body.

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**Extensive variables** depend on the size of the system in question. They are additive.

$$\begin{aligned} M_{1+2} &= M_1 + M_2 \\ N_j^{\alpha+\beta} &= N_j^\alpha + N_j^\beta \\ V^{\alpha+\beta} &= V^\alpha + V^\beta \end{aligned} \quad (4-4)$$

We can define “derived quantities” (or densities) by scaling:<sup>6</sup>

$$\frac{\text{some Extensive quantity}}{\text{some other Extensive quantity}} \quad (4-5)$$

and size of system drops out and these quantities are not additive.

However, the derived intensive quantities still ‘act’ like extensive quantities regarding where they appear in ‘work’ terms:

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<sup>6</sup>I prefer the name derived intensive quantities over the name density. I would prefer to reserve density for those derived extensive quantities that are scaled by dividing through by total volume.

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Extensive variables can be distinguished from intensive variables by the way they add when you add two systems at equilibrium (See Eq. 3-2). Derived quantities don't sum like extensive or intensive quantities, but one can derive a rule for their addition. The trick involves realizing that the derived quantities are "extensive variables in hiding." One can turn them into extensive variables and then use the appropriate rule to add, for instance, consider the combined density,  $\rho_{AB}$  of two bodies with volumes  $V_A$ ,  $V_B$ , and masses  $M_A$ ,  $M_B$ :

$$\begin{aligned}\rho_{AB} &= \frac{M_A + M_B}{V_A + V_B} = \frac{V_A}{V_A + V_B} \frac{M_A}{V_A} + \frac{V_B}{V_A + V_B} \frac{M_B}{V_B} \\ &= \frac{V_A}{V_A + V_B} \rho_A + \frac{V_B}{V_A + V_B} \rho_B = f_A \rho_A + f_B \rho_B\end{aligned}\quad (4-6)$$

where the  $f_i$  are volume fractions. The derived quantities or densities have a "weighted addition" rule.

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Examples of derived intensive quantities are:

$$\rho = \frac{M}{V} \quad (4-7)$$

$$\rho_j = \frac{MW_j N_j}{V N_{\text{avag.}}} \equiv \frac{MW_j \overline{N}_j}{V} \frac{N_{\text{total}}}{N_{\text{avag.}}} \quad (4-8)$$


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This last equation introduces another derived intensive quantity called a **molar** quantity:

$$\frac{\text{Extensive variable}}{\text{Total Number of moles}} = \frac{\text{Extensive variable}}{N^{\text{total}}} \equiv \overline{\text{Extensive variable}} \quad (4-9)$$

For example, molar species number

$$\overline{N}_j = \frac{N_j}{N^{\text{total}}} = \frac{N_j}{N_1 + N_2 + \dots + N_C} \quad (4-10)$$

This quantity is used so often that it gets its own name—*mole fraction* and symbol  $X_j$

$$\bar{U} = \frac{U}{N^{\text{total}}} \quad (4-11)$$

Note on Notation: we use the over-line as the notation to specify that a quantity is molar.

### Partial Quantities

For intensive quantities, it is sometimes useful to associate the contributions of each type of existing chemical species to the value of the intensive quantities. Each separate contribution is called a *partial* quantity, for example for pressure,

$$P_j = X_j P$$

$$(P_1 + P_2 + \dots + P_C) = \sum_{i=1}^C P_i = (X_1 + X_2 + \dots + X_C)P = P \sum_{i=1}^C X_i = P \quad (4-12)$$

$P_j$  is defined as the partial pressure of species  $j$

Question: Does the product of two extensive variables produce a similar extensive variable?

Question: Does the product of two intensive variables produce an intensive variable?

Question: Under what conditions does the product of an intensive variable and an extensive variable produce an extensive variable?

## Equivalence of heat and work

Discussion: Name some ways that one can heat up (i.e. increase the temperature of) a fixed mass of Pb.

The observation that heat and work can independently produce the exact same changes on a body is obvious today. I can't imagine what it is like not to understand this intuitively.

The classical way of explaining this is the following:

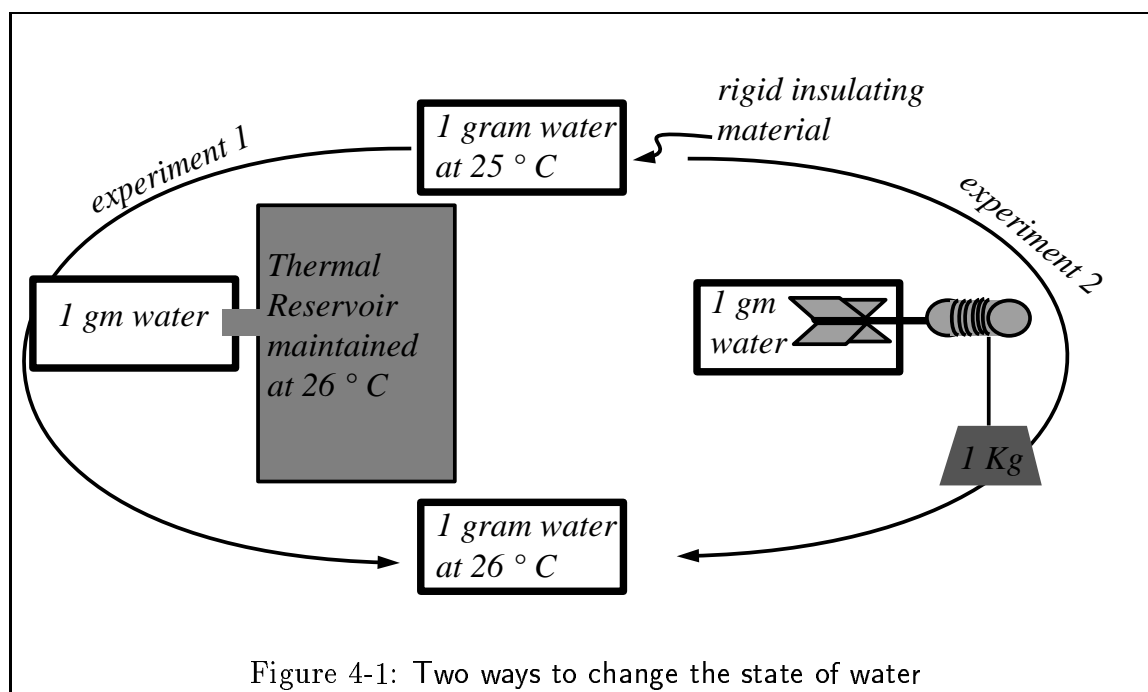


Figure 4-1: Two ways to change the state of water

I've abstracted the following story about James Joule and the introduction of the first law of thermodynamics from Bent's book.



**Figure 4-2: James P. Joule, 1818-89, born in Salford, Lancashire worked in a brewery, painstakingly established the equivalence of heat and work, hero of thermodynamics.**

James Joule is credited with the first careful experiments and analysis that led us to our present understanding of the first law. Joule worked in his family's brewery in Manchester, England and at the age of *nineteen* in 1838 became interested in the improvement of electric motors. He discovered by various means that he could heat a body of water by purely mechanical means: a) by lowering a weight and letting a paddle wheel stir the water; b) by passing electric current through a resistor; c) by compressing a piston immersed in the water; d) by friction from rubbing blocks together. He found that about 800 foot-pounds (*approx* 1 kilojoule) of work could raise the temperature of one pound (.45 kilograms) of water one Fahrenheit degree ( $0.55^{\circ}\text{C}$ ). The result was presented to the British Association in 1843 (Joule was then 24). It was received with "entire incredulity" and "general silence."

In 1844, a paper on the subject was rejected by the Royal Society.

Joule must have had a combination of great confidence in his conclusions, extraordinary temerity, and will. In 1845, he discussed his results and suggested that water at the bottom of a waterfall should have a slight temperature increase from water at the top of a waterfall. He also suggested that data from the thermal expansion of gases indicated that there was a lowest possible temperature that could be achieved—this was the first suggestion of absolute zero on the temperature scale. These results failed to provoke discussion.

Two years passed and once more in 1847, Joule presented his maturing work at an Oxford meeting of the British Association. As Joule later remarked, "... the communication would have [again] passed without comment if a young man has not risen in the section, and by his intelligent observations created a lively interest in the new theory. The young man was William Thomson [later Lord Kelvin] who had two years previously passed at the University of Cambridge with the highest honour, and is now [1885] probably the foremost scientific authority of the age."



In later years Thomson recalled that he was “tremendously struck” by Joule’s paper, and added, “This is one of the most valuable recollections of my life, and is indeed as valuable a recollection as I can conceive in the possession of any man interested in science.”

Thomson has given this account of the historic 1847 Oxford meeting. “...as I listened [to Joule’s paper] I saw that [he] had certainly a great truth and a great discovery, and a most important measurement to bring forward....

“...Faraday was there and was much struck with it, but did not enter fully into the new views. It was many years after that before any of the scientific chiefs began to give their adhesion.”

“... Miller and Graham, or both, were for many years quite incredulous as to Joule’s results, because they all depended on fractions of a degree of temperature, sometimes very small fractions. His boldness in making such large conclusions from such very small observational effects is almost as note-worthy and admirable as his skill in extorting accuracy from them. I remember distinctly at the Royal Society, I think it was either Miller or Graham saying simply he did not believe in Joule because he had nothing but a hundredths of a degree to prove his case by”

In the same account, Thomson adds that soon after the Oxford meeting he was walking near Chamonix at the beginning of a hike at Mt. Blanc in the French Alps, “and whom should I meet walking up but Joule, with a long thermometer in his hand, and a carriage with a lady in it not far off. He told me that he had been married since we had parted at Oxford! and he was going to try for the elevation of temperatures in waterfalls.”

Joule’s paper “On the Mechanical Equivalent of Heat” was communicated by Faraday to the Royal Society in 1849 and appeared in *Philosophical Transactions* in 1850. The last paragraph of this historic paper ends with the statements:

I will therefore conclude by considering it as demonstrated by the experiments contained in this paper:

1. That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force extended.
2. That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken between 55° and 60°F) by 1°F requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lb. through a space of one foot.

A third proposition, suppressed by the publication committee, states that friction consists of a conversion between mechanical work into heat.