1 Sensemaking

Two concepts that are essential to making sense of any answer to a thermodynamics question:

A. intensive/extensive determine how an answer scales with the size of a system. You need to think about this for every answer. (See more details below).

B. dimensions In physics, you need to be aware of, and check, the dimensions of your work, including intermediate answers.

2 Definitions

A. intensive/extensive If you consider two identical systems taken together (e.g. two cups of water, or two identical cubes of metal), each thermodynamic property either doubles or remains the same.

Extensive An extensive property, such as mass will double when you've got twice as much stuff.

Intensive An intensive property, such as density will be the same when you shift from one system to the combination of two identical systems.

We care about extensivity and intensivity for several reasons. In one sense, it functions like dimensions as a way to check our work. In another sense, it is a fundamental aspect of each measurable property, and once you are accustomed to this, you will feel very uncomfortable if you don't know whether it is extensive or intensive. On an exam, you will be docked additional points if you give an answer that can be determined to be incorrect based on intensive/extensive reasoning. You can recover these points if you write a note explaining that you noticed the intensive/extensive issue.

B. heat capacity *(extensive)* C_p is the amount of energy input by heating to raise the temperature of a system held at constant pressure, which means that

$$đQ = C_p dT \tag{1}$$

Similarly for C_V if the system is held at constant volume.

C. specific heat *(intensive)* The heat capacity per unit mass.

D. latent heat *(extensive)* The amount of energy required when heating a system at fixed pressure in order to change it into a different phase (liquid to gas, solid to liquid, or even solid to gas). During an abrupt phase change like these, the temperature does not change, even though the system is given energy by heating.

3 How to measure things

Volume *(extensive)* Measure dimensions and compute it.

Pressure *(intensive)* Force per area. Pressure can equalize if two systems can exchange volume.

Temperature *(intensive)* Find something that depends on temperature, and calibrate it. Alternatively use an ideal gas. Equalizes when systems are in contact.

Energy *(extensive)* Challenging to measure. Can only measure changes in internal energy. Measure work and heat.

$$W = -\int p dV. \tag{2}$$

Entropy *(extensive)* Challenging to measure. Can only measure changes in entropy. Measure heat for a quasistatic process and find

$$\Delta S = \int \frac{đQ}{T}. \tag{3}$$

Heat Energy transferred by heating, from a system its surroundings (or vice versa). In a calorimetry experiment, we might put a hot resistor in contact with a system, so we can transfer energy from the resistor to the system by heating.

Work Work happens when the volume changes quasistatically. No work happens when we see free expansion happening, or if the volume is not changing.

Derivatives Measure changes of one thing as the other changes, with the right stuff held fixed.

4 Physical Laws

First Law (Energy conservation)

$$dU = đQ + đW \tag{4}$$

> **Instructor's guide** PER research on this topic "Student understanding of the first law of thermodynamics: Relating work to the adiabatic compression of an ideal gas" by Loverude et al.

Second Law (Entropy increases)

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \tag{5}$$

Thermodynamic identity

$$dU = TdS - pdV \tag{6}$$

This equation describes how a small changes in U corresponds to small changes in S and V as a substance undergoes a quasi-static process.

5 Equations of State

These are properties of a particular system. These are *only true* for that particular system, and are not true for any other system. Everything related to the ideal gas is in this category. You should ***never*** assume any of these are true unless you are told to assume that.

any ideal gas

$$pV = Nk_BT \tag{7}$$

$$S = Nk_B\left(\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{\frac{3}{2}}\right]\right) \tag{8}$$

Monatomic ideal gas For example, helium, argon, neon...

$$U = \frac{3}{2}Nk_BT \tag{9}$$

Diatomic ideal gas between 250 K - 350 K For example H2, N2 and O2...

$$U = \frac{5}{2}Nk_BT \tag{10}$$

I repeat, you should never assume that any of these equations is true, either in homework or on an exam, unless you are told to assume that.

6 Analyzing processes

When you encounter a process (a way a system changes), there are a number of questions you'll want to ask yourself.

system Identify what you want to call your system, and what the surroundings are.

irreversible Could this process happen in reverse? If not, you know that the entropy of system plus surroundings must go up.

quasistatic Is the process slow enough that the state of the system is well defined at all times? If things are not irreversible, then they almost have to be quasistatic.

heat Does the system heat its surroundings or vice versa? If so, then the entropy must be changing.

work Is something solid moving? Is the volume of the system changing? If so, work is probably being done, and you can figure out what is doing work on what. If your system is doing work, then something else must be getting the energy. ”Free expansion” is an example in which volume changes, but no work is done, because no solid object is moving to have work done to it.

isothermal Is the system being equilibrated with something big so that the temperature is constant? This means that energy almost certainly must be transfered by heating, assuming anything at all is changing. One nice thing about isothermal processes is that if you can find the heat, it's pretty easy to find the entropy, since $1/T$ is constant in $\int \frac{đQ}{T}$.

adiabatic If a system is insulated, then there is no energy transfer by heating.

isochoric If the volume isn't changing, then no work is done. This means that if just about anything is changing, then probably temperature and pressure are both changing.

isobaric If the pressure is fixed, there isn't anything special to be gained at this stage.

Any gas undergoing a quasi-static adiabatic process over a limited temperature range

$$p_i V_i^{\frac{C_p}{C_V}} = p_f V_f^{\frac{C_p}{C_V}}, \tag{11}$$

where p_i and V_i are in the initial pressure and volume, p_f and V_f are the final pressure and volume, and C_p/C_V is the ratio of heat capacities.

7 Math bits

Math identities
Math identities are statements that are mathematically true, such as **"the overlord equation"**:

$$\text{If A is a function of B and C, then} dA = \left(\frac{\partial A}{\partial B}\right)_C dB + \left(\frac{\partial A}{\partial C}\right)_B dC. \tag{12}$$

We sometimes use math identities to "push around" truth from one place to another. For example, we can derive something like:

$$\left(\frac{\partial A}{\partial B}\right)_C = -\frac{\left(\frac{\partial A}{\partial C}\right)_B}{\left(\frac{\partial B}{\partial C}\right)_A} \tag{13}$$

Identifying partial derivatives from equations of differentials
When we have an equation relating total differentials (such as the thermodynamic identity),

$$dU = TdS - pdV, \tag{14}$$

the terms that multiply the dS, dV, etc are partial derivatives.

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S \tag{15}$$

You can show this by comparing the thermodynamic identity with the appropriate overlord equation.

You can do linear algebra using equations that contain total differentials, e.g. substituting one for another. You will need to be able to zap with d to find equations that relate total differentials (see below).

Zapping with d
You should be able to zap a complicated algebraic expression with d using a combination of the following rules:

- zapping common functions with d, especially exponentials and logarithms.
- product rule
- ordinary chain rule

See the three short videos in the Media Gallery (10 minutes total!): Rules for Differentials, Product Rule, Chain Rule.

Finding derivatives from discrete information

You should be able to compute a partial derivative from data in a table or on a contour map. The important point is that a partial derivative is determined by the values of state variables at two ”nearby” states: state 1 and state 2. For computing $\left(\frac{\partial f}{\partial g}\right)_h$ it is essential to choose the two ”nearby” states so that h has the same value in state 1 and state 2. Then you find the values of f and g in the two states and take the ratio of the small changes in these values:

$$\left(\frac{\partial f}{\partial g}\right)_h = \left(\frac{\triangle f}{\triangle g}\right)_h = \left(\frac{f(2) - f(1)}{g(2) - g(1)}\right)_h$$

What counts as ”nearby”? You want the states close enough together that the relationship between the variables in essentially linear, but not so close that when you take the difference between two numbers that are close together you are only getting the error in the measurements. Use good professional judgement and be prepared to explain briefly why you made the choices that you did.

It is always a good idea to plot data from a table to get a sense of the uncertainty in the data: is the data approximately linear? smooth? concave-up or down? are you likely over or underestimating the derivative?

If you are reading the data off a graph, then sometimes (but not always!) the two states lie along a curve on the graph and this derivative will be the slope of the tangent line.

Physical meaning of differentials

You should be able to describe the geometry of a differentials expression as describing the relationship between small changes of various physical/geometric variables. For example:

$$df = \left(\frac{\partial f}{\partial g}\right)_h dg + \left(\frac{\partial f}{\partial h}\right)_g dh \tag{16}$$

tells us that, if g is changing but not h, then small change in f is the rate of change (”slope”) $\left(\frac{\partial f}{\partial g}\right)_h$ times the small change in g.

Manipulating differentials

Any equation obtained by zapping with d is always linear in the differentials, so it is easy to do (linear) algebra on these equations. Here is a list of allowable algebraic manipulations:

- subtract a term from both sides of an equation, which effectively moves a term from one side of an equation to the other, with an appropriate minus sign
- divide both sides of an equation by a partial derivative by turning it upside-down (and keeping the same variable constant)
- substitute one differential’s expression into another

The partial derivatives machine

The PDM is a mechanical physical system that has two ways of getting energy into and out of the system (doing work on each of the two sides). The mathematics of the PDM is analogous to the mathematics of a thermodynamic system for which you can change the internal energy by doing work or by heating. So, there are analogues to all the thermodynamics.