

## Responses to Thermo Recitation 2 “Muddy Cards”

The most common remark was lingering confusion about reversible versus irreversible processes, and calculation of the work thereof: e.g., when are which work equations used? A related question that has come up in office hours is the difference between  $P_{ext}$  and  $P$ .

First, realize that  $P$  refers to the pressure of the *system* – such as the gas – always.  $P_{ext}$  refers to the pressure being applied to the system by the surroundings. In a reversible process they must be equal (in equilibrium) at all times; hence, you can substitute an equation of state such as the ideal gas law in for  $P$ . In an irreversible process,  $P_{ext}$  may change more quickly than  $P$  is able to catch up, so to speak; since it is  $P_{ext}$  that determines mechanical work performed, if it is constant, it is readily taken outside the integral sign.

My answer regarding when one should assume a process is reversible is a pragmatic one: do so when you *need* to do so to solve the problem. In an isobaric process you never do. In an isochoric process there is no work. Along an isotherm, it is useful to do so, and probably not a bad assumption, due to already needing to keep the system in equilibrium with respect to one variable -  $T$ . Finally, in this course, we will not be studying adiabatic expansions/compressions (section 2.10 the book if you are interested).

**Relatedly, how does one calculate work done when changing temperature?**

Work is only done inasmuch as the temperature change causes a corresponding volume change, if it does so. This will typically be calculated from a constitutive equation (e.g.,  $PV = nRT$ ). But a temperature change may transfer heat without the transfer of work.

**Where does  $U = 1.5 nRT$  come from?**

This is true only for an ideal gas (monatomic, at that). It can be derived from statistical mechanics and the kinetic theory of gases, as shown in chapter 33 of Engel & Reid. Recall that  $dU = C_v dT$ , so that tells you something about its relation to classical thermo.

**Why is it useful that mixed partial derivatives of exact differentials are equal?**

I hope that my solution to problem I.3 cleared this up in part. First of all, it makes a useful test for whether something is a state function or not – circular, I know. Second of all, some partial derivatives are much easier to calculate than others! One may be equal to a property like  $C_v$ , whereas another is basically gibberish, conceptually speaking. In other words: it allows you to solve problems given physical data.

**What is specific heat? How does heat capacity relate to boiling points?**

Specific heat is just another name for heat capacity. It is often given in units of energy per *mass* per temperature, rather than energy per mole per temperature. At phase

changes, heat capacity is considered undefined (or infinite), because it is the ratio of differential heat transferred and differential temperature change – which is zero.

High boiling points and high heat capacities can be related. In the case of water, both are due to the extensive hydrogen bonding network: it must be broken for evaporation (i.e., boiling) to occur, and energy input to heat liquid water to a higher temperature may be ‘wasted’ on bending of hydrogen bonds.

**Regarding the “units?” question – please be more specific next time, as I’m not sure what in particular you are asking.**

**Regarding pedagogical suggestions: thank you, I will try to incorporate them.**