ESCI 341 – Atmospheric Thermodynamics
Lesson 3 – The First Law of Thermodynamics

References: *Introduction to Theoretical Meteorology*, Hess
Physical Chemistry (4th edition), Levine
Thermodynamics and an Introduction to Thermostatistics, Callen
The Elements of Classical Thermodynamics, Pippard

Reading: Petty, Chapter 5

THE LAWS OF THERMODYNAMICS

- **The four 'laws' of thermodynamics are essentially postulates or axioms that are assumed to be true, and have never (so far) been seen to fail.**
- **For this course we are primarily concerned with the First and Second Laws of Thermodynamics. However, we briefly define and describe each of them below**

ZEROTH LAW

- **The *Zeroth Law of Thermodynamics* states that if two systems are each separately in equilibrium with a third system, then the first two systems are also in equilibrium with each other**

FIRST LAW

- **The *First law of Thermodynamics* is nothing more than a statement that energy is conserved.**

SECOND LAW

- **The *Second Law of Thermodynamics* has several possible equivalent statements. Two of them are:**
  - **The entropy of an isolated system can never decrease.**
  - **It is impossible for an engine operating in a cyclic process to convert energy into work with 100% efficiency.**
- **We show later in this course that the two statements are indeed equivalent.**

THIRD LAW

- **The *Third Law of Thermodynamics* is the least robust of the laws of thermodynamics. There are several different statements of the Third Law. Among them are:**
  - **The entropy change of a substance goes to zero as temperature approaches absolute zero.**
  - **The entropy of a pure substance is zero at absolute zero.**
- **A consequence or result of the First, Second, and Third Laws is that it is impossible to reduce the temperature of a substance to absolute zero (0 K) in a finite number of steps.**
  - **In other words, it would take an infinite number of steps to reach absolute zero, so therefore, it is unattainable.**
- **The unattainability of absolute zero is sometimes regarded as being another alternate statement of the Third Law of Thermodynamics, however, it is actually a consequence of the First, Second, and Third Laws (see Levine, pp. 159 for details if interested).**
- **As of 2009 the coldest temperature achieved is 3×10^{-9} K.**

THE FIRST LAW OF THERMODYNAMICS IN DETAIL

- **The first law of thermodynamics expresses the conservation of energy. It is given as**

$$dU = dQ + dW.$$

- **The first law states that the internal energy of a system can be changed either through heating or through work.**
- **Using intensive properties, the first law becomes**

$$du = dq + dw.$$

- **Our convention will be that heat <u>added</u> to the system and work <u>done on</u> the system will be positive.**
  - **Thus, work done *by* the system on its surroundings will be negative.**

P-V WORK

- **Work is defined as force acting over a distance,**

$$dW = \{\vec{F} \cdot d\vec{x}.$$

- **If a gas expands *reversibly* against a pressure, *p*, the work done by the gas is given by the pressure multiplied by the change in volume, *V*, or**

$$dW = -pdV. \qquad \text{MERGEFORMAT}$$

  - **The stipulation of reversibility is required to preclude the effects of friction, turbulence, etc.**
  - **The negative sign is included because work is being done *by* the system.**

- **The first law is then written**

$$dU = dQ - pdV, \qquad \text{MERGEFORMAT}$$

  - **In terms of specific quantities, the first law is**

$$du = dq - pd\alpha, \qquad \text{MERGEFORMAT}$$

  where α is the specific volume (*V/m*, or ρ^{-1}).

- ***NOTE*: In the "old days" it was common to define positive work as work done "by" the system, so that the first law would be $dU = dQ - dW$, and the work term would be defined as $dW = pdV$. Modern convention is to define positive work as work done "on" the system, so that $dU = dQ + dW$ and $dW = -pdV$. Either convention leads to the correct form of expression (1), so it really doesn't matter, as long as you are consistent.**
- **The first law in this form tells us that if a gas expands then its internal energy must either decrease, or heat must be added to it in order to keep the internal energy from decreasing.**
  - **In an adiabatic process, no heat is added or subtracted. Therefore $dq = 0$. This means that if a gas expands adiabatically its internal energy (and hence, its temperature) will decrease.**

EXERCISES

1. **Prove that for a volume of <u>arbitrary</u> shape that the work done in expanding the volume by a differential volume, *dV*, is *pdV*. Hint: Imagine everywhere on the surface of the volume that the surface is pushed out an amount $d\vec{n}$, where $\vec{n}$ is a vector whose direction is everywhere normal to the surface.**

2. **a. What is the minimum amount of work done by you in blowing up a spherical party balloon to a diameter of 8 inches? Assume standard sea-level pressure.**

   b. Why is this the minimum amount of work?