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

**References:** Introduction to Theoretical Meteorology, Hess Physical Chemistry (4<sup>th</sup> edition), Levine Thermodynamics and an Introduction to Thermostatistics, Callen

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:
  - o 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.
  - o 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  $3 \times 10^{-9}$  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,

$$dW = \vec{F} \bullet d\vec{x} \,.$$

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

$$dW = -pdV \,. \tag{1}$$

- Equation (1) is only valid if the process is *quasi-static with respect to* <u>mechanical equilibrium</u>.
  - The system does not have to be near thermal equilibrium in order to use
    Eqn. (1), as long as it is close to being in mechanical equilibrium.
- o The negative sign is included because work is being done by the system.
- The first law is then written

$$dU = dQ - pdV, \qquad (2)$$

o In terms of specific quantities, the first law is

$$du = dq - pd\alpha, \tag{3}$$

where  $\alpha$  is the specific volume (*V*/*m*, or  $\rho^{-1}$ ).

- <u>NOTE</u>: 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?