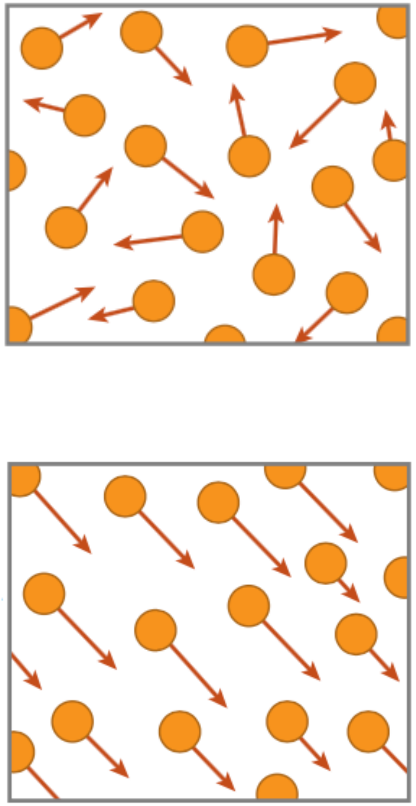
Unit 4 Review 1

FIRST LAW OF THERMODYNAMICS, HEAT, ENTHALPY

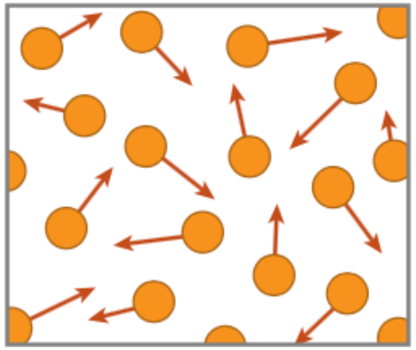
Thermodynamics Basic Definitions

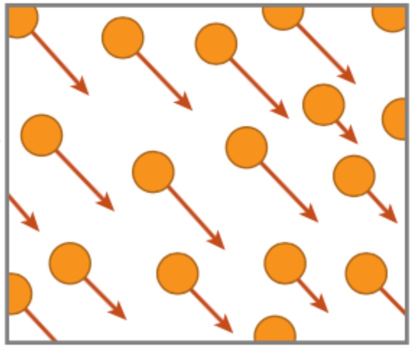
- **Heat (q):** energy derived from random molecular motion (always travels from high T to low T)
- **Work (w):** the energy derived from organized molecular motion (in chemistry, mostly as a result of compression or expansion at constant pressure)
- **Internal Energy (U):** the total energy of a system, the surroundings, or the universe (depends on the subscript)
- **Enthalpy (H):** the heat content of a system (usually depicted as ΔH; heat flow at constant pressure, q_p)



Thermodynamics Basic Definitions

- **Heat (q) = $mC_s\Delta T$**
- **Work (w) = $-P\Delta V$**
- **Change in Internal Energy (ΔU) = q + w**
- **Change in Enthalpy (ΔH) = q_p**





Heat Flow: System vs. Surroundings

- We define our environment in thermodynamics as the system and the surroundings. The system is the direct environment of the reaction and the surroundings is everything outside of this.
- Important: we often measure chemical reactions from the perspective of the surroundings. Therefore, when a reaction produces heat, we are actually measuring the change in temperature of the surroundings – not the system

$q > 0$; endothermic (+), heat is absorbed

$q < 0$; exothermic (-), heat is released

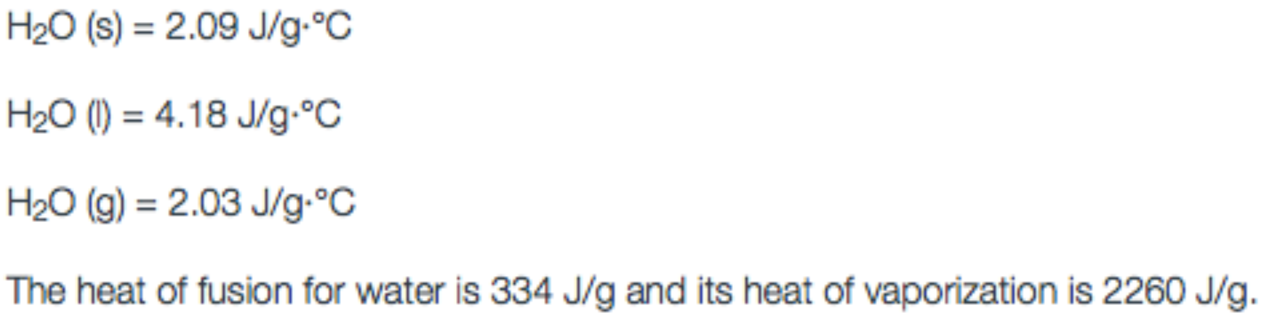
$w > 0$; work energy in, work is done on the system (+)

$w < 0$; work energy out, work is done by the system (-)

Heat Flow: Heating Curves

Suppose you are melting a 10g ice cube from -10°C to 110°C at constant pressure (1 atm). How can we use what we know about thermodynamics to quantify the total heat of this change?

- We must understand that heat flow can apply to a temperature change or no temperature change and **these are calculated differently**



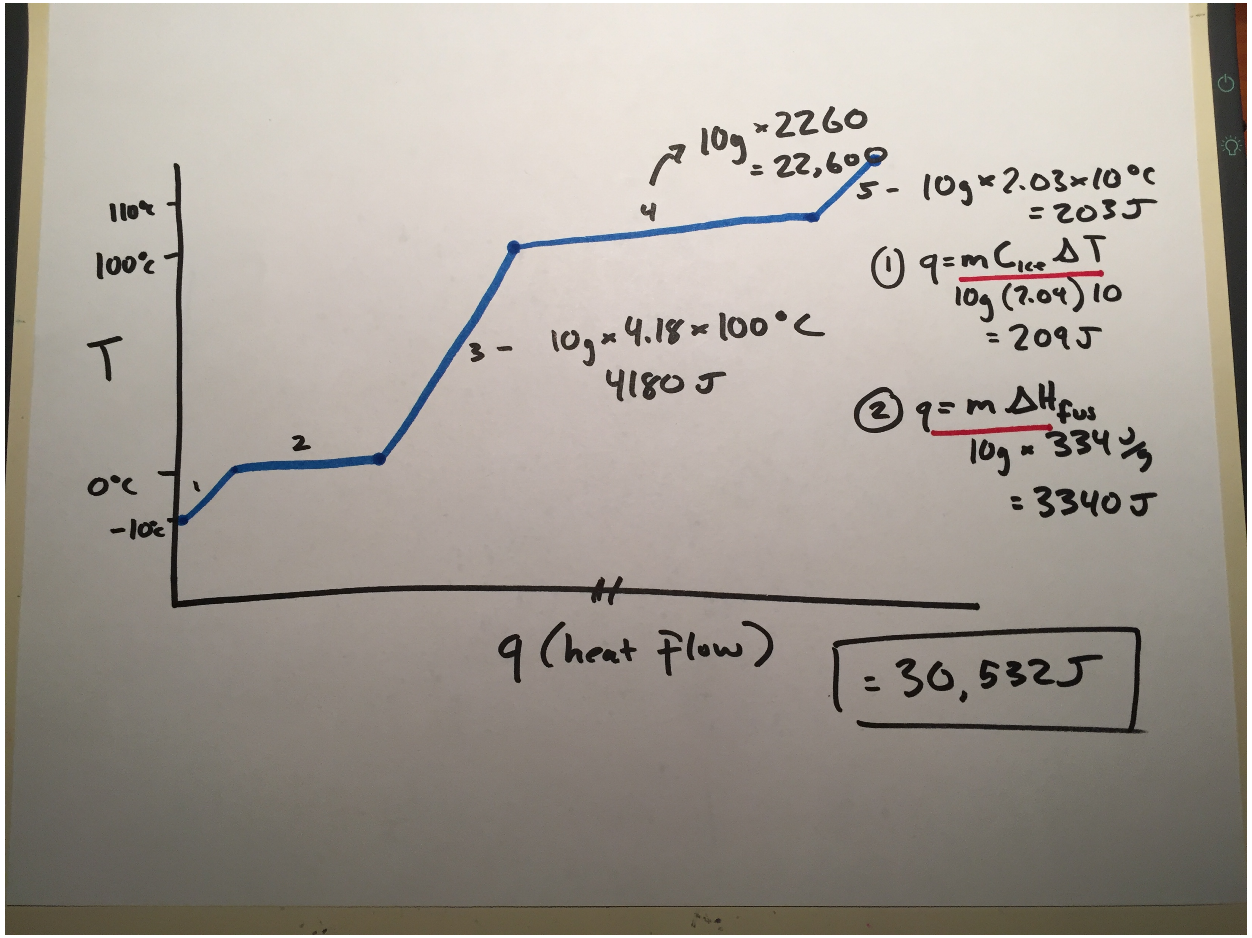
H_2O (s) = 2.09 J/g·°C

H_2O (l) = 4.18 J/g·°C

H_2O (g) = 2.03 J/g·°C

The heat of fusion for water is 334 J/g and its heat of vaporization is 2260 J/g.

Heat Flow: Heating Curves



3 - $10g \times 4.18 \times 100°C$
4180 J

4 → $10g \times 2260$
= 22,600

5 - $10g \times 2.03 \times 10°C$
= 203 J

① $q = \underline{m C_{ice} \Delta T}$
$10g (2.04) 10$
= 209 J

② $q = \underline{m \Delta H_{fus}}$
$10g \times 334 J/g$
= 3340 J

$\boxed{= 30,532 J}$

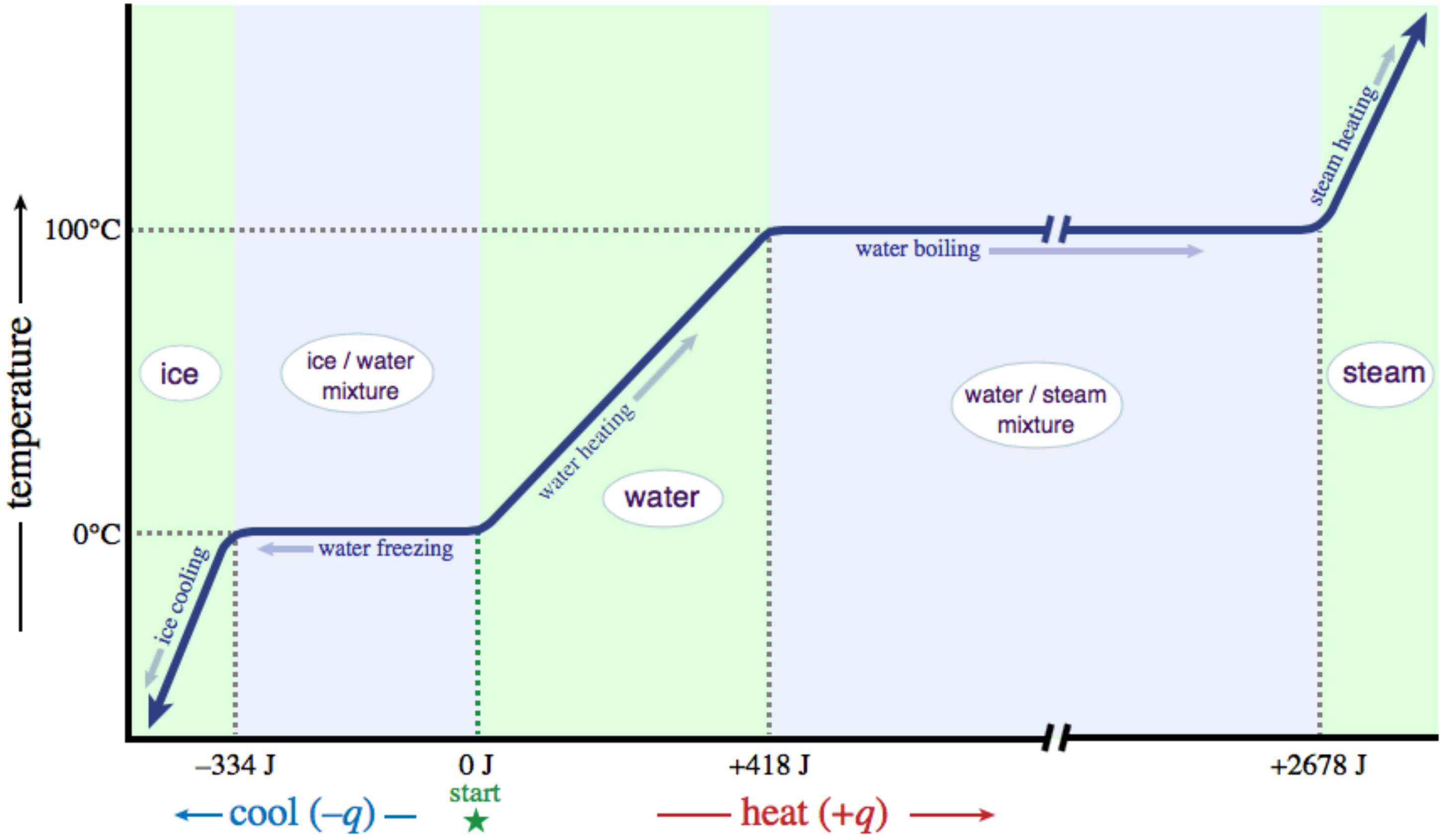
Heat of a Temperature Change

$q = mC\Delta T$

Heat of a Phase Change

$q = m\Delta H_{phase\text{-}change}$

Heat Flow: Heating Curves



Heat of a Temperature Change

$q = mC\Delta T$

Heat of a Phase Change

$q = m\Delta H_{\text{phase-change}}$

The First Law of Thermodynamics

- The energy of the universe is always conserved
- The conclusions of this law are:
  1. The internal energy change of the system is the sum of the heat and work
  2. The internal energy loss of the system is the equal to energy gain of the surroundings
  3. The internal energy change of the universe is zero and there is no energy or matter leaving

$$\Delta U_{universe} = 0$$

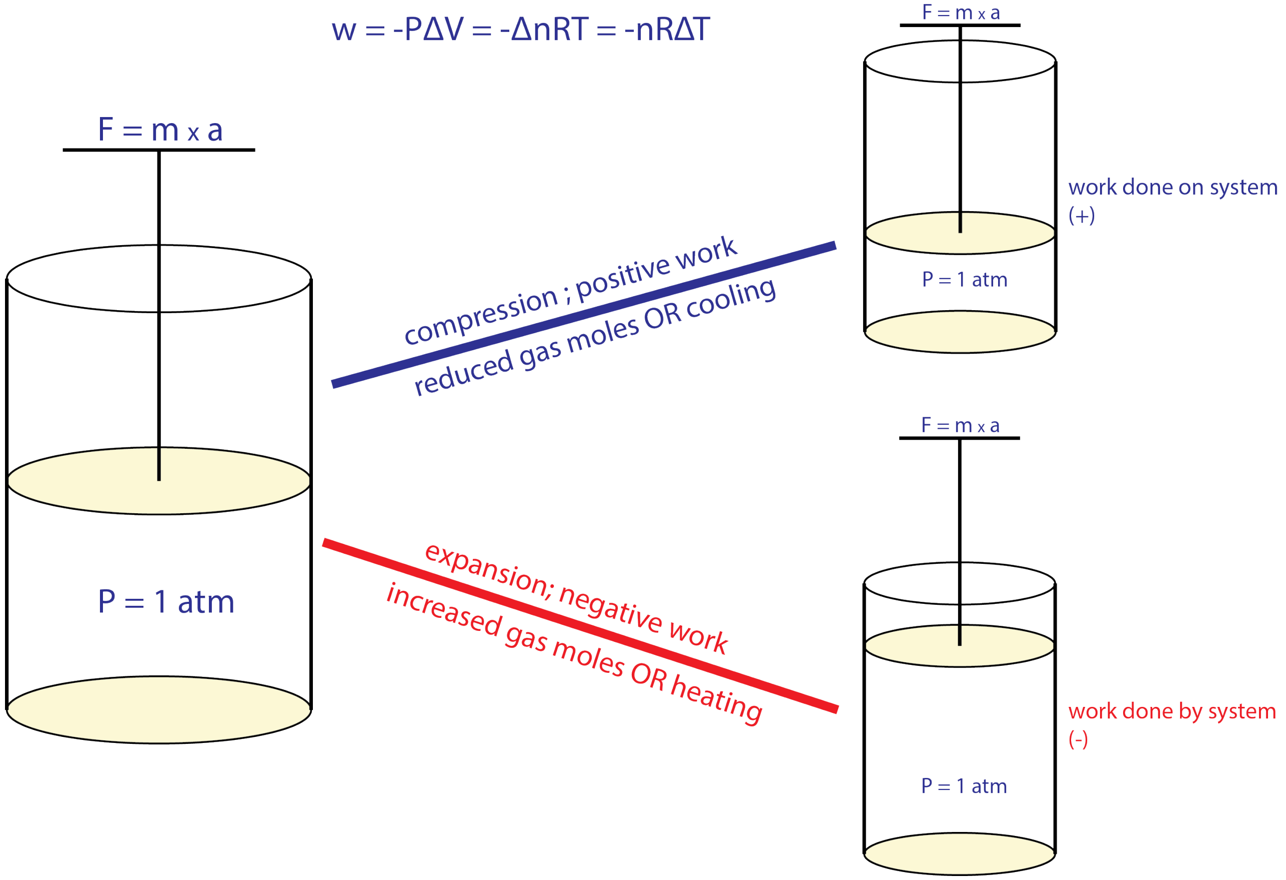
$$\Delta U_{sys} = q + w$$

$$\Delta U_{sys} = -\Delta U_{surr}$$

Visualizing Chemical Work

- Work in chemistry is most often related to what we call “PV” work, where $w = P\Delta V$
- We often think of experiments measuring “PV” work in the context of using a piston
- Pistons exert a variable force to maintain a constant pressure. This pressure is used to determine the work done by or on the system
- **When you are compressing your sample, you are doing work on the system (positive)**
- **When your sample expands, your system is doing work on the surroundings (the piston) to maintain the constant pressure (negative)**

$$w = -P\Delta V = -\Delta nRT = -nR\Delta T$$



Chemical Work Question

Calculate the work in the combustion of hexane at standard conditions. Is work done on or by the system?

$$2C_6H_{14(l)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(l)}$$

Chemical Work Question

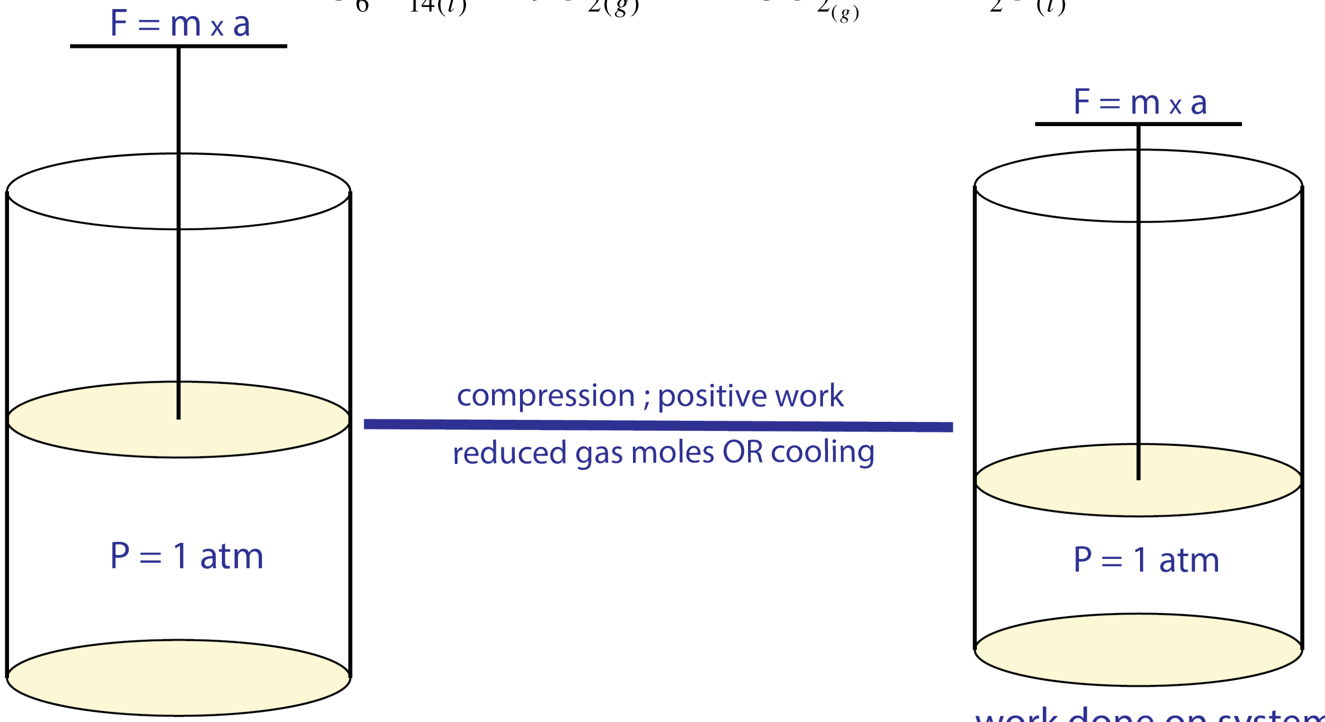
Calculate the work done in the combustion of hexane at RT and 1 atm.

$$2C_6H_{14(l)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(l)}$$

$$w = -\Delta nRT$$

$$w = -(-7moles)(8.314\frac{J}{molK})(298.15K)$$

$$w = 17351J = 17kJ$$



work done on system
(+)

Chemical Work Question

If the enthalpy of combustion of hexane is -4163kJ/mol, what is the change in internal energy for this process at RT?

$$2C_6H_{14(l)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(l)}$$

$$w = 17351J = 17kJ$$

Chemical Work Question

If the enthalpy of combustion of hexane is -4163kJ/mol, what is the change in internal energy for this process at RT?

$$2C_6H_{14(l)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(l)}$$

$$w = 17351J = 17kJ$$

$$\Delta U = q + w = q - \Delta nRT$$

$$\Delta U = -4163kJ + 17kJ = -4146kJ$$

Chemical Work Question

Calculate the work in the combustion of hexane at 100°C. Is work done on or by the system?

$$2C_6H_{14(g)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(g)}$$

Chemical Work Question

Calculate the work in the combustion of hexane at 100°C.

$$2C_6H_{14(g)} + 19O_{2(g)} \rightarrow 12CO_{2_{(g)}} + 14H_2O_{(g)}$$

$$w = -\Delta nRT$$

$$w = -(5moles)(8.314\frac{J}{molK})(373.15K)$$

$$w = -15511J = -15.5kJ$$

The “Complicated” Stuff

- **We can calculate the internal energy of moving particles based on the temperature and complexity of the molecule**
- The motion of a particle that contributes to is energy can be described as translational, rotational, or vibrational. We refer to these as the “modes” of the energetic motions.
- For each mode of motion, we write the molar energy as: $U_{\sin gleMode} = \frac{1}{2}RT$
- Therefore, the total internal energy is the sum of the available modes of motion

Monatomic Gases (3 Modes)

- Monatomic gases have only translational motion in 3 dimensions: x, y, and z.
- **Therefore, the internal energy can be written as:**

$$U_{monatomic} = \frac{3}{2} RT$$

Linear Gases (5 Modes)

- Linear gases have both translational motion (3: x, y, and z) and rotational motion with two modes of freedom. This is a total of 5 modes.
- **Therefore, the internal energy can be written as:**

$$U_{linear} = \frac{5}{2}RT$$

Complex Gases (6 Modes)

- Non-linear gases have both translational motion (3: x, y, and z) and rotational motion with all three modes of freedom. This is a total of 6 modes.
- **Therefore, the internal energy can be written as:**

$$U_{complex} = \frac{6}{2}RT = 3RT$$