

19-1: The First Law of Thermodynamics

In PHY181 (see chapters 9 & 10), we developed the principle of the **Conservation of Energy**. Consider applying this to a container of gas:

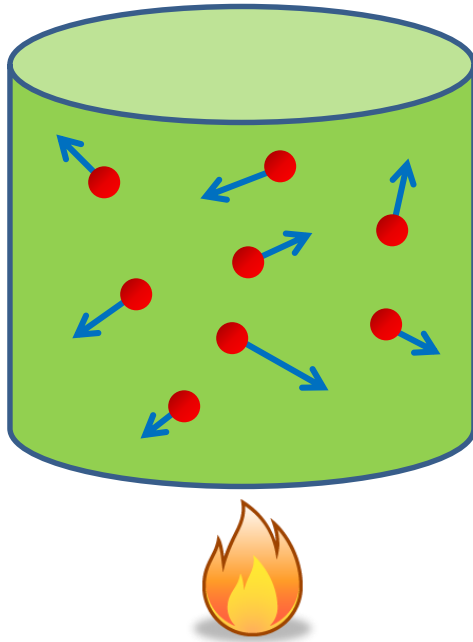
$$\Delta E_{\text{sys}} = \Delta E_{\text{mech}} + \Delta E_{\text{th}} = W_{\text{ext}}$$

From 181: $E_{\text{mech}} = K + U$ (of the entire system)

New Idea: $E_{\text{th}} = \text{Thermal Energy}$

(Energy contained in the random motions of the particles in the system)

$W_{\text{ext}} = \text{Work done by external forces}$
(can change either the mechanical or the thermal energies)



PhET
Gas Properties

Now, as your author points out, this is incomplete.

What happens when a flame is placed under the gas?

The temperature and hence the thermal energy increases. **This is what we mean by Heat, a transfer of energy by thermal interaction.**

PhET
Gas Properties

Conservation of Energy

So, a more complete statement of the Conservation of Energy for the system is:

$$\Delta E_{\text{sys}} = \Delta E_{\text{mech}} + \Delta E_{\text{th}} = W + Q$$

where **Q** is the energy transferred into or out of the system as Heat.

Back in PHY181: we looked at problems where there was no change in thermal energy or work done by dissipative forces; Thus, our energy conservation equation was:

$$\Delta E_{\text{mech}} = \Delta K + \Delta U = 0$$

Now, in PHY182: we want to look at problems where neither the bulk kinetic nor the potential energies of the system change, but the thermal energy can change:

$$\Delta E_{\text{th}} = W + Q$$

This form of Conservation of Energy is called The First Law of Thermodynamics.

The First Law answers the question: *“how do you change the thermal energy of of a system?”*

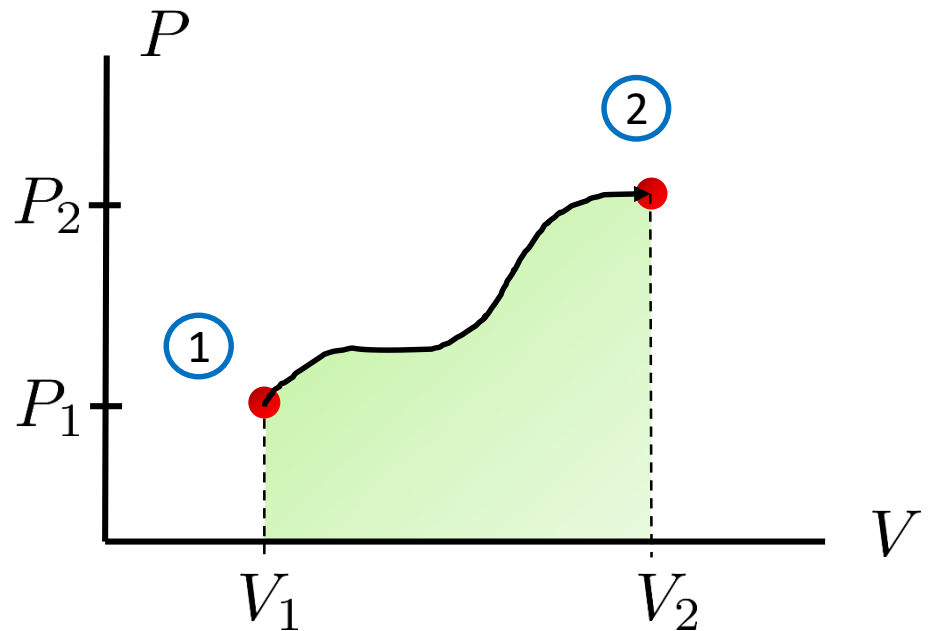
Answer: “you do Work on it or you Heat it”

Work for a Thermodynamic System

Your author shows that for a system composed of a gas going from some initial state **i** to some final state **f**, the **Work Done on the Gas** is:

$$W = - \int_{V_i}^{V_f} p dV$$

Now, if we represent this on a PV diagram:



$$W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} p dV = -(\text{area under the } PV \text{ curve})$$

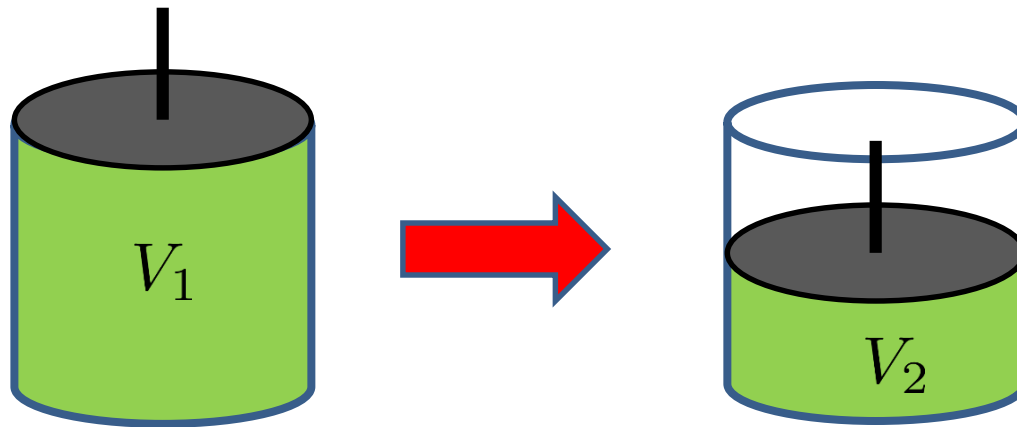
Note: the work done in going from state 1 to state 2 depends on the path followed.

Work for a Thermodynamic System

$$W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} p dV = -(\text{area under the } PV \text{ curve})$$

Does this negative sign make sense?

Consider compressing a gas with a piston:



What should happen to the thermal energy of the gas?

PhET
Gas Properties

It should go up?

$$\Delta E_{\text{th}} = W = - \int_{V_1}^{V_2} p dV \sim -(p > 0)(dV < 0) > 0$$

So, the change in thermal energy is greater than zero, and energy is transferred to the gas.

Whiteboard Problem 19-1

A 2000 cm³ container holds 0.10 mol of helium gas at 300°C; call this **State 1**. The gas is to be compressed to **State 2** which has a volume of 1000 cm³.

- At the **LC prompt**, sketch this process on the PV grid if the compression is Isobaric (Constant Pressure).
- Calculate the work done for the isobaric compression. **(LC)**
- At the **LC prompt**, sketch the process on the PV grid if the compression is Isothermal (Constant Temperature).
- Calculate the work done for the isothermal compression. **(LC)**

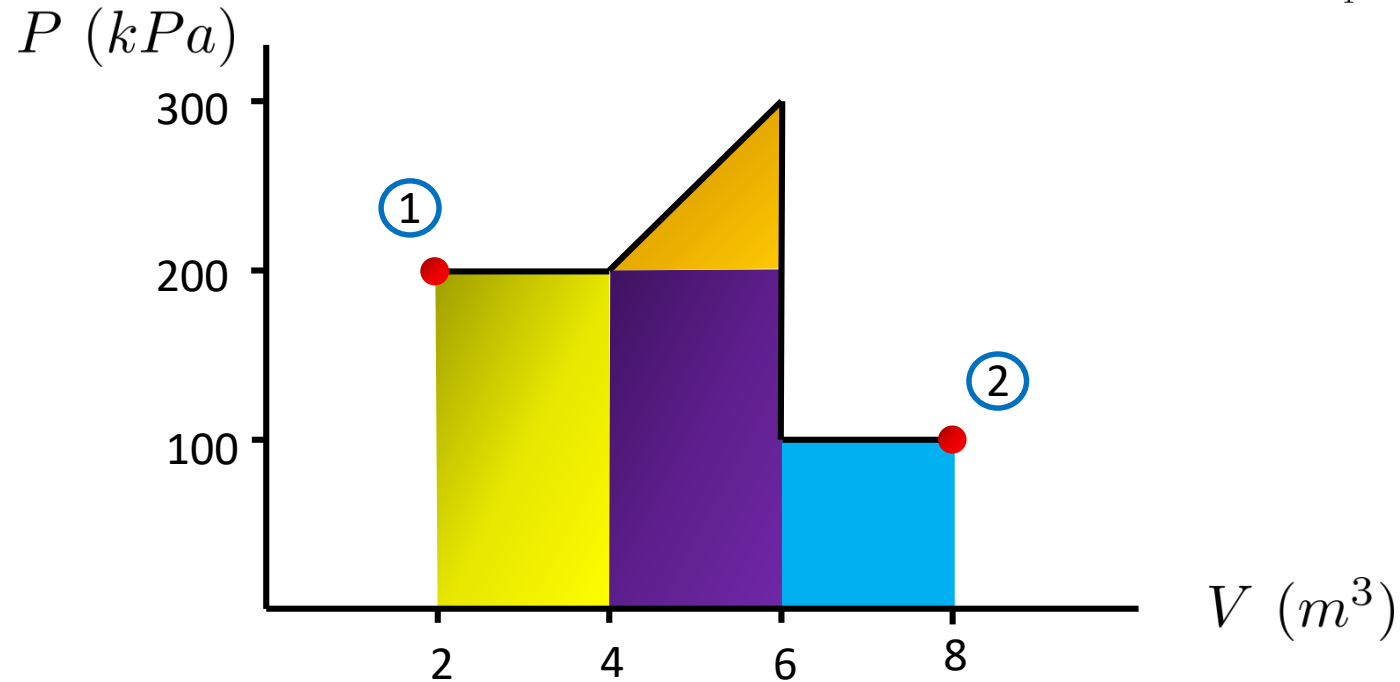
Do not use your equation sheet or textbook for this problem; all you need is the definition:

$$W = - \int_{V_i}^{V_f} p dV$$

In the future, when you have to calculate the work done in an isothermal or isobaric process, go ahead and use the formulae from the equation sheet, but you should do them using the definition at least once!

Caution: Don't be fooled by something like this

Calculate the work done on the gas going from 1 to 2: $W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} p dV$



How do you do this? Just calculate areas!

$$W_{1 \rightarrow 2} = -(\text{area under the } PV \text{ curve})$$

$$= -[(2)(200 \times 10^3) + (2)(200 \times 10^3) + \frac{1}{2}(2)(100 \times 10^3) + (2)(100 \times 10^3)]$$

$$= -1.1 \times 10^6 \text{ J}$$

This is an actual exam problem that I had as a student long long ago in a university far far away. No, I didn't get it right!

Heat

Recall what the **First Law of Thermodynamics** says:

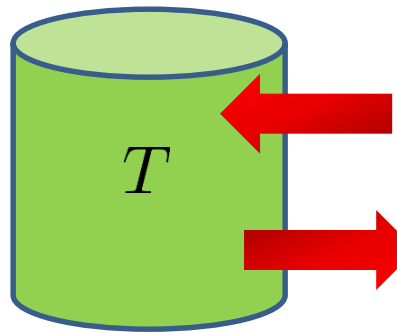
$$\Delta E_{\text{th}} = W + Q$$

It tells us the ways that we can **change the thermal energy of a system**:

1.) **Work** $W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} p dV = -(\text{area under the } PV \text{ curve})$

- Environment does work on system: $W > 0$, and thermal energy increases
- System does work on environment: $W < 0$, and thermal energy decreases

2.) **Heat** is energy transferred due to a temperature difference.



For $T < T_{\text{env}}$

Energy is transferred to the system, $Q > 0$, thermal energy increases.

T_{env}

For $T > T_{\text{env}}$

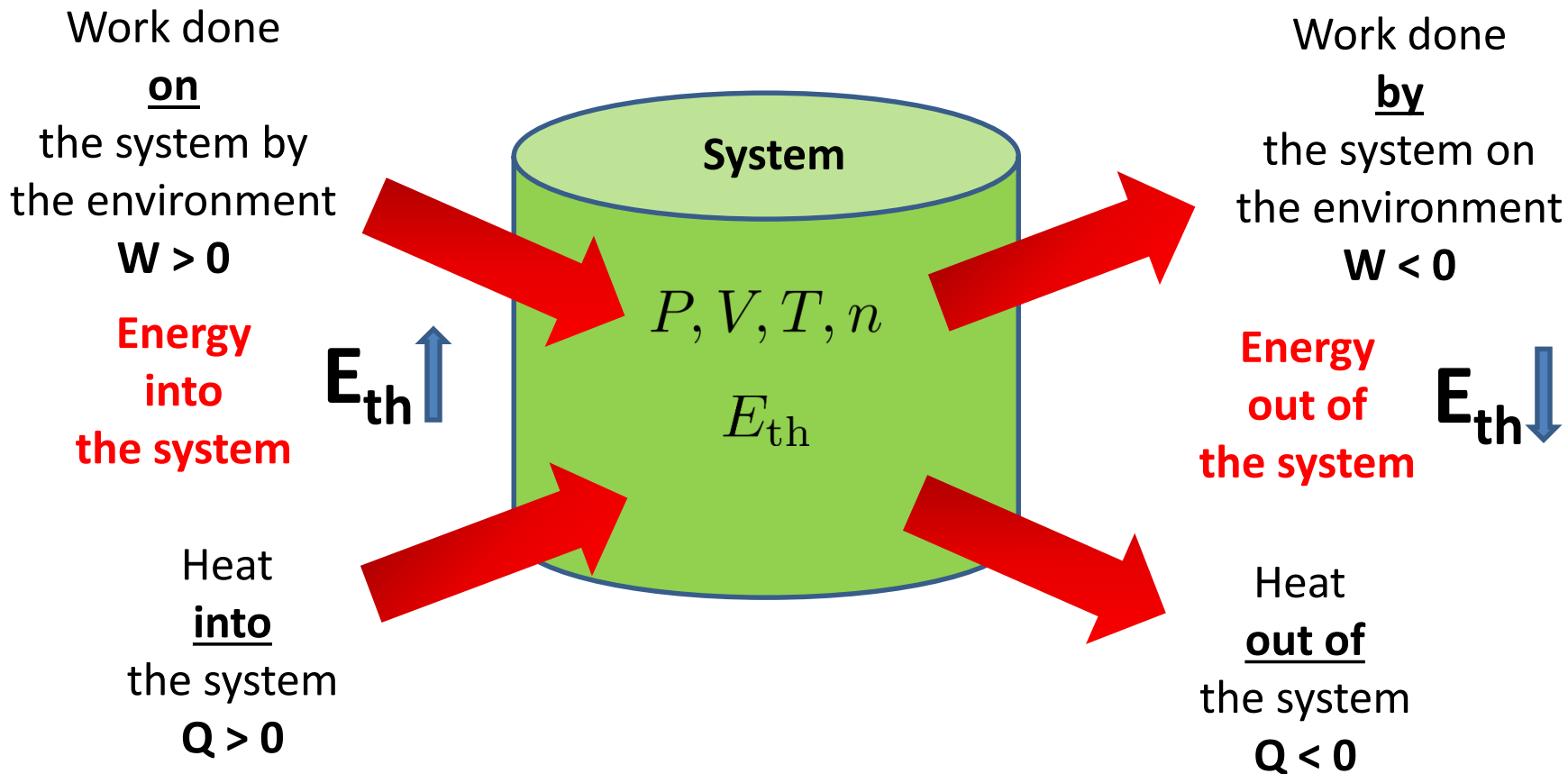
Energy is transferred out of the system, $Q < 0$, thermal energy decreases.

Read the discussion in Section 19.3.3 carefully about heat, temperature, and thermal energy. They are different, but related quantities, and we sometimes confuse them in our everyday language. Also, we haven't really yet defined just what heat is and what temperature measures!

The First Law of Thermodynamics: Pictorially

$$\Delta E_{\text{th}} = W + Q$$

(balances the energy coming into or going out of a system)



Important Note: $P, V, T, n,$ & E_{th} are State Variables (properties of the system)
 Q & W are NOT state variables

What Happens when the Thermal Energy changes?

When work is done on or by the system, or heat comes into or out of the system, what happens?

Many things can happen, but the **two most important** are:

(you already know this; what happens to your teapot on the stove?)

1. **The temperature changes.**
2. **The phase (solid, liquid, or gas) changes.**

Temperature Change:

When the thermal energy changes, there is a proportional change in temperature that **depends on the mass of the system and material properties of the system:**

$$\Delta E_{\text{th}} = Mc\Delta T$$

Where: M = the mass of the system

$$\Delta T = T_f - T_i$$

c = the specific heat of the substance (units: $\frac{J}{kg \text{ } ^\circ C}$ OR* $\frac{J}{kg \text{ } K}$)

(Note: the specific heat is the amount of energy required to raise the temperature of 1 kg of a substance by one degree, either Celsius or Kelvin)

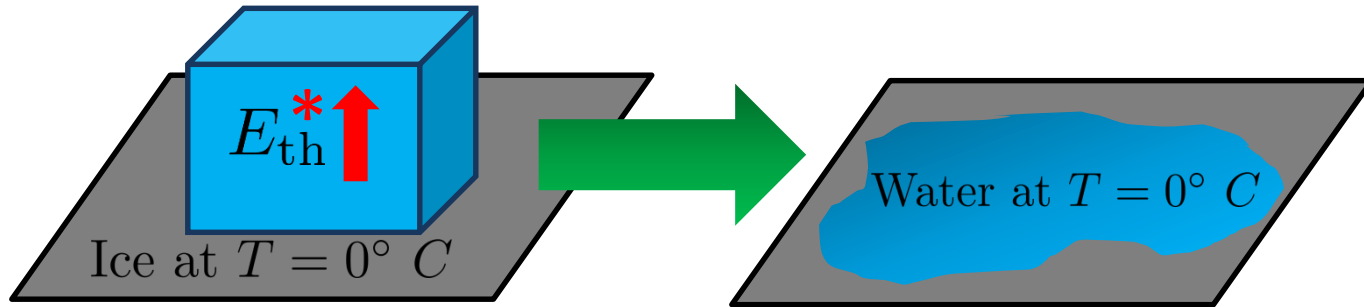
Sometimes we see this in moles: $\Delta E_{\text{th}} = nC\Delta T$ where C = Molar specific heat

* **Why can either temperature units be used?** it's ΔT , the change in temperature

What Happens when the Thermal Energy changes?

Phase Changes: Sometimes changing the thermal energy of a system causes a change in the phase of the system (without changing the temperature)

e.g. what happens to an ice cube left out on the counter:



In this case, if the increase in energy doesn't raise the temperature, where does it go?

The energy is used to break the strong bonds of the solid.

Define: **Heat of Transformation, L** = amount of energy required to transform 1 kg of the substance through the phase change

So, for mass M , the heat needed to achieve the transformation is: $Q = ML$

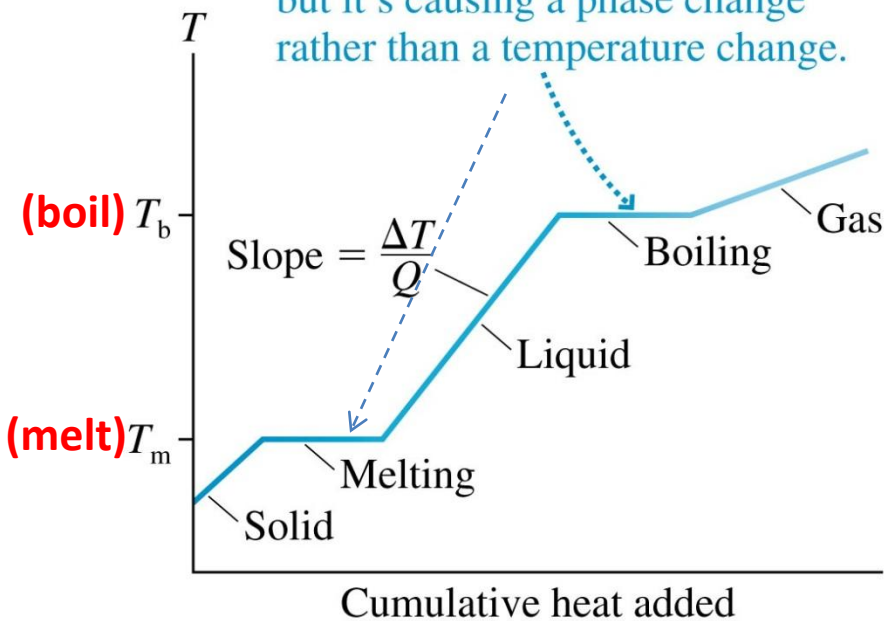
**For the case of a melting ice cube, the change in thermal energy is usually due to heat added to the ice; although it doesn't have to be.*

What Happens when the Thermal Energy changes?

(more on temperature and phase changes)

So, for a substance like water, its temperature would change like this as heat is added:

The system's thermal energy is increasing as heat energy is added, but it's causing a phase change rather than a temperature change.



We will be concerned with the solid/liquid (Fusion) and the liquid/gas (Vaporization) phase changes.

So, the heat needed for a phase change is:

$$Q = \begin{cases} \pm ML_f & \text{for solid} \leftrightarrow \text{liquid} \\ \pm ML_v & \text{for liquid} \leftrightarrow \text{gas} \end{cases}$$

Where:

L_f = heat of fusion

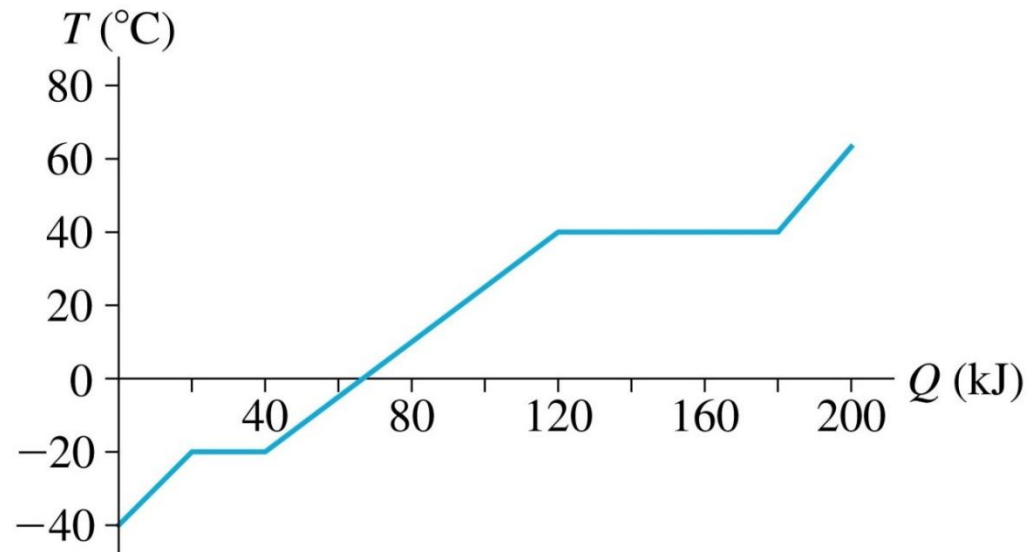
L_v = heat of vaporization

For some substance, i.e. L_f and L_v depend on the material.

Whiteboard Problem 19-2

An experiment measures the temperature of a 500g substance while steadily supplying heat to it. It starts out as a solid, melts to liquid, and then vaporizes to a gas. The figure below shows the results of the experiment. **What are:**

- a) **The melting temperature?**
- b) **The boiling temperature?**
- c) **The specific heat in the solid phase? (LC)**
- d) **The specific heat in the liquid phase? (LC)**
- e) **The heat of fusion?**
- f) **The heat of vaporization? (LC)**



Whiteboard Problem: 19-3

A 5.0 g ice cube at -20°C is in a rigid, sealed container from which all the air has been evacuated. **How much heat is required to change this ice cube into steam at 200°C ? (LC)**

Necessary data:

TABLE 19.3 Melting/boiling temperatures and heats of transformation

Substance	T_m ($^{\circ}\text{C}$)	L_f (J/kg)	T_b ($^{\circ}\text{C}$)	L_v (J/kg)
Nitrogen (N_2)	-210	0.26×10^5	-196	1.99×10^5
Ethyl alcohol	-114	1.09×10^5	78	8.79×10^5
Mercury	-39	0.11×10^5	357	2.96×10^5
Water	0	3.33×10^5	100	22.6×10^5
Lead	328	0.25×10^5	1750	8.58×10^5

** There is no need to memorize data like this. For homework, just use these tables from your text, and on an exam, data like this will be supplied with the problem.*

For the specific heat of steam, since the volume is held constant, use $c = 2009 \text{ J/kg K}$.

Hint: to keep track of the heat that you are calculating, write it out in words before you write any equations.

TABLE 19.2 Specific heats and molar specific heats of solids and liquids

Substance	c (J/kg K)	C (J/mol K)
Solids		
Aluminum	900	24.3
Copper	385	24.4
Iron	449	25.1
Gold	129	25.4
Lead	128	26.5
Ice	2090	37.6
Liquids		
Ethyl alcohol	2400	110.4
Mercury	140	28.1
Water	4190	75.4

The First Law for Solids and Liquids

When there is no phase change, the first law for a solid or liquid is:

$$\Delta E_{\text{th}} = Q + W = Mc\Delta T$$

But, to a very good approximation, solids and liquids are **incompressible**, so:

$$W = - \int PdV = 0 \text{ since } dV = 0$$

So, **for solids and liquids***, we have a simple relation that gives the resulting change in temperature for a given amount of heat added to or removed from the system:

$$Q = Mc\Delta T$$

remember: $\Delta T = T_{\text{final}} - T_{\text{initial}}$

**For gases, the volume can change and the work can be non-zero; we'll consider gases in the next class.*

Whiteboard Problem 19-4

A 500 g sphere made of an unknown metal is heated to 300°C, then dropped into a beaker containing 300 cm³ of mercury at 20.0°C. A short time later, the mercury temperature stabilizes to 99.0°C.

Identify the metal. (LC)

TABLE 19.2 Specific heats and molar specific heats of solids and liquids

Substance	c (J/kgK)	C (J/molK)
Solids		
Aluminum	900	24.3
Copper	385	24.4
Iron	449	25.1
Gold	129	25.4
Lead	128	26.5
Ice	2090	37.6
Liquids		
Ethyl alcohol	2400	110.4
Mercury	140	28.1
Water	4190	75.4

Obviously, you are to identify the metal by determining its specific heat.

If you're in PHY184, you'll do this experiment in a few weeks, but you'll use water instead of mercury.