Lecture 3: 09.14.05 The first law of thermodynamics

Today:

Reading: Engel and Reid: 2.5, 2.6, 2.7, 2.9, 3.1

Last Time

- Thermodynamic variables:

  INTENSIVE : INVARIANT W/SIZE OF THE SYSTEM   T, P, ...

  EXTENSIVE : VARY LINEARLY W/SIZE (# MOLES) IN THE SYSTEM

  e.g., V, U, S, ...

- Thermodynamic systems:

  CAN IT PASS AT BOUNDARY?   ENERGY   HEAT   WORK   MOLECULES

	ENERGY	HEAT	WORK	MOLECULES
ISOLATED	N	N	N	N
CLOSED	Y	Y	Y	N
ADIABATIC		N	Y	(N)
OPEN	Y	Y	Y	Y

- Thermodynamic processes:

  ISOTHERMAL — CONSTANT T

  ISOBARIC — CONSTANT P

  ADIABATIC — NO HEAT TRANSFER

Irreversible processes

- Natural processes typically occur in only 1 direction spontaneously

  ENTROPY OF UNIVERSE INCREASES IN THE PROCESS

  ↳ REVERSING THE PROCESS WOULD VIOLATE THE 2ND LAW

  o These are *irreversible* processes

Experiment	Process	Observation of irreversibility
Add a drop of food coloring to a glass of water	Diffusion	Droplet never re-forms spontaneously
Expansion of a gas into a vacuum	FREE EXPANSION	GAS WILL NEVER SPONTANEOUSLY RE-COMPRESS
Cooling of a hot object placed in a cold room	HEAT TRANSFER	HEAT NEVER SPONTANEOUSLY FLOWS COLD → HOT
Melting of a solid at T = Tm + 100°	MELTING ABOVE Tm	NEVER, LIQUID RESOLIDIFY SEE @ $T > T_m$

Irreversible processes are driven in the one allowed direction by the second law.

Work and heat change the internal energy of a system

PERFECT DIFFERENTIAL   — INEXACT DIFFERENTIAL

The first law: conservation of energy in thermodynamic calculations

- Internal energy, like kinetic and potential energy that you first encounter in physics, is conserved. Energy lost from a system is not destroyed; it is passed to its surroundings. The first law of thermodynamics is simply a statement of this conservation. The first law, mathematically, is:

INFINTESSIMAL CHANGE
IN INTERNAL ENERGY:

$$dU = dq + dw$$
$$\text{HEAT} \quad \text{WORK}$$

← DEFINES EXISTENCE OF THE FUNCTION INTERNAL ENERGY

- Stated in simple language, the first law says that a change in internal energy is exactly accounted for by summing the contribution due to heat transferred (into or out of the system) and the work performed (on or by the system).

- The first law introduces the two ways of changing the energy of a system: via ***heat transfer or work***.

Sign conventions in the first law

- A source of confusion to new students of thermodynamics is the sign on dq and dw- particularly because different textbooks define different sign conventions for work. We will adopt the following conventions:

$$\Delta U = U_f - U_i = q + w$$
$$\text{HEAT} \quad \text{WORK}$$

HEAT TRANSFER INTO THE SYSTEM : $\Delta U > 0$ $q > 0$

"   "   OUT OF   "   "   : $\Delta U < 0$ $q < 0$

WORK DONE ON THE SYSTEM : $\Delta U > 0$ $w > 0$

"   "   BY   "   "   : $\Delta U < 0$ $w < 0$

Defining work and heat

Definition of work

- The meaning of mechanical work is somewhat intuitive; it is energy spent in applying a mechanical force to produce a displacement- a change in size of a system. You are familiar with mechanical work where F is a mechanical force and dx is a change in the length of a (one-dimensional) system, such as a spring.

$$dw = F \cdot dx$$
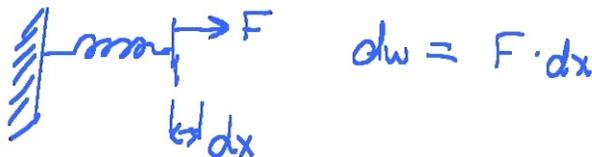
- Where dw is the rate work is performed in creating some infintessimal change in the extent of the system dx against the force F which resists that change.

o   Work can take on many forms other than mechanical work. Some examples of interest for
materials science & engineering include:

Examples of work in materials

Type of work	Thermodynamic Force, "*F*"	Change in system's extent "*dx*" in response to this force (displacement):
Work of hydrostatic pressure	• P	• $-dV$
Work of polarization	• $\vec{E}$ ELECTRIC FIELD	• $d\vec{D}$ ELECTRIC DISPLACEMENT (CHANGE IN POLARIZATION)
Chemical work	• μ CHEMICAL POTENTIAL	• dn OR dN # MOLECULES
Work of surface energy	• γ SURFACE ENERGY OR SURFACE TENSION	• dA INTERFACIAL AREA

A = area of interface

Spreading droplet gives rise to area change   dA
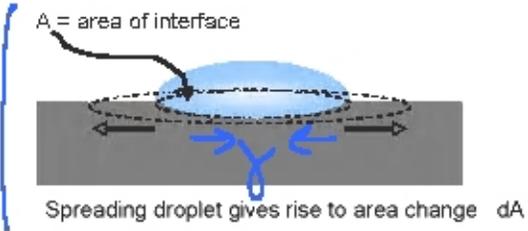
•   Applying pressure changes the extent of the system's volume *V*. Applying an electric
field changes the extent of the system's charge- each of these different kinds of work has
a general form Fdx. We will discuss some of the important forms of work in more detail a
few lectures from now.

Definition of heat

- We can use the first law and the definition of work given above to define heat: $dU = dq + dw$

$$dU = dq + dw \Big/ {}_0$$

HEAT IS THE <u>WORKLESS</u> TRANSFER OF ENERGY

↳ ENERGY PASSED BETWEEN INTERNAL DEGREES OF FREEDOM!
BOND STRETCHES, VIBRATIONS, ROTATIONS...

> - Heat is thus energy transferred during a process, *not* a property of the system.

Heat and work only refer to processes of energy transfer (!!!)

THINGS <u>NOT</u> TO SAY:

    THE SYSTEM HAS 5J OF HEAT.

    THE SYSTEM HAS 20J OF WORK.   ✗ NO

HEAT AND WORK ARE NOT CONSERVED...

Energy transfer
dq

Energy transfer
dw
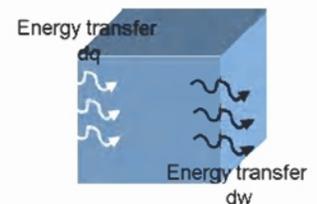
No guarantee heat in = heat
out or work in = work out

Equivalence of work and heat

- The first law can be thought of as a statement of energy conservation, but it is also a statement of the equivalence of work and heat. (Eqn 1) says that I could change the internal energy of a system by some amount (suppose the internal energy is increased 5 Joules, for concreteness) in two entirely different ways:

  o Perform 5 J of work on the system with no heat transfer at the boundaries of the system.

$$\Delta U = q + w = 0 + 5J = 5J \quad \boxed{\text{ADIABATIC}}$$

  o Transfer 5 J of heat into the system while performing no mechanical work (or any other form of work).

$$dw = -P\,dV \Big/ {}_0$$

$$\Delta U = q + w = 5J + 0 = 5J \quad \boxed{\text{ISOCHORIC}}$$

  o Combining knowledge of the type of process occurring with the first law allows one to calculate changes in internal energy directly from measurable quantities like heat and work.

- You may be intuitively comfortable with the idea that mechanical work can convert to heat through processes such as friction- Joule was the first to rigorously test this theory. Others following Joule confirmed that *all* forms of work- not just mechanical work- can be converted to heat.

Limitations on the conversion of heat into work

WE WILL REVISIT
↑ THIS IDEA IN 2ND LAW...

Conversion of heat -> work: IMPOSSIBLE : MANIFESTATION OF THE SECOND LAW
100%!   (PREVENTS PERPETUAL MOTION 'OF THE SECOND KIND')

Conversion of work -> heat: POSSIBLE   RUB 2 STONES TOGETHER: WORK→HEAT
100%!   ↳ $\Delta U = 0$ $q + w = \Delta U$

- When we formally introduce the second law, we will show that it prohibits the opposite process: heat from converting 100% converted into work with no loss of energy to the surroundings. (more on this in lecture 4…)

Heat and work in reversible processes

P-V work in reversible processes

- Pressure on a system performs work at a rate that is well defined only if the work is done extremely slowly, such that the system is in equilibrium at all times and none of the mechanical work being done is converted to heat.
  - This is referred to as a *quasi-static process*- it is *reversible.*
  - In such a process, the increment of work performed for an infintessimal change in volume is given by:
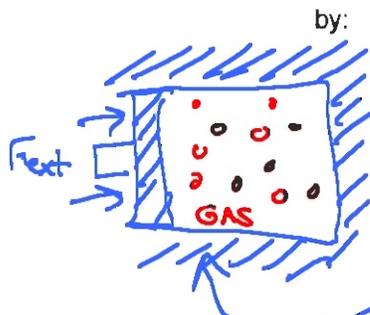
HYDROSTATIC WORK
IN A REVERSIBLE PROCESS :

$$dw = -P dV \leftarrow \text{PRESSURE OF GAS}$$
$$= -P_{ext} dV \leftarrow \text{REVERSIBLE}$$

$$P_{ext} = \frac{F_{ext}}{A}$$

AREA OF PISTON

  - The total work for a quasi-static process is readily calculated by integrating:

- We can only integrate $-P_{ext}dV$ when the process is reversible!

$$V_A \rightarrow V_B \qquad W = \int dw = \int_{V_A}^{V_B} -P dV$$

Heat transfer is linked to an entropy change in reversible processes: first encounter with the second law

- Our first real encounter with entropy comes in examining heat transfer in a reversible process, which provides one definition of entropy. We have mentioned that the second law dictates that entropy increases in spontaneous processes- *but the second law first confirms the existence of a state function- entropy*, which is defined as:

REVERSIBLE PROCESS
DEFINITION OF ENTROPY :

$$dS = \frac{dq_{rev}}{T}$$

ABSOLUTE TEMPERATURE (KELVIN SCALE)

$$K = {}^{\circ}C + 273$$

$$\text{e.g., } 20\,{}^{\circ}C \longrightarrow 293\,K$$

$$\text{UNITS OF ENTROPY? } dS = \frac{[\text{ENERGY}]}{[\text{TEMPERATURE}]} = \frac{J}{K}$$

- o For practical calculations, we see that the units of entropy are the units of heat (energy) divided by temperature. We will discuss the definition of *temperature* next time; for now, let's just state that the temperature in all thermodynamic equations refers to absolute temperature on the Kelvin scale (*K*). Thus the units of entropy are *Joules/K*.

- The reversible process definition of entropy provides a means to measure entropy changes during reversible processes. It is the heat change in a system divided by the system's temperature.

- The definition also allows us to show the link between entropy and internal energy. Combining the first law with the reversible process definition of entropy gives us:

$$dU = dq + dw$$

$$\Big\downarrow \text{ REVERSIBLE PROCESS}$$

$$\boxed{dU = TdS - PdV} \quad \text{FIRST LAW}$$

- o In a reversible process where no mechanical work is performed, *dU = TdS*.

Path dependence vs. path independence of work, heat, and other thermodynamic functions

Path independent variables: State functions

- We have introduced several thermodynamic functions:

    - Internal energy $U = U(S,V,N)$ — STATE FUNCTIONS
    - Entropy $S = S(U,V,N)$ (EXACT DIFFERENTIAL)
    - Pressure $P = P(V,N,T)$
    - Etc.

        - We've just seen how the internal energy depends on S and V for the case of reversible processes. We will show in a few lectures how U also depends on N.

- We have also introduced heat and work:

    - Heat q increment of heat transferred; $đq$ NOT STATE FUNCTIONS
    - Work w increment of work: $đw$ (INEXACT DIFF)

- The thermodynamic functions above are distinct from work and heat: $U, S,$ and P are examples of *state functions*, while q and w are **not** state functions

3 Characteristics of state functions using the ideal gas law as an example

o	**1: State functions are models for materials**

- A special type of state function relates P, V, and T for a material: such a state function is called an **equation of state**. An example we will return to later: the P-V state function of an **ideal gas**:
    - The ideal gas equation of state can be derived by making two assumptions:
        - **The molecules do not interact**
        - **Each atom/molecule acts as a point mass**

IDEAL GAS : ① EQUATION OF STATE : $\overline{PV = nRT}$ ← STATE FUNCTION

② $U = f(T)$ (ONLY)   ↑ GAS CONSTANT

→ DERIVED FROM MOLECULAR MODELS, OR EMPIRICAL DATA

- R = gas constant = 8.3144 J/mole K $= 0.082057$ L·atm/mole·K

Example comparison of ideal gas law behavior with real (experimentally determined) gas behavior:

Isotherms for CO_2 are shown at (a) 426 K and (b) 310 K using the van der Waals equation of state (red curve), the Redlich-Kwong equation of state (brown curve), and the ideal gas equation of state (green curve). The orange dots are accurate values taken from the NIST *Chemistry Webbook.*
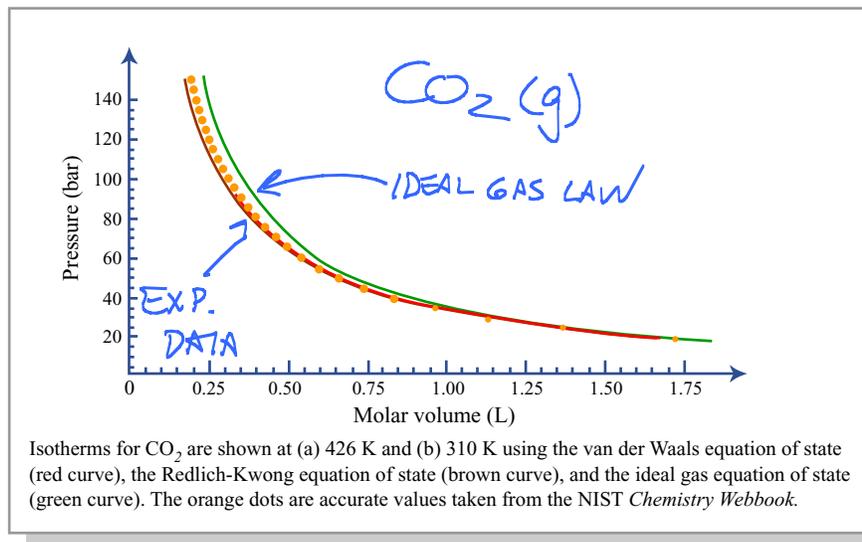
Figure by MIT OCW.

o   **2: If I know 3 variables, the fourth is determined by a state function**

e.g.: $PV = nRT$ $P, n, T:$ $V = \dfrac{nRT}{P}$

o   **3: State functions are path independent**:
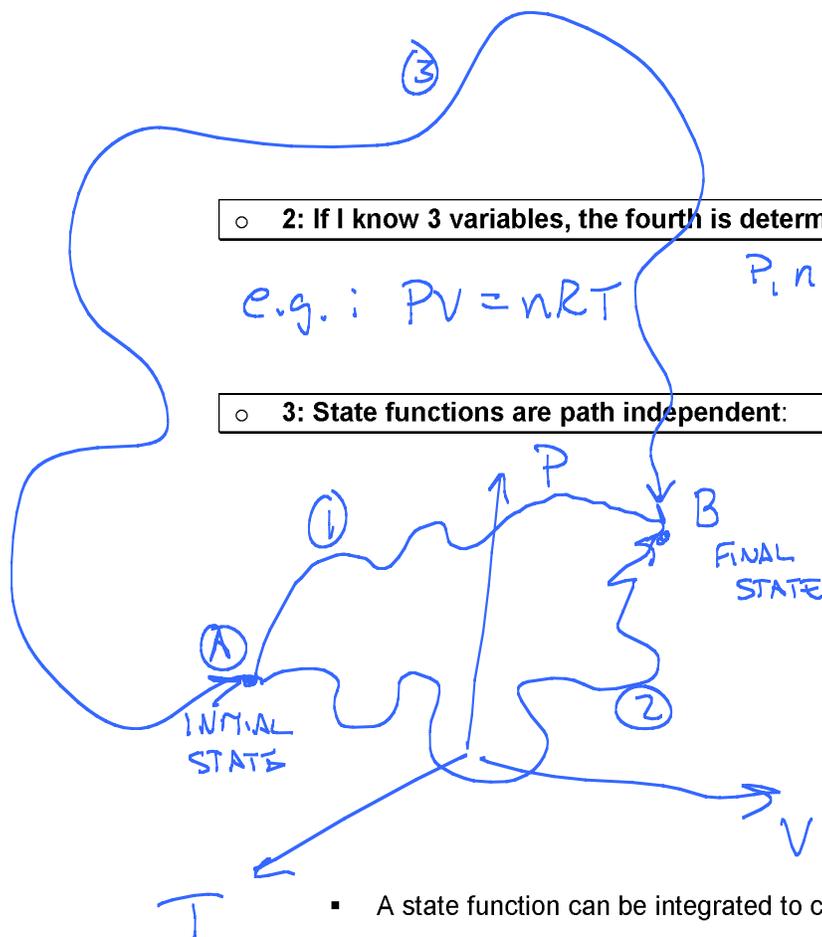
$\Delta U = U_f - U_i$

$= \Delta U_1 = \Delta U_2$

CYCLIC PROCESS : ① $A \to B$
                           ② $B \to A$

$\Delta U = \Delta U_1 + \Delta U_{2\,rev} = U_B - U_A - U_B + U_A = 0$

▪   A state function can be integrated to calculate changes in the value of the function:

- Integration of a state function over a cyclic process gives a change of zero in the value of the state function.

- **Path-dependent functions like heat and work, on the other hand, can only be integrated in reversible processes**.

Path dependent variables: heat and work

- Work and heat are not state functions; they are path dependent- what does this mean? In most physical situations, we are concerned with a quantity of heat or work transferred into or out of a material, which causes a change from one state of the material to another. Path dependence implies that the amount of work or heat needed to make the change depends on *how* the process was performed, not just what state the material started in and ended in.

A simple example: path dependence of P-V work[2]

- If mechanical work is performed on a material by placing it under pressure extremely slowly- such that none of the work is converted to heat (e.g. due to friction) and the system is in equilibrium at each moment, then the work performed is given by:

- Suppose I have a block of material that I put under various conditions, varying the pressure the material is under and it's volume. I do this to change from a state A (P_1, V_1) to state B (P_2, V_2) by two different paths, as illustrated below:
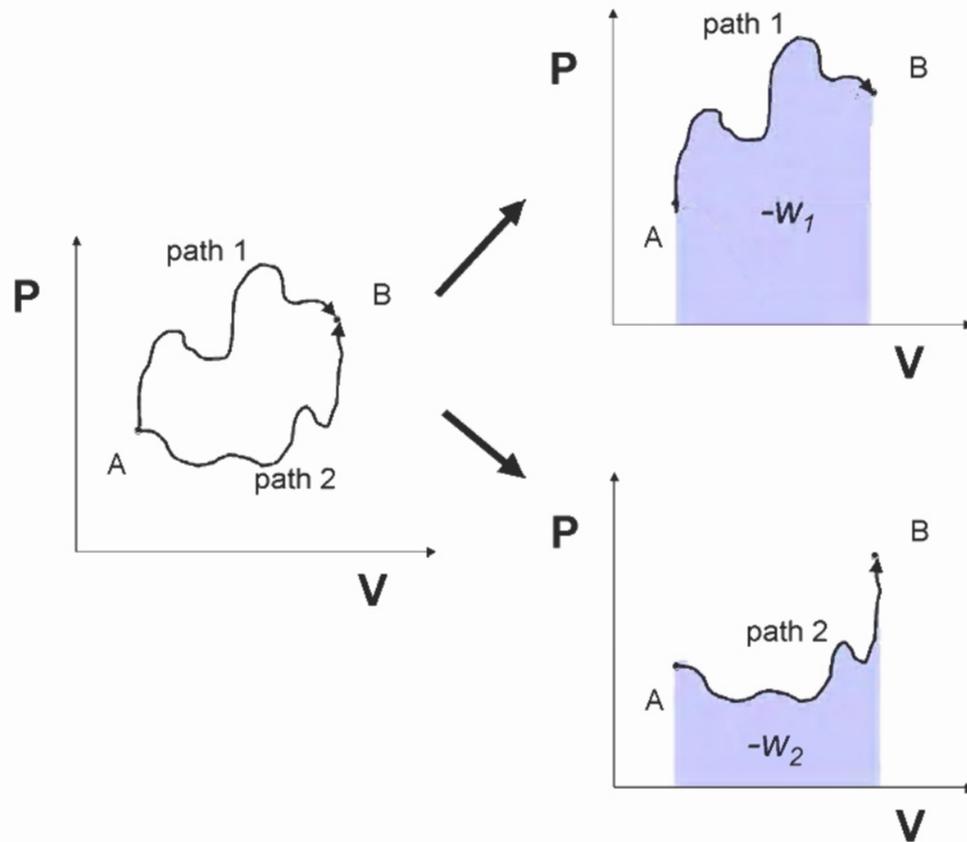
- Since I performed this work extremely slowly (without waste of any of the work as heat), we can calculate the total work for each path by integrating:

$$w_1 = \int_{path1} -PdV$$

- We can clearly see from the graphical representation that the work done along path 1 will be significantly different from that along path 2: *the total work is path dependent.*

References

1.   Engel, T. & Reid, P. Physical Chemistry (Benjamin Cummings, San Francisco, 2006).
2.   Denbigh, K. The Principles of Chemical Equilibrium (Cambridge University Press, New York, 1997).