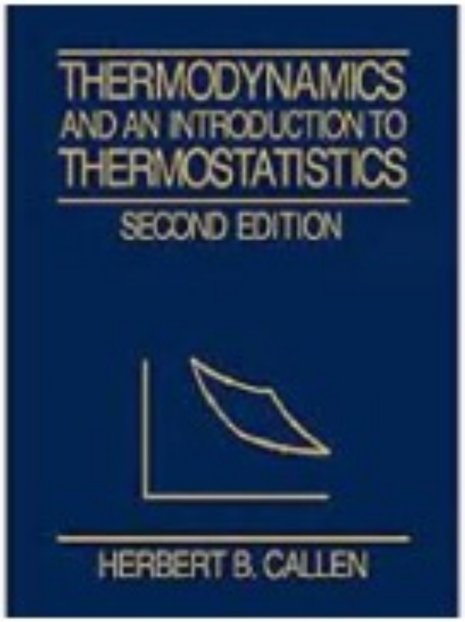
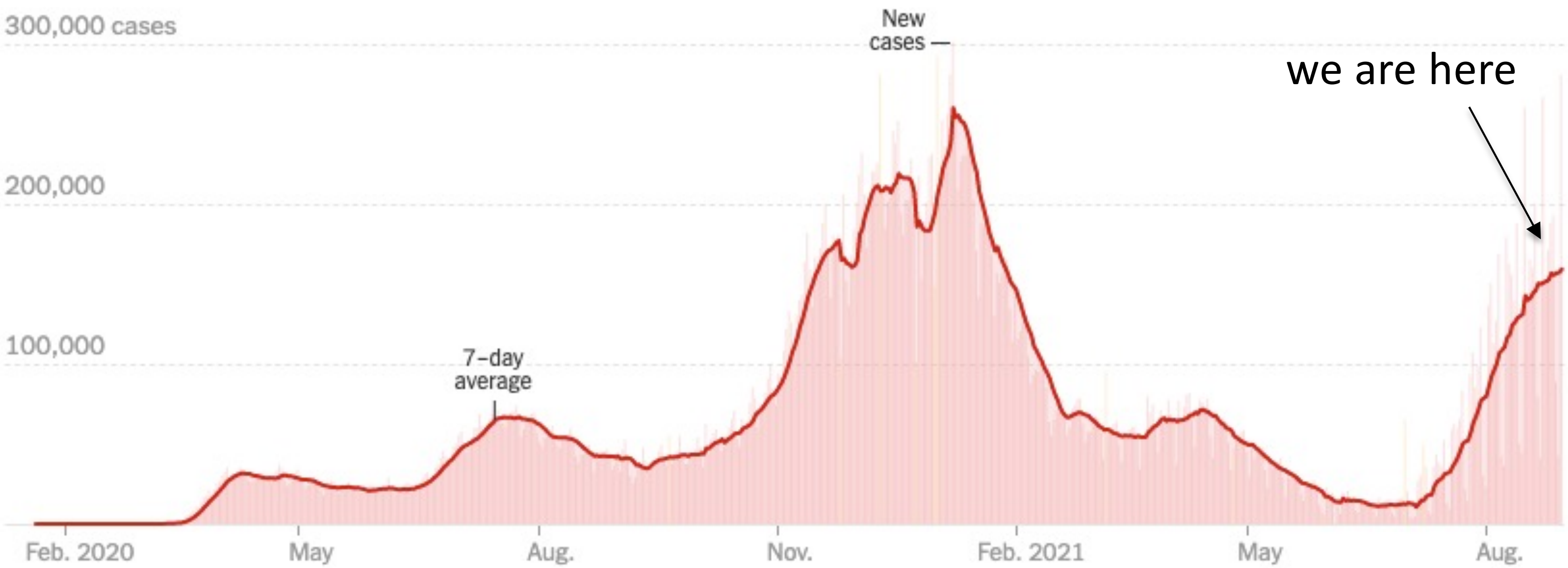
Phys 408: Thermodynamics /Statistical Mechanics

- Course web address: rossgroup.tamu.edu/408page.html
  Syllabus is now posted there, and I have a few printed copies here. (More information such as slides, HW will be posted on web as we go along.) or try http://people.tamu.edu/~jhross/
- Grading: 1 midterm + 1 final, also Homework.
  Homework presentations: about 3 each week, extra credit opportunity. I will ask for volunteers after I assign homework/choose problems. More information to come.
- Reading: Ch. 1 this week, to be followed by ch. 15.
- Note about lectures/slides: I sometimes use powerpoint, sometimes just whiteboard. Slides I will post but you should take notes; I don't put everything on slides.
- I will also record lecture for those needing to quarantine or be absent.


THERMODYNAMICS
AND AN INTRODUCTION TO
THERMOSTATISTICS
SECOND EDITION
HERBERT B. CALLEN

<< Callen text

Covid safety:



NY Times

?

we would like
to make it here

Please do your part, this is a dangerous time for many people.

Thermodynamics : macroscopic thermal physics

First part of text: ch. 1 to read first

Statistical mechanics : microscopic, ”atoms up” properties.

Starting with ch. 15, coming next

>> Here we deal with with collections or “ensembles” of particles or objects.

Thermodynamics : macroscopic thermal physics

Entropy (S), $dS = \frac{\delta Q}{T}$, heat flow vs. temperature: Clausius, Carnot mid 1800's.

Statistical mechanics : microscopic, "atoms up" properties, but applied in statistical way.

Boltzmann: $S = k_B \ln \Omega$; Ω = countable number of states to be explored by particles in system.

>> Here we deal with with collections or "ensembles" of particles or objects.

Some applications:

- Fermi & Bose gases: quantum behavior underlies everyday behavior of metals, nuclei & nuclear matter, neutron stars.
- Quantum information theory, connection to black hole entropy, Hawking radiation etc.
- "Quantum thermodynamics"; entanglement vs. random/statistical behavior of interacting systems.

Quantities and Variables:

Processes

Q = Heat; Spontaneous energy flow into system, not by changing external variables.

W = Work done on system; energy transfer to system via changing external variable.

most obvious example: mechanical, e.g. by piston ($W = -P\,dV$.)
work also includes all energy transfer processes other than heat flow.

Refer to specific processes (change along a specific path) Reversible *or* irreversible.

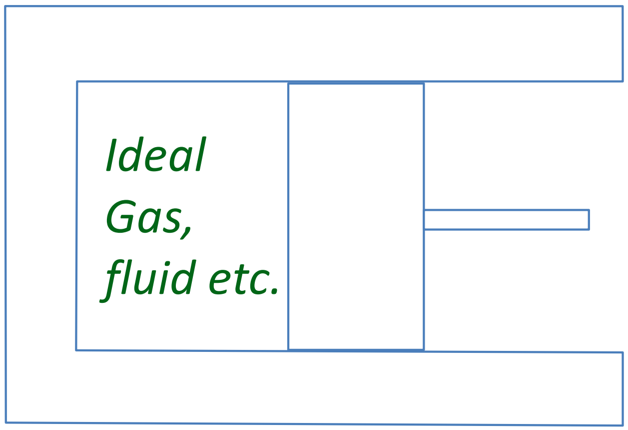
State function

U = Total internal energy.

- Total of all energy contained in system
- Includes Potential + Kinetic energy of thermal motions, electronic or other internal excitations, etc.

Example

(*N* = const inside)



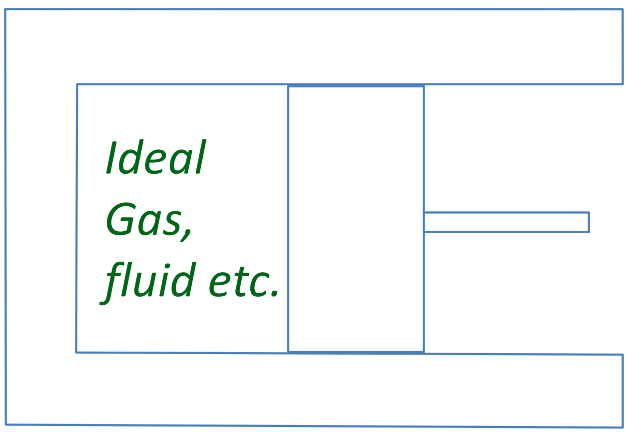
Expand <u>suddenly</u> to 2x volume.

sign of *Q*, *W*? ΔU? ΔT?

Perfectly Insulated cylinder ("<u>**Adiabatic Process**</u>") $Q = 0$

Example

(*N* = const inside)



Expand suddenly to 2x volume.

sign of Q, W? ΔU? ΔT?

0 0 ? 0 if *ideal gas*

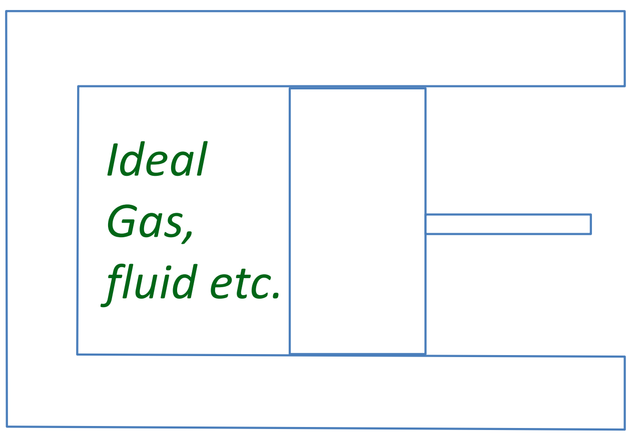
Perfectly Insulated cylinder ("**Adiabatic Process**") $Q = 0$

W = Work done on system; energy transfer to system via changing external variable. *$W = -P\,dV$ only for a controlled process; path dependent energy transfer*

- **First law (conservation of energy):**

$$\Delta U = Q + W$$

(N = const inside)



Expand <u>suddenly</u> to 2x volume.

sign of Q, W? ΔU? ΔT?

0 0 ? 0 if *ideal gas*

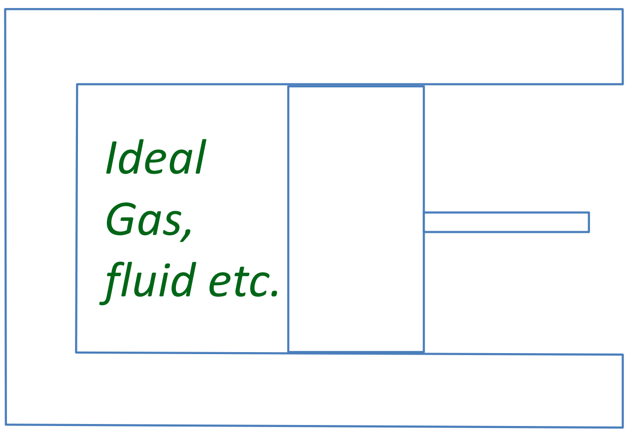
Perfectly Insulated cylinder (“**Adiabatic Process”**) Q = 0

W = Work done <u>on system</u>; energy transfer to system via changing external variable. *W = – $P\,dV$ only for a <u>controlled process</u>; path dependent energy transfer*

- **First law (conservation of energy):**

$$\Delta U = Q + W$$

(*N* = const inside)



Expand <u>suddenly</u> to 2x volume.

sign of Q, W? ΔU? ΔT?

0 0 ? 0 if *ideal gas*

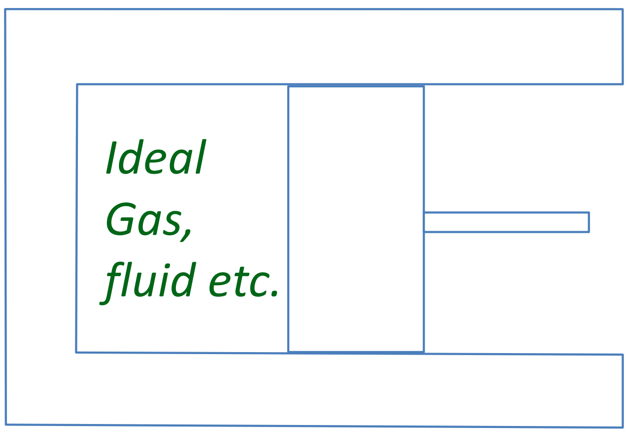
Further process: <u>slowly</u> return piston to original position.

Does system return to its original state?

- **First law (conservation of energy):**

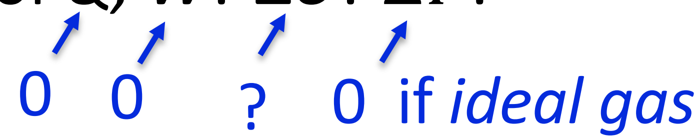
$$\Delta U = Q + W$$

(*N* = const inside)



Expand suddenly to 2x volume.

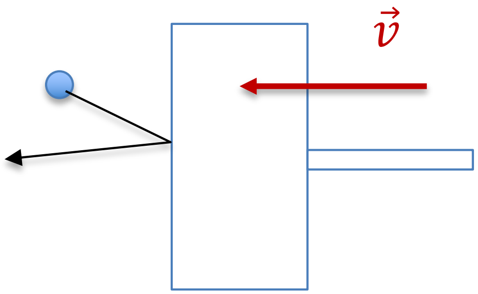
sign of Q, W? ΔU? ΔT?



Further process: slowly return piston to original position.

Does system return to its original state?

Uncontrolled process: increases entropy of the system (and we find, *applied heat* does the same thing)



& note microscopic kinetic equivalent of mechanical work

Entropy (*S*):

- Incorporates the concept of "disorder", although in *energy* states as well as simply physical disorder: This is statistical mechanics physical basis for *S*.
- In thermodynamics, find that $dS = dQ/T$ for a controlled process; heat flow always increases *S*. But *uncontrolled* processes also increase entropy in absence of heat flow.
- In our example, from these definitions can see that *S* increased, and there is no way to reverse the process!

- **First law (conservation of energy):**

$$\Delta U = Q + W$$

U = State function; $\Delta U \equiv U_2 - U_1$

- *More specific notation*:

$$dU = đQ + đW$$

< Q & W processes don't act as independent variables

- *Generalized work*:

e.g. Mechanical work

For controlled process only, $W = -\int P dV$.

alternatives $-\mu_o VHdM$; $-P\Delta E$; …

also <u>chemical work</u> by change of # particles to define soon.

variables define <u>multi-dimensional space</u>

Thermodynamic Variables:

P, V : Pressure (intensive) and Volume (extensive)

Extensive: proportional to system size. e.g. depends on the *physical extent* of system.

Intensive: Independent of system size

N, H, M we have seen.

Note text notation: $I = MV$ total magnetic moment

Which are extensive/intensive?

Multi-component system: N_1, N_2, … e.g. $N_2 + O_2$ or nuclear matter

T = Temperature. (Same as familiar quantity, formal definition to come)

U = Internal energy.

S = Entropy *Extensive quantity*

Thermodynamic Variables:

P, V : Pressure (intensive) and Volume (extensive)

Extensive: proportional to system size. e.g. depends on the *physical extent* of system.

Intensive: Independent of system size

N, H, M we have seen.

Note text notation: $I = MV$
total magnetic moment

Which are extensive/intensive?

Multi-component system: $N_1, N_2, \ldots$ e.g. $N_2 + O_2$ or nuclear matter

T = Temperature. (Same as familiar quantity, formal definition to come)

U = Internal energy.

S = Entropy *Extensive quantity*

Note extensive/intensive pairs are intrinsically coupled:

$$dU = TdS - PdV + \mu dN$$

1st law as later defined (ch. 2); maintains proper *size scaling*.

Chapter 1 & Postulates:

Assumptions for now:

- "Very large" system size: System variable assumed to have a specific value (fluctuations we consider later). Huge number of internal variables we can then neglect with regards to macroscopic measured quantities.

- System in equlibrium: Thermodynamic variables unchanging in time. Non-equilibrium thermodynamics beyond this course.

- Quasistatic processes: Idealization, assuming changes in state are sufficiently slow that system proceeds through a series of equilibrium states. Kinetic view: particles disturbed e.g. during piston motion relax completely to thermal average behavior before new particles engage the piston. (but note, adiabatic processes might proceed relatively quickly)

- Also general assumption is made of unbounded available set of *energy excitations*. (Excludes only special cases.) We will see, this means temperature is only a positive quantity.

Postulate 1:

System in equlibrium:

- Postulation that equilibrium state *exists*.
- Equilibrium state is *characterized completely by quantities U, V, and the particle numbers* N_1, N_2, ...

Postulate 1:

"ergodic system": will eventually and spontaneously explore all regions of phase space (or all quantum states) accessible to it. [Not true for truly isolated quantum system]

System in equlibrium:

- Postulation that equilibrium state *exists*.
- Equilibrium state is *characterized completely by quantities U, V, and the particle numbers* N_1, N_2, ...

3-dimensional variable space needed for 1-component thermal system. (But a different set of 3 may also be chosen)

Entropy postulates:

2) Entropy (*S*) *exists* as extensive quantity; Among all other initial states reachable from equilibrium state (depending on *U, V, N*), equilibrium state has <u>Maximum Entropy</u>.

3) Entropy is additive for subsystems (separate adjoined regions, or e.g. different particle types), and increases as *U* increases.

4) Nernst theorem: S = 0 at T = 0.