Physics 846 - Winter 2009-10

Instructor: David Stroud
Grader: Ranjan Laha
Text: Pathria, Statistical Mechanics, 2nd ed. (required)
      Callen, Thermodynamics and an Introduction to Thermodynamics, 2nd ed. (recommended)

Grading:
1 MT (~25%)
1 Final (~40%)
HW (~35%)

Course homepage: http://www.physics.ohio-state.edu/~stroud/p846.html

Probably ~5 weeks thermo (maybe less)
5 weeks stat mech

Relevant chapters of the two books:
Callen: chapters 1-7 (8, 9 unk.)
Pathria: chapters 1-4
Other books (see course web page)

I will mostly follow Callen, in treating thermo, with connections to conventional statements of the Laws of Thermodynamics, as I go along.
Def. A "simple system" is one which is macroscopically homogeneous, isotropic, unchanged, large enough that surface effect can be neglected, and not acted on by electric, magnetic, or gravitational fields.

Thermodynamic equilibrium: A state of a macroscopic system that does not change as a function of time. A more formal statement is given by Callen's Postulate I. Each particular state of simple systems (called equilibrium states) which do not change macroscopically are completely characterized by the internal energy $U$, the volume $V$, and the mole numbers $N_1, \ldots, N_r$ of the constituents (i.e., the chemical constituents).

Side remark: What is "internal energy"? It is just what we mean by the total energy of a system, relative to that of some "fiducial state".

Another side remark: Often hard to tell if a system is in equilibrium (e.g., window glass).
Comment: "macroscopic" and "microscopic"

Macroscopic: referring to a large chunk of material (e.g. volume V, mass, total internal energy U, etc.)

Microscopic: on an atomic (or smaller) scale

Thermodynamics: general relationships between micro-macroscopic quantities

Stat mech: Connection between macroscopic quantities and microscopic ones.

\[ U = \text{internal energy} \]
\[ V = \text{volume} \]

Mole number \( N_i \): what is it?

It is the number of moles of a given component \(( 1 \text{ mole} = 6.02 \times 10^{23} \text{ molecules} = \text{Avogadro's number of molecules})\)

Extensive parameter: If we imagine some system divided into subsystems, an extensive param of the system is the sum of the extensive params of the subsystems.

Examples: \( U, V, N_i \)

Walls and constraints: These are walls or objects which separate a system from its surroundings.

Can have walls which are restrictive with respect to \( V, U, N_i \)

Restrictive wrt \( V \): Rigid walls

Restrictive wrt \( U \): see below

Restrictive with respect to \( N_i \): impermeable or semipermeable
Suppose we have a system with two subsystems as below:

Suppose wall is rigid and impermeable. It can still let energy flow through in the form of 'heat' in this case it is called isothermal. If it does not allow energy through at all in the form of heat, it is called an adiabatic wall.

If we have a system surrounded by an impermeable adiabatic wall, the only way $U$ of the system can change is if work is done on it, or it does work (e.g. by expanding it). Furthermore, we can measure the amount of work done on a system using the theory of mechanics (e.g. $W = F \cdot d$), to get determine the change in energy of a system surrounded by adiabatic walls (and impermeable walls). So: energy differences are measurable.

In fact, any two systems with the same mole numbers can be joined by some mechanical process, at least in one direction. Hence, $U$ can be measured to within a constant.
Let us say we have a simple system and there is some process taking that system from state A to state B. Suppose we have measured $U_B - U_A$.

Then

$$U_B - U_A = \Delta W_M + \Delta Q$$

$$= \text{work done on system + heat flowing into system}$$

This equation defined $\Delta Q$.

Suppose we knew go from state A to state B by a series of very small steps, which are taken to occur very slowly so that system stays in equilibrium throughout. This is called a quasi-static process. Then we may write for an infinitesimal step

$$dW_M = -PdV$$

where $P =$ pressure

E.g. see below:

\[\text{Force produced by piston} = P \text{ per unit area}\]

\[\text{work done} = P \cdot A \cdot dx = -P dV \text{ since } V \text{ is getting smaller}\]
we write \( dW \) rather than \( dW_\text{m} \) because there is no state variable \( W \).

Then

\[ dU = -P\,dV + \delta Q \]

where \( \delta Q \) = heat flowing into system

or \( \delta Q = dU + P\,dV \) at constant mole #’s.

Both \( dW \) and \( \delta Q \) are measured in units of energy.

**Example:** A gas has the property that if enclosed in an adiabatic container, \( P \) and \( V \) are related by

\[ P^2 V^5 = \text{const}. \]

Find the quasi-static work in each of the three processes below:

- **Process A to D:**
- **Process B to C:**
- **Process C to B:**
Process \( AB \) (along adiabat):

\[ U_B - U_A = W_{AB} = - \int_{V_A}^{V_B} P \, dV \]

We have \( PV^{5/3} = P_A V_A^{5/3} \)

So \( P = P_A \left( \frac{V_A}{V} \right)^{5/3} \)

\[ U_B - U_A = - \int_{V_A}^{V_B} P_A V_A^{5/3} \frac{dV}{V^{5/3}} \]

\[ = \frac{3}{2} P_A V_A^{5/3} \left( V_B^{2/3} - V_A^{2/3} \right) \]

\[ = \frac{3}{2} (25 - 100) = -112.5 \text{ J} \]

And Process \( ADB \):

\[ W_{ADB} = W_{AD} + W_{DB} = W_{AD} \]

\[ = -10^5 (V_B - V_A) = -10^5 \left( 8 \times 10^{-3} - 10^{-3} \right) \]

\[ = -700 \text{ J} \]

\[ U_B - U_A = W_{ADB} + Q_{ADB} \]

\[ \Rightarrow Q_{ADB} = U_B - U_A - W_{ADB} = -112.5 \text{ J} + 700 \text{ J} \]

\[ = 587.5 \text{ J}. \]
\[ W_{ACB} = W_{AC} + W_{CB} \]
\[ = W_{CB} = - \frac{10^5}{32} \left( 8 \times 10^{-3} - 10^{-3} \right) \]
\[ = -\frac{700}{32} J \approx 21.9 J \]

And hence
\[ \Phi_{ACB} = U_B - U_A - W_{ADB} = (12.5 + 21.9) = 90.6 J \]

Finally,
\[ W_{AB} = - \int_{A}^{B} P \, dV \text{ along straight line} \]
\[ W_{AB} = - \int_{A}^{B} \left[ P_A + \frac{P_B - P_A}{V_B - V_A} (V - V_A) \right] dV \]
\[ = - \left\{ P_A V + \frac{1}{2} \frac{P_B - P_A}{V_B - V_A} V^2 - \frac{P_B - P_A}{V_B - V_A} V_A V \right\}^{B}_{A} \]
\[ = -P_A (V_B - V_A) + \frac{1}{2} \frac{P_B - P_A}{V_B - V_A} (V_B - V_A)^2 - \frac{P_B - P_A}{V_B - V_A} V_A (V_B - V_A) \]
\[ = -360.9 J \text{ upon plugging in numbers} \]

So
\[ \Delta Q = \Delta U - \Delta W = U_B - U_A - \Delta W \]
\[ = -4248.4 J \]
\[ = -360.9J \text{ eventually} \]

So \( \Delta Q = 428.4J. \)

(b). Suppose we have paddle which causes gas to increase pressure at rate

\[ \frac{dP}{dt} = \frac{2}{3} \frac{w}{V} \times \text{(torque)} \]

Show that this permits us to measure energy diffs. at const. vol.

**Sol:** We have \( \frac{dP}{dt} \frac{dU}{dt} = \text{(torque)}w \)

(\( \text{power delivered by a torque}\) from mechanics)

(non-quasistatic energy transfer)

Hence

\[ \frac{dP}{dt} = \frac{2}{3} \frac{dU}{dt} \]

or

\[ dP = \frac{2}{3} \frac{dU}{dt} \]

\[ dU = \frac{3}{2} V dP \]

So at fixed volume \( \Delta U = \frac{3}{2} V \Delta P \)

\[ U_A - U_C = \frac{3}{2} V_A (P_A - P_C) = 145.3 \text{ J} \]

\[ U_D - U_B = \frac{3}{2} V_D (P_D - P_B) = 1162.5 \text{ J} \]
Can now connect any two points in PV plane to get energy diffs. — either by adiabats, or by isochrones (const. vol.)

Hence, can get any \( \Delta U \)'s: (and any \( \Delta Q \)'s)

\[
\Delta Q_{AD} = \Delta U_{AD} - \Delta W_{AD}
\]

\( \Delta U_{AD} = U_A - U_D \) now known
\( \Delta W_{AD} \) already calculated

\( \Rightarrow \) get all partial heats

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Basic problem of thermodynamics:

Prob: How to find equilibrium state of a closed composite system after removal of interplay constraints

\[
N_1^{(1)}, V_1^{(1)}, U^{(1)} \quad N_1^{(2)}, V_1^{(2)}, U^{(2)}
\]

\( \text{constraint (e.g. piston wall)} \)
Entropy maximum postulates

There exists a function (called the entropy)
which depends on extensive parameters which
is defined for equilibrium states,
which is maximum among possible

The closed system arranges itself so as to maximize
the entropy.

(Goes with Postulate I: equilibrium state is completely
defined by \(U, N_i, V\))

i.e. given \(U, N_i, V\)
we know that there is
one state.

What is the entropy? We assume

- It is extensive i.e. \(S = S_1 + S_2\) for
  two subsystems

and (6) It vanishes in any state for which

\[
\left( \frac{\partial U}{\partial S} \right)_{V, N_i, V_r} = 0 \quad \text{(i.e. at temp } T = 0)
\]

(Nernst hypothesis)

Also assume \(S\) continuous, differentiable, monotonically increasing function of \(U\).
Meaning will arise as we go along:

**Consequences of extensivity:**

We have in general  
\[ S = S(U, V, N_1, \ldots, N_r) \]

for a system with \( r \) subcomponents.

**Extensivity:** If we make the same system \( \lambda \) times larger, it follows
\[
S(\lambda U, \lambda V, \lambda N_1, \ldots, \lambda N_r)
\]
\[\quad = \lambda S(U, V, N_1, \ldots, N_r)\]

**Monotonicity:** 
\[
\frac{\partial S}{\partial U}(U, V, N_1, \ldots, N_r) > 0 \quad \text{(will imply)}
\]
\[\quad \implies T > 0\]

Also, can invert \( S \) to get
\[ U(S, V, N_1, \ldots, N_r) \]

called the fundamental relation.

(Called this because if you know \( S \) you can get all thermodynamic quantities.)

Scaling to molar quantities
\[ S(U, V, N_1, \ldots, N_r) = N S\left(\frac{U}{N}, \frac{V}{N}, \frac{N_1}{N}, \ldots, \frac{N_r}{N}\right) \]
\[ = N S(U, V, N_1, \ldots, N_r) \]
\[ = U = \frac{U}{N} \quad \text{and} \quad n_i = \frac{N_i}{N} \]

For one-component system
\[ S = S(U, V, N) = N S\left(\frac{U}{N}, \frac{V}{N}, 1\right) \]
\[ = N s(U, V) \]
Equilibrium conditions

We had

\[ S = S(U, V, N_1, \ldots, N_r) \]

or

\[ U = U(S, V, N_1, \ldots, N_r) \]

Some calculus:

\[ dU = \left( \frac{\partial U}{\partial S} \right)_{V, N_1, \ldots, N_r} dS + \left( \frac{\partial U}{\partial V} \right)_{S, N_1, \ldots, N_r} dV \]

\[ + \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_1, \ldots, N_{i-1}, N_{i+1}, \ldots, N_r} dN_i \]

Derivatives called intensive parameters

Definition:

\[ \left( \frac{\partial U}{\partial S} \right)_{V, N_1, \ldots, N_r} \equiv T \quad \text{("temperature")} \]

\[ - \left( \frac{\partial U}{\partial V} \right)_{S, N_1, \ldots, N_r} = +P \quad \text{("pressure")} \]

\[ \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_1, \ldots, N_{i-1}, N_{i+1}, \ldots, N_r} = \mu_i \]

"Electrochemical potential"
\[ dU = TdS - PdV + \sum_{i=1}^{r} \mu_i \, dN_i \]

Case I:  \( dN_i = 0 \)

\[ dU = TdS - PdV = \tilde{\Delta}Q + \tilde{\Delta}W_M \]

\[ \tilde{\Delta}W_M = -PdV \]

\[ \tilde{\Delta}Q = TdS = \text{quasistatic heat flow} \]

\[ \sum_{i=1}^{r} \mu_i \, dN_i = \tilde{\Delta}W_C = "\text{quasistatic chemical work}" \]

\[ dU = \tilde{\Delta}Q + \tilde{\Delta}W_M + \tilde{\Delta}W_C \text{ energy dimensions} \]

Equations of state: We have relations like

\[ T = T(S, V, N_1, ..., N_r) \]
\[ P = P(S, V, N_1, ..., N_r) \]
\[ \mu_i = \mu_i(S, V, N_1, ..., N_r) \]

Not all independent (see below).

Theorem: \( T(\lambda S, \lambda V, \lambda N_1, ..., \lambda N_r) = T(S, V, N_1, ..., N_r) \)

Proof: We have \( U(\lambda S, \lambda V, ..., \lambda N_r) = \lambda U(S, V, N_1, ..., N_r) \)
\[
\frac{\partial}{\partial s} u(\lambda s, \lambda v, \ldots, \lambda N_r) = \lambda \frac{\partial u}{\partial s}(s, v, \ldots, N_r)
\]

\[
= \lambda T(s, v, \ldots, N_r)
\]

\[
= \frac{\partial (\lambda s)}{\partial s} \frac{\partial}{\partial (\lambda s)} u(\lambda s, \lambda v, \ldots, \lambda N_r)
\]

\[
= \lambda T(\lambda s, \lambda v, \ldots, \lambda N_r)
\]

or \( T(\lambda s, \lambda v, \ldots, \lambda N_r) = T(s, v, \ldots, N_r) \) \( \text{q.e.d.} \)

So temp. of system is unchanged on enlargement by factor \( \lambda \)

This is an alternative way of defining an intensive parameter.

\( P, \xi, \eta \) are also intensive parameters.

Single-component systems: molar quantities:

\[
U = U^\infty(s, v, N)
\]

\[
= N U\left(\frac{S}{N}, \frac{V}{N}, 1\right) \quad \text{(taking} \lambda = \frac{1}{N})
\]

\[
= Nu(S, v) \quad u = U\left(\frac{S}{N}, \frac{V}{N}, 1\right)
\]

\[
\lambda = \frac{S}{N}; \; v=\frac{V}{N}
\]
Then \[ du = \left( \frac{\partial u}{\partial s} \right)_V ds + \left( \frac{\partial u}{\partial v} \right)_s dv \]
\[ \left( \frac{\partial u}{\partial s} \right)_V = \left( \frac{\partial}{\partial S/N} \right)_{V,N} \]
\[ \left( \frac{\partial u}{\partial v} \right)_s = \left( \frac{\partial}{\partial q/V/N} \right)_{S,N} \]

So \[ du = T ds - P dv \]

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**Entropy extensive parameters:**

Instead of writing \( U = U(S, V, N_1, \ldots, N_r) \) we could have written \( S = S(U, V, N_1, \ldots, N_r) \).

Then \[ dS = \left( \frac{\partial S}{\partial U} \right)_{V,N_1,\ldots,N_r} dU \]
\[ + \left( \frac{\partial S}{\partial V} \right)_{U,N_1,\ldots,N_r} dV \]
\[ + \sum_{i=1}^{r} \left( \frac{\partial S}{\partial N_i} \right)_{U,V,N_1,\ldots,N_{i-1},N_{i+1},\ldots,N_r} dN_i \]

But we also have \[ du = Tds - Pdv + \sum \mu_i dN_i \]