Homework Schedule
Email Single PDF to ailee@ucsd.edu

• Due Oct. 8 (Monday, 12 noon)
  – Ch. 1, Problem 11
  – Ch. 2, Problem 2
• Due Oct. 22 (Monday, 12 noon)
  – Ch. 3, Problem 1 (typo in answer key), 3
  – Ch. 4, Problem 4, 5
• Midterm Oct. 31 (in class)
• Due Nov. 5 (Monday, 12 noon)
  – Ch. 5, Problem 3, 7 (erratum in 7d)
• Due Nov. 14 (Wednesday, 12 noon)
  – Ch. 6, Problem 4, 6
• Due Nov. 19 (Monday, 12 noon)
  – Ch. 7, Problem 3 (not graded, outline approach only, discuss)

What did we learn in Ch. 1?
• What P, T, U are for a fluid
• What an ideal gas is
• How P, T, v relate for an ideal gas (and we call this relationship an equation of state)
• What chemical components constitute the atmosphere (for homosphere <110 km)
• What the hydrostatic balance is
• How p, T vary with z for observed, “standard,” isopycnic, isothermal, constant lapse-rate atmospheres

Lecture Ch. 2a
• Energy and heat capacity
  – State functions or exact differentials
  – Internal energy vs. enthalpy
• 1st Law of thermodynamics
  – Relate heat, work, energy
• Heat/work cycles (and path integrals)
  – Energy vs. heat/work?
  – Adiabatic processes
  – Reversible “P-V” work → define entropy

Curry and Webster, Ch. 2 pp. 35-47
Van Ness, Ch. 2

Key Combined 1st+2nd Law Results
• 1st Law: \( du = dq + dw \); \( u \) is exact Eq. 2.8
  • \( du = dq_{rev} + pdv \) (expansion only) p. 56
  • Define Enthalpy: \( H = U + PV \) Eq. 2.12
• 2nd Law: \( [dq_{rev}/T]_{int.cyc} = 0 \) Eq. 2.27
  • Define Entropy: \( d\eta = dq_{rev}/T \) Eq. 2.25a
  • \( Td\eta = dq_{rev} \; du = Td\eta - pdv \)
  • Define Gibbs: \( G = H - T\eta \) Eq. 2.33
• \( dg = dh - Td\eta \; - \eta dT \; = (du + pdv + vdp) - Td\eta - \eta dT \) p. 58
• \( (\delta p/\delta t)_{g} = \eta /v \) Eq. 2.40

Other Kinds of Energy
What is the difference between \( E \) and \( U \)?
• In addition to changes in internal energy, a system may change
  – Potential energy for height change \( \Delta z \)
  – Kinetic energy for velocity change \( \Delta v \)
  – Nuclear energy for mass change \( \Delta m \)

\[
\Delta E = \Delta U(p,V,T) + \frac{1}{2} m \Delta v^2 - c^2 \Delta m = Q + W
\]

if \( \Delta E = \Delta U(p,V,T) \), then \( \Delta U(p,V,T) = Q + W \)

Van Ness, p. 13

Lord Kelvin (a.k.a William Thomson)

James P. Joule

The First Law of Thermodynamics
\[
dU = dq + dw
\] (2.7)

Consequences

| Significance of work values \( W_{rev} = -W \) | Reversible
| Definition of energy \( Q = 0 \Rightarrow W = 0 \) | Adiabatic
| Conservation of energy \( Q = 0, W = 0 \Rightarrow \Delta E = 0, K_{i} = K_{f} \) | State function
| Impossibility of perpetual motion machine \( Q = 0, \Delta E = 0 \Rightarrow W = 0 \) | See also 2nd law!
| (Relativity) \( \Delta E = mc^2 \) | Proof for homework...
Exact Differentials

State functions are exact differentials.

- The first law thus states that although $dU$ and $dW$ are not exact differentials, their sum $dU + dW$ is an exact differential and thus a thermodynamic state variable.

- An exact differential $dQ$ has the following properties:
  1. The integral of $dQ$ about a closed path is equal to zero ($\oint dQ = 0$).
  2. For $Q(x,y)$, we have $dQ = \left( \frac{\partial Q}{\partial x} \right) dx + (\frac{\partial Q}{\partial y}) dy$ where $x$ and $y$ are independent variables of the system and the subscripts $x$ and $y$ on the partial derivatives indicate which variable is held constant in the differentiation.

Heat Capacity

It is convenient to define a new function called the enthalpy, $H$, by:

$$H = U + pV$$

- Difference b/w $U$ and $H$:
  - $U$ depends on $v$,
  - $H$ depends on $p$

- Specific heats [a.k.a. heat capacity]
  - $c_v$ is constant $v$ $\frac{du}{dt} = \frac{2}{3} \frac{dv}{dt}$
  - $c_p$ is constant $p$ $\frac{dh}{dt} = \frac{2}{3} \frac{dp}{dt}$

Heat Capacity

For all gases:

$$du = c_v dt + \left( \frac{B}{T} \right) dv$$

$$dh = c_p dt + \left( \frac{B}{T} \right) dp$$

For an ideal gas, it has been shown experimentally that $\left( \frac{B}{T} \right) = 0$, so that internal energy is a function only of temperature for an ideal gas, i.e., $u = u(T)$. It can also be shown that $dh = 0$ and $h = h(T)$. This implies that for ideal gases:

$$du = c_v dt$$

$$dh = c_p dt$$

What does $c_v$ differ from $c_p$ quantitatively? In a constant-pressure process, some of the added heat must be expended in doing work on the surroundings, while in a constant-volume process, all of the heat is devoted to raising the temperature of the substance. Therefore it takes more heat per unit temperature rise at constant pressure than at constant volume, and $c_p > c_v$. The difference between $c_p$ and $c_v$ can be evaluated from cycles:

Work

- Expansion work $W = -pdV$ or $w = -pdv$
  - Lifting/rising
  - Mixing
  - Convergence
- Other kinds of work?
  - Electrochemical (e.g. batteries)

Cycles

- Work and heat are path-dependent transfers
  - Work $W$
  - Heat $Q$

- State functions are unique "states"
  - Internal energy $u$
  - Enthalpy $H$
  - Entropy $S$
  - Helmholtz free energy $A$
  - Gibbs energy $G$
Adiabatic
"First Law"
Reversible
"Internal Energy"
Ideal Gas
\[
p_1 V_1 T_1 = \frac{R}{\gamma} = p_2 V_2 T_2
\]
\[
\Delta u = c_v dT
\]
\[
W = -p dV
\]
\[
\Delta u = Q + W
\]
Reversible, Adiabatic
Frictionless
Low P, High T
\[
\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma}{\gamma-1}}
\]
Entropy
• Is there a way to quantify “useful” energy?
• Need a measure that is conserved, exact, unique
• While Q is not exact, Q\text{rev} is exact
  – Reversible heat is limit of maximum work done
  – Since path is specified, cyclic integral is 0
There exists an additive function of state known as the equilibrium entropy, which can never decrease in a thermally isolated system.

Lecture Ch. 2b
• Entropy
• Second law of thermodynamics
• Maxwell’s equations
• Heat capacity
• “Meteorologist’s entropy”

Curry and Webster, Ch. 2 pp. 47-62
Van Ness, Ch. 5-7

Curry and Webster, Ch. 2 pp. 47-62
Van Ness, Ch. 5-7
Consider the first law of thermodynamics in its integral form (2.18b) for a reversible process:

\[ dq = cp dT - dp \]

The two terms on the right-hand side of (2.23) are by definition exact differentials, and their sum must be an exact differential. Therefore \( dq \) is an exact differential.

The entropy of an isolated system cannot decrease.

\[ \Delta S_{\text{system}} \geq 0 \]

\[ \Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dQ}{T_{\text{system}}} \]

**Clausius’ Inequality**

\[ \Delta \eta_{re} \geq 0 \]

which is known as Clausius’ inequality. For a reversible process we cannot have \( \Delta \eta_{re} < 0 \), since we would have \( \Delta h_{re} < 0 \) upon reversing the process, which would violate Clausius’ inequality. Therefore, \( \Delta \eta_{re} = 0 \) for all reversible changes for the system.

No process exists in which heat is extracted from a source at a single temperature and converted entirely into useful work, leaving the rest of the world unchanged.

**Maxwell’s Equations**

Since \( dq \), \( dh \), \( ds \), and \( dp \) are exact differentials, they obey the Euler conditions (2.9). Therefore from (2.31), (2.32), (2.34) and (2.36) we obtain the following set of useful relations called Maxwell’s equations:

\[ \left( \frac{\partial f}{\partial T} \right)_p = \left( \frac{\partial G}{\partial T} \right)_p \]

\[ \left( \frac{\partial f}{\partial S} \right)_T = \left( \frac{\partial G}{\partial S} \right)_T \]

\[ \left( \frac{\partial f}{\partial T} \right)_S = \left( \frac{\partial H}{\partial T} \right)_S \]

\[ \left( \frac{\partial f}{\partial S} \right)_T = \left( \frac{\partial H}{\partial S} \right)_T \]

\[ \left( \frac{\partial f}{\partial p} \right)_T = \left( \frac{\partial F}{\partial p} \right)_T \]

\[ \left( \frac{\partial f}{\partial p} \right)_S = \left( \frac{\partial F}{\partial p} \right)_S \]

\[ \left( \frac{\partial f}{\partial T} \right)_p = \left( \frac{\partial G}{\partial T} \right)_p \]

\[ \left( \frac{\partial f}{\partial S} \right)_T = \left( \frac{\partial G}{\partial S} \right)_T \]

\[ \left( \frac{\partial f}{\partial T} \right)_S = \left( \frac{\partial H}{\partial T} \right)_S \]

\[ \left( \frac{\partial f}{\partial S} \right)_T = \left( \frac{\partial H}{\partial S} \right)_T \]

\[ \left( \frac{\partial f}{\partial p} \right)_T = \left( \frac{\partial F}{\partial p} \right)_T \]

\[ \left( \frac{\partial f}{\partial p} \right)_S = \left( \frac{\partial F}{\partial p} \right)_S \]