

Key Features of the Course

- Text: Atkins & Jones, NOT Peck et al.
- Lab: much different, see Lab syllabus
 - 101H/113 Lab Manual **NOT** required!
- Term Paper - required for honors courses.
 - Topic deadline: Feb. 24th
 - Outline deadline: Mar. 31st
 - Due date: April 19th
- Homework, posted on web, 18% of grade
 - Groups of 4 (voluntary)

Key Features of the Course

- The gap between Honors and Non-honors section is larger than most other honors classes.
- I will conduct regular evening Q&A sessions, the attendance of which is entirely voluntary.
- Rigorous science classes require that you NOT have to cram for exams – rather, you should be using the homework as part of a way to keep up with the material.

Are you in the Right Course?

- I assume that you are already familiar from your high school course(s) with the concepts in the introductory "Fundamentals" sections of the textbook.
- Review this material; for Chem 102H sections A, D, G, H, I, J, K, and L are relevant (other sections were prerequisite to Chem 101H).
- Elementary principles of differential and integral calculus will also be assumed.
- If you are concerned that you may not be adequately prepared to succeed in this course, please consult with me during the first week of class.

*Thermodynamics:
First Law & Calorimetry
First up: Work, Heat, Energy*

CHEM 102H
T. Hughbanks

Reading, etc.

- Chapter 6 starting today!
- Homework will be posted on the class web site:
- <http://www.chem.tamu.edu/rgroup/hughbanks/courses/102H/chem102H.html>
- These lecture outlines, calendar of exam dates, syllabus, etc... also posted.

Definitions, etc.

- Early part of Chapter 6 deals with a lot of terms: system, surroundings, universe, etc.
- Read the material carefully; the material is a bit abstract. I'll try to discuss aspects of "work" and "heat" carefully, though in practice chemists don't really have to think about "work" all that often.

Quick Definitions

Universe = System + Surroundings

System = That part of the universe we wish to study; Surroundings = everything else

Open System: Exchanges both matter and energy with surroundings (often 'real world')

Closed System: Exchanges energy, but not matter, with surroundings (idealized)

Isolated System: no exchange of matter or energy with surroundings (more idealized)

Changes of state & state functions

- In thermodynamics, we usually talk about some change in a system. A change in a property X is just

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

- X is called a state function if the value of ΔX depends only on the initial and final states, & not on the path taken between them.

State Functions

- Common state functions include P, V, T, n , p ,...
- Equations of State: show the mathematical relationships between state variables (e.g., $PV = nRT$ approximates real gases).
- Most books, including ours, use the convention that state functions are represented as capital letters. Lower case letters are usually not used for state functions.

Path Independence of State Functions

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

- This does not specify what might happen between initial and final states.
- ΔX is “path independent.” We can imagine any process from initial to final states.

Energy, Heat, Work, ...

- Definitions not always same as in ordinary use
- Distinctions between these important
- Our discussion will be limited - you will get more careful view in other courses

Energy (U)

- Often defined as “the ability to do work.”
- Lots of different forms of energy, as we have seen: potential, kinetic, light, etc.
- We look mainly at chemical energy, which is the energy stored in the chemical bonds in a substance or released when such bonds are formed. Chemical energy can be converted into other forms of energy.

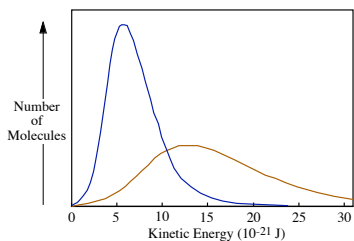
Internal Energy

- We often discuss the change in “internal energy” (or just the change in energy) of a system.
- Our text uses ΔU for this.
- We rarely talk about U itself, because there is no absolute scale for energies.
- Other books often use ΔE for the change in internal energy.

Review: Gas Temperature & Kinetic Energy

- T is proportional to the average kinetic energy of the molecules in a gas.
- Ideal gas (per mole): $KE_{\text{avg}} = (3/2)RT$
- At a given T , different gases have **same** average KE.
- See Chapter 4 in Atkins & Jones (p. 146) or Chapter 12 in Whitten, Davis, & Peck, 6th ed.

K.E. Distributions: Effect of T



Both curves are for N_2 . One is at $T = 300\text{ K}$ and one is at $T = 900\text{ K}$. Which is which?

Molecular Speeds

- Given by Maxwell-Boltzmann distribution function
- $KE_{\text{avg}} = (3/2)RT = (1/2) m u_{\text{avg}}^2$
⇒ Average speed = $u_{\text{avg}} \propto (T/m)^{1/2}$
- Light or Hot → fast
- Heavy or Cold → slow

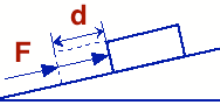
Heat (q)

- “A transfer of thermal energy into or out of a system.”
- Note that heat and temperature are not the same thing. Temperature is a measure of thermal energy, while heat is a change in thermal energy. Heat always “flows” from regions of higher T to those with lower T.
- Also note that heat does not always produce a change in T....

Work (w)

- Thermodynamic definition: “energy transfer accomplished by a force moving an object some distance.”
- Work = force × distance; $w = F \times d$
- If nothing moves, no work is done!

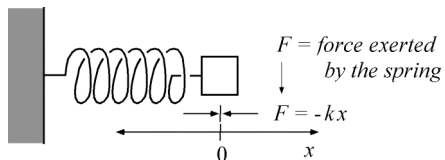
$$\begin{aligned} F \times d &= (\text{mass} \times a) \times d \\ &= \text{kg} \times (\text{m/s}^2) \times \text{m} \\ &= \text{kg} \times (\text{m}^2/\text{s}^2) \\ &\sim \text{mass} \times v^2 \sim \text{K.E.} \end{aligned}$$



Work Example: Storing energy in a Spring

- Work = force \times distance; $w = F \times d$

$$dw = kx \, dx$$



$$w = \int_0^x dw = k \int_0^x x' dx' = \frac{k}{2} x^2$$

Work in chemical reactions?

- Usually, the only form of work which is done in a chemical process is "PV-work," or "work of expansion or compression."
- This is given by
$$w = -P_{\text{ex}} \Delta V$$
 (note the sign) when P_{ex} , the external pressure, is constant.
- If P_{ex} varies as the process occurs, we need calculus to find that w is the integral of $-P_{\text{ex}} dV$

PV-work

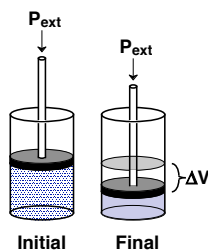
Units Check

- Pressure \sim Force/Area
- Volume \sim Area \times Distance
- PV \sim Force \times Distance
- \sim Energy (or Work)

Work is done on system

$$w = -P_{\text{ex}} \Delta V > 0 \text{ because}$$

$$V_{\text{final}} < V_{\text{initial}}$$



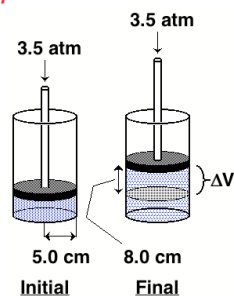
Example

- An automobile piston with a radius of 5.0 cm is displaced by 8.0 cm after firing. How much work is done (on the system) in each firing stroke if the external pressure is 3.5 bar?

Set up the problem

- Get necessary info:

$$\begin{aligned}\Delta V &= \pi r^2 \cdot d \\ &= \pi (5.0)^2 \cdot 8 \text{ cm}^3 \\ &= 628.3 \text{ cm}^3 \\ &= 0.6283 \text{ L}\end{aligned}$$



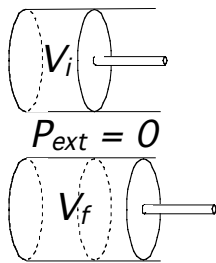
Adiabatic Processes

- Both the previous examples involve nearly **adiabatic** processes.
- Adiabatic**: occurring with no transfer of heat, $q = 0$.
- In adiabatic processes, all the energy change is due to work done on ($w > 0$), or by ($w < 0$) the system.

Isothermal Processes

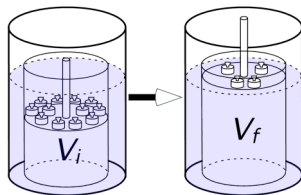
- If the temperature of the system remains constant throughout a process, it is said to be **isothermal**.
- (Nearly) isothermal processes are carried out by keeping the system in good thermal contact with a large “bath” in the surroundings. When the bath is large compared to the system, the system’s temperature varies little.

Free Expansion - No Work



- If we allow the volume of the gas in the piston to expand against no external pressure, it does no work “pushing” external gases aside. (We’re neglecting work of moving the piston head itself.)

Reversible Isothermal Expansion

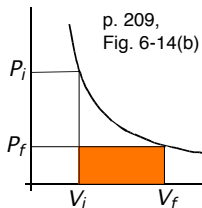


Gradually decrease pressure, by removing one weight at a time.

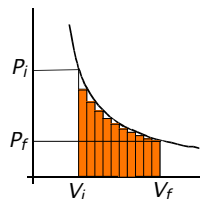
Note, since $T = \text{const.}$,
 $P_i V_i = P_f V_f$

- If we gradually decrease the pressure while keeping the apparatus in a large bath, expansion will be nearly reversible and nearly isothermal.

Irreversible vs. (nearly) Reversible

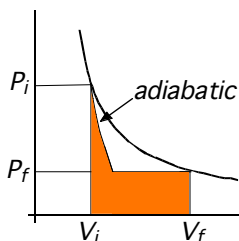


Pressure lowered in one step (remove all weights)



Pressure lowered in incremental steps

More realistic Scenario



It is easier to release pressure quickly, before heat has time to transfer. A more realistic pair of changes is first an adiabatic expansion of the gas, then adding heat to bring back to the initial temperature.

Isothermal Ideal Gas Expansion

- Suppose we carry out a reversible expansion of an ideal gas at constant temperature. When reversible, $P = P_{\text{ex}}$.

for each infinitesimal step of the expansion, $dw = -PdV$

$$w = \int_{V_i}^{V_f} dw = - \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$w = -nRT \ln \frac{V_f}{V_i}$$

- As we've discussed, actually performing an expansion this way is not easy.

Heat capacity: relating q & T

- If we change T at constant P : $q = nC_p\Delta T$
- n is number of moles of the substance
- ΔT is change in temperature
- C_p is "molar heat capacity" of the substance

$$C_p = \frac{q_p}{\Delta T}$$

(remember, measurements at constant P)

- Also often see $q = mc\Delta T$, especially in physics & engineering books. Here c is called "specific heat." Just different units!

Heat capacity: relating q & T

- If we change T at constant V : $q = nC_v\Delta T$
- n , ΔT have same meaning as before
- C_v is "constant-volume heat capacity":

$$C_v = \frac{q_v}{\Delta T}$$

(remember, measurements at constant V)

- Which is bigger, C_v or C_p ?

We'll see about that...

First Law of Thermodynamics

- "The energy of the universe is constant."

- $\Delta U_{sys} + \Delta U_{surr} = 0$

- Focus on system:

$$\Delta U_{sys} = q + w$$

- U is a state function, q and w are NOT state functions.

Signs of q & w

- $w > 0$ when work is DONE ON the system
- $q > 0$ when heat is ADDED TO the system
- These are scientist's definitions, engineers often change the sign of w . (When that definition is used, then $\Delta U = q - w$. We will never use that definition.)

C_V vs. C_P for an Ideal Gas

Let's compare heating an ideal gas under constant V and constant P:

$$P_1, T_1, V_1 \xrightarrow{\Delta V = 0} P_2, T_2, V_1$$

$$P_1, T_1, V_1 \xrightarrow{\Delta P = 0} P_1, T_2, V_2$$

We are starting from the same state, and heating to the same final temperature (NOT the same final state!)

What do we know about q , w , ΔU in each case?

C_V vs. C_P for an Ideal Gas

The heat capacities are defined under just these conditions:

$$P_1, T_1, V_1 \xrightarrow{\Delta V = 0} P_2, T_2, V_1 \quad q_V = C_V \Delta T$$

$$P_1, T_1, V_1 \xrightarrow{\Delta P = 0} P_1, T_2, V_2 \quad q_P = C_P \Delta T$$

In the constant V case, no work is done

$$\therefore \Delta U_V = q_V = C_V \Delta T$$

For one mole of ideal gas, $U = (\frac{3}{2})RT$,
therefore, $C_V = (\frac{3}{2})R$

Problem

- Imagine an ordinary room filled with an ideal gas. Recall that $\Delta U = C_V \Delta T$, where C_V is the molar constant-volume heat capacity.

Q: If C_V is constant over a certain range of temperatures, how does the energy of the gas *in the room* change as we increase the temperature in that range?

C_V vs. C_P for an Ideal Gas

The heat capacities are defined under just these conditions:

$$P_1, T_1, V_1 \xrightarrow{\Delta V = 0} P_2, T_2, V_1 \quad q_V = C_V \Delta T$$

$$P_1, T_1, V_1 \xrightarrow{\Delta P = 0} P_1, T_2, V_2 \quad q_P = C_P \Delta T$$

In the constant V case, no work is done

$$\therefore \Delta U_V = q_V = C_V \Delta T$$

C_V vs. C_P for an Ideal Gas

For the process at constant P:

$$T_1 V_2 = T_2 V_1 \Rightarrow T_1 V_2 - T_2 V_1 = 0$$

$$T_1 V_2 - (T_2 - T_1) V_1 - T_1 V_1 = 0 \quad (\text{algebra trick: add zero})$$

$$T_1 (V_2 - V_1) - (T_2 - T_1) V_1 = 0 \Rightarrow T_1 \Delta V = V_1 \Delta T$$

$$\Delta V = \frac{V_1}{T_1} \Delta T$$

Final temperature, T_2 , is the same for both processes. Since $U = U(T)$, $\Delta U_V = \Delta U_P$.

C_V vs. C_P for an Ideal Gas

For the process at constant P:

$$\Delta U_P = q_P + w_P = C_P \Delta T + w_P =$$

$$C_P \Delta T - \int_{V_1}^{V_2} P_1 dV = C_P \Delta T - P_1 \Delta V$$

$$\Delta U_V = \Delta U_P \Rightarrow C_V \Delta T = C_P \Delta T - P_1 \Delta V$$

$$C_V \Delta T = C_P \Delta T - P_1 (V_1/T_1) \Delta T = (C_P - R) \Delta T$$

$$C_P = C_V + R = \frac{5}{2} R$$

Physical Origin of C_V

- Each translational *degree of freedom* contributes $(1/2)R$ to the heat capacity
- For gas molecules with more than one atom, rotational and vibrational motion can be places to “store energy”.
- Diatomics and linear polyatomics: 2 rotational *degrees of freedom*: $(1/2)R$ each.
- All other degrees of freedom are *vibrational*. At high temps, these each contribute R.
- In all gases, $C_P = C_V + R$

Examples: C_V and C_P of Some Gases

- Estimate C_V and C_P for one mole of each of the following gases: H₂, N₂, O₂, F₂, I₂, CO₂, H₂S, CH₄, C₂H₂
(3.5•R = 29.10 J•K⁻¹•mol⁻¹)
(4.0•R = 33.26 J•K⁻¹•mol⁻¹)
- Experiment (C_P in J•K⁻¹•mol⁻¹ at 298 K):
H₂: 28.82 N₂: 29.12 O₂: 29.36
F₂: 31.30 I₂: 36.90 CO₂: 37.11
H₂S: 34.23 CH₄: 35.31 C₂H₂: 43.93
