Lecture 4: 09.16.05 Temperature, heat, and entropy

Today:

Reading: Engel and Reid: 1.3, 2.4, 3.2

ANNOUNCEMENTS :

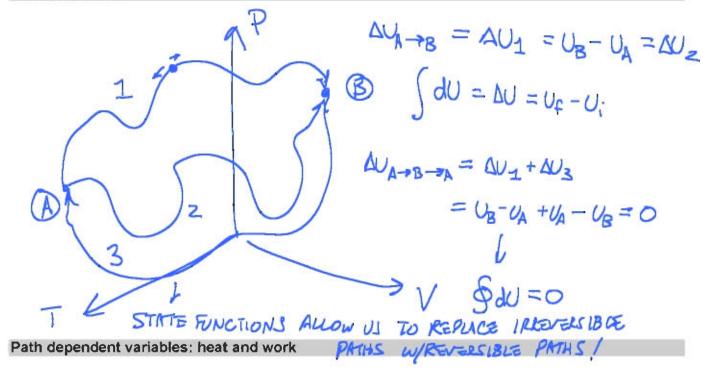   PS1 DUE TUESDAY 5 pm (8-425) OR TURN IN
          DURING RECITATION

     WEDNESDAY : CLASS WILL END EARLY (2:30 pm)

     [MONDAY NO CLASS...]

Last time

State functions

$$\Delta U_{A \to B} = \Delta U_1 = U_B - U_A = \Delta U_2$$

(B) $\int dU = \Delta U = U_f - U_i$

$$\Delta U_{A \to B \to A} = \Delta U_1 + \Delta U_3$$

$$= U_B - U_A + U_A - U_B = 0$$

$$\oint dU = 0$$

STATE FUNCTIONS ALLOW US TO REPLACE IRREVERSIBLE

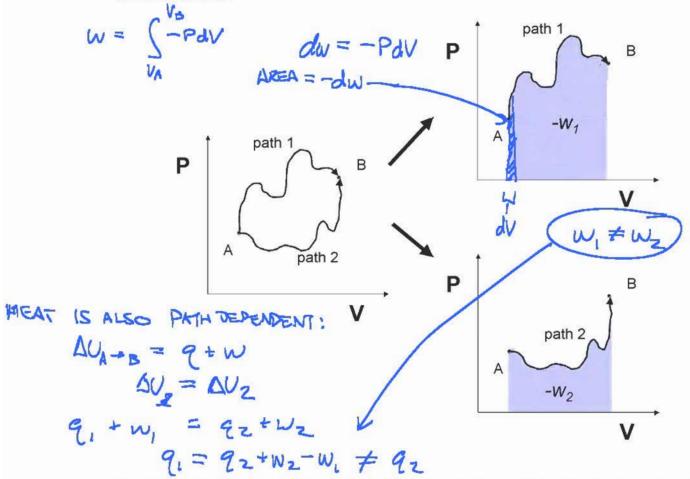### Path dependent variables: heat and work   PATHS w/REVERSIBLE PATHS !

- 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[1]

- 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:

REVERSIBLE : $dw = -PdV$

$$\int dw = w = \int_{V_A}^{V_B} -PdV$$

- 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:

$$W = \int_{V_A}^{V_B} -PdV$$

$$dw = -PdV$$

$$AREA = -dw$$

P path 1 B

$-W_1$

A

$$\frac{w}{dv}$$

V

$$W_1 \neq W_2$$

P path 1 B

A path 2

V

P B

path 2

A $-W_2$

V

HEAT IS ALSO PATH DEPENDENT:

$$\Delta U_{A \to B} = q + w$$

$$\Delta U_1 = \Delta U_2$$

$$q_1 + w_1 = q_2 + w_2$$

$$q_1 = q_2 + w_2 - w_1 \neq q_2$$

- 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.*

LET PATH 3 = PATH 2 IN REVERSE

PATH 1 + PATH 3 : $\oint dw = w_1 + w_3 \neq 0$

defining *temperature*

- Can you define temperature? HOW DO YOU KNOW WHEN A MATERIAL HAS AN ELEVATED TEMPERATURE?

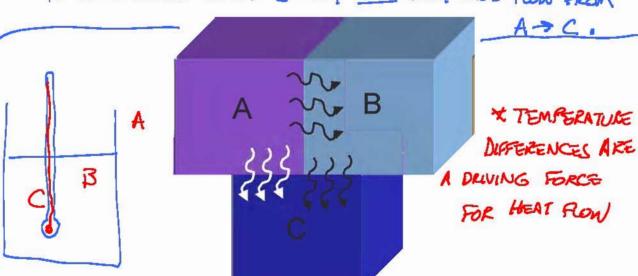 → PHYSICAL SENSATION OF HOTNESS!

  BUT: T ≠ HEAT   T ≠ ENERGY

The zeroth law of thermodynamics

- In the first lecture, we introduced the concept that thermodynamics is 'ruled' by 4 empirical laws, and now we'll discuss another of these, called **the zeroth law** - which will help us to define temperature:

  o **Zeroth law:** IF 3 SYSTEMS ARE IN THERMAL CONTACT (THEY CAN EXCHANGE HEAT), AND IF HEAT FLOWS FROM A→B, AND IF HEAT FLOWS FROM B→C, THEN HEAT WILL FLOW FROM A→C.

  * TEMPERATURE DIFFERENCES ARE A DRIVING FORCE FOR HEAT FLOW

  o The **temperature** is defined as *that which is equal when heat ceases to flow between these samples.*

  o Last time, we saw that entropy changes are related to heat transfer in reversible processes. The first law for a reversible process is:

MATHEMATICAL DEFINITION:

$$dU = đq + đw$$

$$\downarrow Rev$$

$$dU = TdS - PdV$$

STATE FUNCTION: $U = U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

MATHEMATICAL PROP OF STATE FCTS!

- For a process where no work is performed (isochoric process), $dU = TdS$. This gives us another way to define temperature:

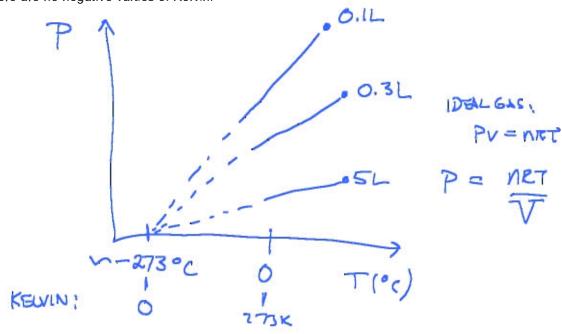$$T \equiv \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial U}{\partial S}\right)_{NO\ work}$$

The absolute temperature scale

- All thermodynamic calculations use the absolute temperature scale, measured in units of Kelvin (no degree symbol!)

- The Celsius scale with which we are most familiar in everyday life was derived by defining the temperature at which water freezes as 0 degrees. Last time, we introduced the absolute (Kelvin) temperature scale in defining the units of entropy- a scale with a zero point and no possibility of a lower temperature- without much discussion of where it comes from.

   o The Celsius and Kelvin scales are related by:

(Eqn 4)
$$X°C = X + 273.15K$$

- The value of 273.15K in the conversion comes from a historical convention: that the triple point of water- the unique temperature where liquid, ice, and vapor are in equilibrium with one another, would be defined as 273.16K (the triple point is also 0.01°C, hence the relationship given).

- The thermodynamic temperature scale is called absolute temperature because it has an 'absolute' zero. There are no negative values of Kelvin.
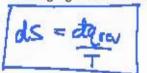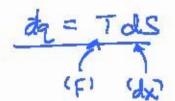
Consequences of the relation between temperature, heat, and entropy: heat capacity

The difference between heat and temperature

- Why do we need to define the property of temperature independently of heat? Why doesn't the temperature of a material simply quantify the amount of heat transferred to it?

    ○ Looking again at the reversible process definition of entropy:

$$\text{REV. PROCESS}: \quad \boxed{dS = \frac{dq_{rev}}{T}} \qquad \underline{dq = T\,dS} \qquad \text{HEAT} \xleftrightarrow{} \begin{array}{c} T \\ S \end{array}$$
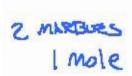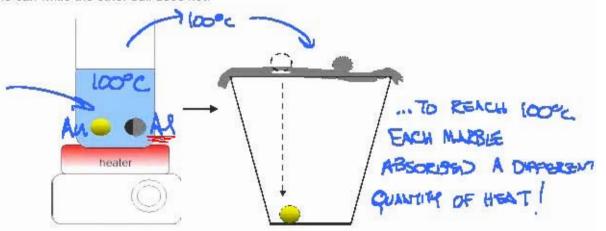
$$(F) \quad (dx)$$

   - Temperature may be thought of as a *thermodynamic force*, and entropy its *conjugate displacement* (that aspect of the system that responds to the force) when no mechanical work is being performed by the system.

Defining heat capacity

- The following experiment can be done: Consider two roughly marble-sized balls of equal mass, one made of gold and one made of aluminum, both heated to a uniform temperature of 100° C. The two balls are placed on a strip of wax suspended over an open can. The Au ball melts through the strip of wax and falls into the can while the other ball does not.

2 MARBLES
1 mole
100°C
Au   Al
heater
→100°c

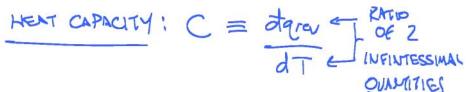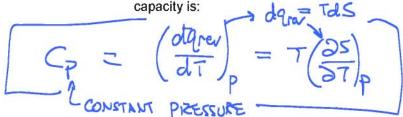...TO REACH 100°C EACH MARBLE ABSORBED A DIFFERENT QUANTITY OF HEAT!

    ○ Why would two metals heated to the same temperature have a different ability to melt the wax strip? The answer lies in the equation above relating temperature and heat, which indicates that *two metals at the same temperature have not necessarily received the same amount of energy-* since the amount of heat transferred into the balls is equal to the product of their temperature and their entropy change dS. This is another outcome of the link between temperature, heat, and entropy.

- Physically, it is due to differences in composition, structure, and bonding between atoms and molecules in different materials. **We measure this difference in responses to heat transfer by the thermodynamic property** *heat capacity*.

- Heat capacities are defined depending on the type of process a system is exposed to: constant-pressure or constant volume.
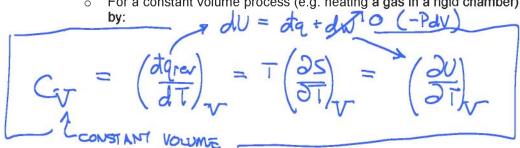
HOW DO WE ACCOUNT FOR DIFFERENT ABILITIES FOR HEAT ABSORPTION?

HEAT CAPACITY: $C \equiv \dfrac{dq_{rev}}{dT}$ ← RATIO OF 2 INFINITESSIMAL QUANTITIES

- In a constant pressure process (e.g. heating a bar in a beaker on the lab bench), the heat capacity is:

$dq_{rev} = TdS$

$$C_P = \left(\frac{dq_{rev}}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

CONSTANT PRESSURE

- For a constant volume process (e.g. heating a gas in a rigid chamber), the heat capacity is given by:

$dU = dq + dw \rightarrow^0 (-PdV)$

$$C_V = \left(\frac{dq_{rev}}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$
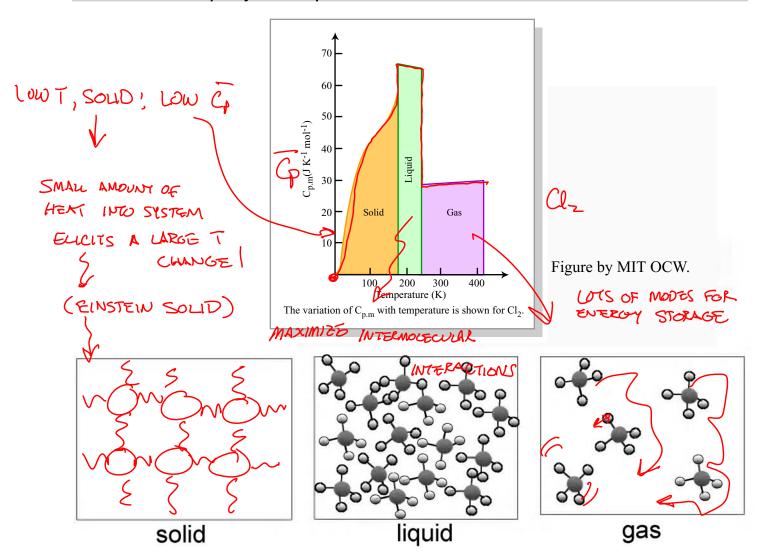
CONSTANT VOLUME

- What do the equations tell us? A material with a low heat capacity will experience a large temperature change (dT) for a small transfer of heat (dq). A material with a large entropy at a given temperature will also have a high heat capacity.

  - **Heat capacity measures the ability of a material to store energy transferred as heat:** Recalling our 'physical' notion of entropy as a measure of the degrees of freedom available to the molecules in the material, this implies that materials with more molecular degrees of freedom (ability for molecules to translate, vibrate, rotate, etc.) have higher heat capacities.

- **UNITS:** Experimental heat capacities are often given in units of J/mole•K (molar heat capacity) or J/g•K (the latter are called specific heat capacities or specific heats).

$$C_P = \left(\frac{dq}{dT}\right)_P = \frac{[ENERGY]}{[TEMP]} = \frac{J}{K}$$

MOLAR HEAT CAPACITY: $\overline{C_P} = \dfrac{C_P}{n} = \dfrac{J}{mole \cdot K}$

Behavior of heat capacity with temperature

(handwritten) LOW T, SOLID! LOW $\bar{C_p}$

(handwritten) SMALL AMOUNT OF HEAT INTO SYSTEM ELICITS A LARGE T CHANGE!

(handwritten) (EINSTEIN SOLID)

$\bar{C_p}$

$C_{p.m}$ (J K^{-1} mol^{-1})

Solid   Liquid   Gas

Temperature (K)

(handwritten) Cl_2

Figure by MIT OCW.

(handwritten) LOTS OF MODES FOR ENERGY STORAGE

The variation of $C_{p.m}$ with temperature is shown for Cl_2.

(handwritten) MAXIMIZED INTERMOLECULAR INTERACTIONS

solid   liquid   gas

(Harmonic oscillator model: Chabay[3])

Constant Pressure Heat Capacity of some materials at T = 298K at 1 atm pressure[4]

Material	State of aggregation	$\overline{C_P}$ (J/mole•K)	C_p (J/ g•K)
Pyrex (silicate)	Solid	0.836	
C (diamond)	Solid	6.23	0.519
Fe	Solid	8.44	0.444
C (graphite)	Solid	8.57[5]	0.713
Al	Solid	24.3	0.899
Au	Solid	25.4	0.129
N_2 (g)	Gas	29.12[6]	1.04
N2	Gas	29.28	
O_2	Gas	29.33	0.916
CO_2 (g)	Gas	29.33[6]	0.667
H_2O (g) (unstable at 298K)	Gas	33.57[6]	1.865
H_2O (s- ice- unstable at 298K)	Solid	37.66	2.092
H_2O (l)	Liquid	75.31	4.184
CH_2OH (ethyl alcohol)	Liquid	112.9	3.64

(handwritten) 20°C

CH$_3$-(CH$_2$)$_5$-CH$_3$ (n-heptane)	Liquid	224.6	

- o Heat capacities can be very different between materials with similar bonding (e.g. two metals Au and Fe), materials with the same atomic constituents but different atomic arrangements (e.g. diamond and graphite), and between the same material in different states of aggregation (e.g. liquid water vs. ice).

Figure removed for copyright reasons.
See "3D Diamond" link at http://www.tg.rim.or.jp/~kanai/chemistry/index-e.shtml
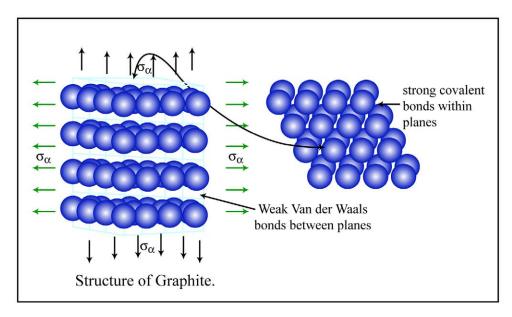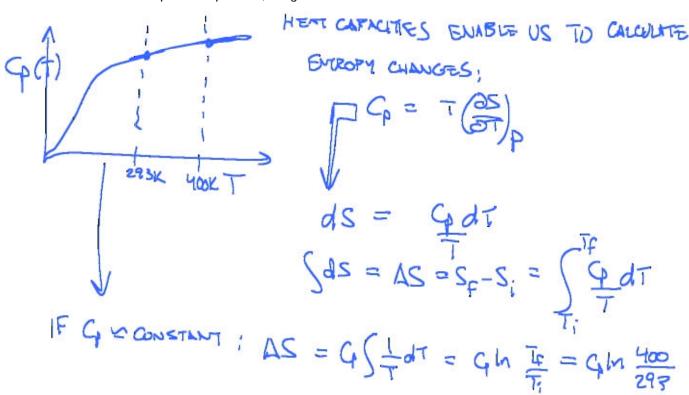

Figure by MIT OCW.

Calculations with heat capacities

- Knowledge of heat capacities allows us to perform calculations of internal energy and entropy from simple experimental measurements. Given either a value for the heat capacity (assumed constant over the temperature range of interest) or an empirical formula for the dependence of the heat capacity with temperature, we can directly compute absolute entropies.

The Third Law and calculation of absolute entropies

- The third law, like the other laws of thermodynamics, is derived from empirical observations made by scientists studying the behavior of thermodynamic systems. The third law derived from experiments looking at the behavior of heat capacities and entropy at lower and lower temperatures. One statement of the third law is:
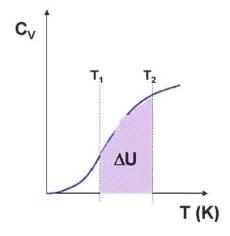
  - **The third law:**

    THE ENTROPY OF A PERFECT CRYSTAL AT 0K IS ZERO.

    $$S_{T=0K} = 0$$

- We can make use of the defined zero-point of entropy (and heat capacities) to calculate absolute entropies: For example, if we change the temperature of an aluminum sample from T=293K to T=400K by a constant pressure process, we get:

HEAT CAPACITIES ENABLE US TO CALCULATE ENTROPY CHANGES;

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$dS = \frac{C_p \, dT}{T}$$

$$\int dS = \Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_p}{T} \, dT$$

IF C_p ⊾ CONSTANT;

$$\Delta S = C_p \int \frac{1}{T} \, dT = C_p \ln \frac{T_f}{T_i} = C_p \ln \frac{400}{293}$$

  - …Note that because the heat capacity approaches 0 at 0K, it would be unwise to assume C_P is a constant when integrating starting at $T=0K$.

Calculation of internal energy changes

- We've so far only been able to calculate changes in internal energy for ideal gases using the first law combined with the ideal gas law. The heat capacity gives us a means to determine changes in internal energy for arbitrary materials if we know the dependence of the heat capacity on temperature. For a constant volume process:

References

1.   Denbigh, K. The Principles of Chemical Equilibrium (Cambridge University Press, New York, 1997).
2.   Carter, W. C. (2002).
3.   Chabay, R. & Sherwood, B. Matter & Interactions.
4.   Dill, K. & Bromberg, S. Molecular Driving Forces (New York, 2003).
5.   Gaskell, D. R. Introduction to Metallurgical Thermodynamics (Hemisphere, New York, 1981).
6.   Lupis, C. H. P. Chemical Thermodynamics of Materials (Prentice-Hall, New York, 1983).