Giancoli Ch19: Heat and the First Law of Thermodynamics

1 Heat as Energy Transfer

- Heat is not a substance (the failed caloric theory)

- 1 calorie(cal)[1]= amount of energy required to raise the temperature of 1 kg of water by 1 degree celsius[2]

- Heat: energy transferred $\because \Delta$ temperature

- SI unit of heat: Joules

- Mechanical equivalence of heat: work done$\rightarrow$ increase in temperature (1 cal = 4.186 Joules)

2 Internal Energy

- Internal (Thermal) Energy: total energy of all molecules

- Temperature: measure of average thermal E_k of individual molecules [3]

- Internal Energy of an Ideal Monoatomic Gas Assumptions:

  1. If more than one atom in a molecule than need to consider rotational E_k ,vibrational E_k, E_p. But still only α on T
  2. Real Gas: largely dependent on T but also has a bit of dependence on P,V
  3. Liquid, Solids: Complicated Internal energy $\because$ take into consideration electrical bond energy

$$E_{int} = \Sigma E_{k \quad translational} = N(\frac{1}{2}m\bar{v}^2) \tag{1}$$

$$= N(\frac{3}{2}kT) \tag{2}$$

$$= \frac{3}{2}nRT \tag{3}$$

3 Specific Heat

$$Q = mc\Delta T$$

- for solids and liquids, the value of c somewhat dependent on T and a bit on P

$\because$ c is a function of T $\rightarrow c(T)$ we write heat as:

$$dQ = mc(T)dT \qquad \rightarrow \qquad Q = \int_{T_1}^{T_2} mc(T)dT$$

---

[1] 1kcal= Calorie

[2] Also British Thermal Unit (BTU)= The amount of energy required to raise the temperature of 1lb of water by 1 degree F

[3] Remember that heat is ONLY dependent on temperature

- but for $\Delta T \to 0$ we treat c as constant

- Gas more complicated

4 Calorimetry

- Closed system: no mass in or out (but can energy exchange)

- **Isolated** system if no energy in or out of its boundaries

- Isotropic tendency within system

- Conservation of energy valid for isolated closed sys (often if not $\to$ approx)

- heat gained = heat lost

- Consider all sources of energy transfer

- Calorimetry : quantitative measurement of heat exchange

- "method of mixtures" : calculate specific heat by mixing

5 Latent Heat

- is the energy released or absorbed by a system during a constant temperature process.

- Typical ex. is energy involved in change of phase

- Heat of fusion (L_f): heat required to change 1 kg of substance (s) $\to$ (l) [4]

- Heat of vaporization (L_v) : heat required to change 1 kg of substance (l) $\to$ (g) [5]

- heat involved in phase change= Q =mL where L: latent heat of the particular process and substance

- The value of L_v increases slightly with a decrease in temperature.(?) When water evaporates, since the energy required comes from the water itself (L_v) so its internal energy $\therefore$ T $\downarrow$. (ex. sweating)

- Energy is used for bond breakage/ formation in molecules instead of used to increase average kinetic energy. And $\because$ (l) $\to$ (g) is a more violent reorganization than (s) $\to$ (l) $\therefore$ usually $L_v > L_f$

6 The First Law of Thermodynamics

- heat : transfer of energy due to a difference in temperature

- work : transfer of energy tat is not due to a temperature difference

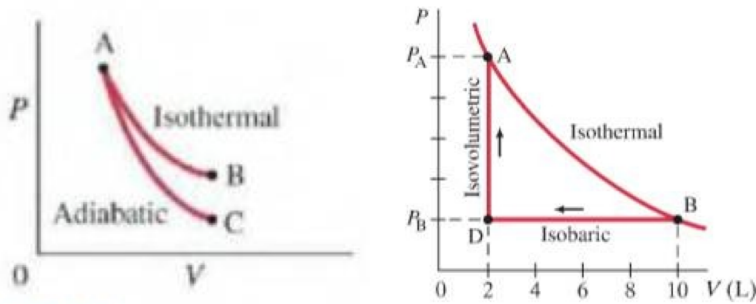- First law of thermodynamics
$$\Delta E_{int} = Q - W \tag{4}$$

where Q: net heat **added** to the system
W: net work done **by** the system

---

[4]$L_f, water = 3.33 \times 10^5 J/kg$
[5]for water, 2260 kJ/kg

- restatement of conservation of energy → applies only to closed system

- if open system, must taken into account the internal energy due to increae of decrease in the amount of matter.

- Isolated system : W=Q=0 (no heat or work on sys) ∴ $E_{int} = 0$

- State variable: describe the state of a system [6]

- Also useful to write as $dE_{int}=$ dQ - dW [7]

- For a **moving** system with potential energy,

$$\Delta K + \Delta U + \Delta E_{int} = Q - W \tag{5}$$

7 Work Calculation

Area under PV graph:

7.1 Isothermal processes ΔT=0

- Isotherm : curves on isothermal PV graph

- Ideal gas ∴ PV= constant at every point on graph

- Heat reservoir: a body whose mass is so large that T ≈ constant when heat is exchanged

- quasistatically : moving so slow (i.e. static) that T doesn't signficifantly change

- $E_{int} = \frac{3}{2}nRT$ ∵ mass, T unchanged ∴ E_{int} unchanged
$E = Q - W = 0 \quad \rightarrow \quad Q = W$
work done by gas in an isothermal process = heat added to gas

7.2 Adiabatic Processes (Q=0)

- situation: short Δt or well insulated

- ∵ 1st law of thermo : $\Delta E_{int} = -W$

- ex) Adiabatic compression → T ↑→ Diesel fuel mixture ignite spontaneously [8]

---

[6]Q , W are NOT state variables
[7]dQ and dW are not exact differential
[8]1st law of thermo also holds for Isobaric and Isovolumetric (Isochoric) Processes

7.3 Work Done in Volume Changes

Work and heat are not property of a system, they are not only dependent on final and initial but also depend on type of process ("path independent") $dW = \mathbf{F}d\mathbf{l} = PAd\mathbf{l} = PdV$ where $d\mathbf{l}$ point into the gas
Isobaric

- Area under PV graph is rectangle $W = P(V_f - V_i)$

- as volume change in gas, P=P_b throughout $\rightarrow P = \frac{nRT_b}{V_b}$

- divide both side by $V_b \rightarrow \therefore W = nRT_b(1 - \frac{V_a}{V_b}$ [9]

Isothermal

$$W = \int dW = \int PdV = nRTln\frac{V_b}{V_a} \tag{6}$$

Free Expansion
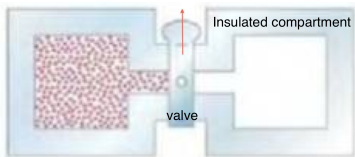
- a method of adiabatic expansion with W=0

- release valve: gas move from one compartment to another $\because$ gas does not move any obj $\therefore$ W=0

- $\therefore$ by 1st law $\rightarrow \Delta E_{int} = 0 \rightarrow \Delta T = 0$

- Using this method, we experimentally show that $\Delta T \rightarrow 0$ but $\neq 0$ $\therefore \Delta E_{int}$ does not depend solely on T but also a bit on P and V

- Rapid process [10] $\therefore$ state variables in intermediate stages are not well define $\rightarrow$ can not be plotted on PV diagrams

8 Molar specific heat for gas Equipartiton of E

- molar specific heat (C): heat required to raise 1 mol of gas by 1 deg Celsius @ constant V & P

- depend on process : isobaric (C_p) ,isochoric (C_v) $Q = nC_v\Delta T$ [11]

- $M = molarmass = \frac{m}{n} = [\frac{g}{mol}]$

- $C_v = Mc_v$

- value of C are $\approx$ same for different gas wih same # of atoms per mcl

---

[9]Remeber to always define what exactly is our system
[10]instead of being quasistatic
[11]ditto for C_p for these equ in this section

8.1 $C_p - C_v = R$

8.2 Equipartition of Energy

- more # of atoms in mcl $\to$ more Degrees of freedom $\to$ molar specific heat $\uparrow$

- **Principle of equipartiton of Energy**: energy is shared equally among the active Dof and each active Dof of a mcl has $E_{avrg} = \frac{1}{2}kT$

- Diatomic: 3 Dof translational +2 Dof rotational

- @ high T: diatomic gas has 2 new Dof from electrical,spring-like,vibrational $E_k \to C_{v,\text{diatomic}} = \frac{7}{2}$

- @ low T : almost no E_k rotational $\to$ 3 Dof

- this phenomenom is explained by Brownian motion , which gives molecules its discrete nature. Discrete Dof at discrete T $\to$ quantized minimum energy

- Can apply princple of equipartition to solids too!

- $C_{\text{any solid @ high T}}$ $\approx$ Dulong and Petit value= 3R
  $\because 3E_k + 3E_p$ spring-like in crystalline structure

9 Adiabatic Expansion of gas

Deriving relation between P and V of quasi-static adiabatic expansion of an ideal gas

10 Heat Transfer

10.1 Conduction

- transfer of E_k through molecular collisions

-
$$\frac{dQ}{dt} = -kA\frac{dT}{dx} \tag{7}$$

- negative sign $\because$ Q flow is opposite to direction of temperature gradient

- conductor: large k ; insulator : small k

- Thermal resistance (R-value): measure of thermal property in building material: $R = \frac{thickness}{k}$

10.2 Convection

- heat flow by mass movement of large number of molecules over large distances

- forced convection (ex: forced-air furnace)

- Natural convection $\because$ density difference

10.3 Radiation

- doesn't require matter as medium

- rate at which an object radiates energy $\alpha \qquad T^4$

- Stefan-Boltzmann equation : σ=Stefan-Boltzmann constant=$5.67 \times 10^{-8} W/m^2 \cdot K^4$

$$\frac{\Delta Q}{\Delta t} = \epsilon \sigma A T^4 \tag{8}$$

- $\epsilon=$ emissivity ($0 \leq \epsilon \leq 1$)

  - somewhat α on T
  - good emmiter (dark)L absorb almost all radiation ($\epsilon \approx 1$)
  - obj not only emit but also absorb radiated energy $\therefore$good emmitter is also a good absorber
  - Opposite: shiny surfaces

- obj emmit $\rightarrow$ surrounding absorb $\rightarrow$ surrounding emmit
  $\therefore$Net rate radiant heat flow from obj= $\frac{\Delta Q}{\Delta t} = \epsilon \sigma A(T_1^4 - T_2^4)$where T_2 temp of surroundings

- we can't use this to calculate Sun's radiant heat , $\because$ Sun is point source not a "surrounding"

- Solar constant= amount of energy from Sun striking Earth's atmosphere =1350 W/m^2

$$\frac{\Delta Q}{\Delta t} = (1350W/m^2)\epsilon A cos\theta \tag{9}$$

where θ =angle between Sun's rays and the area's normal

- ex) seasons, thermography

11 Question

1. pg 526 The value of L_v increases slightly with a decrease in temperature.(?) What is the prupose of this anyways? if water only evaporate at 100 degree, why should we care about L_v at other temperature?