

Lecture six

The first law of thermodynamics

Application of 1st law of thermodynamic

The energy balance of a system –as a consequence of 1st law of thermodynamic is a powerful tool to analyse the exchanges of energy between the system and its environment. Here is a summary of 1st law of thermodynamic formulation in the different types of thermal processes:

$$\Delta U = q - W$$

Thermodynamic processes and their characteristics		
Constant pressure	$w = -P_{ex} \Delta V$	$\Delta U = q + w$
Constant volume	$w = 0$	$\Delta U = q$
Isothermal (constant temperature)	$w = -q$	$\Delta U = 0$
Adiabatic (no heat flow)	$w = \Delta U$	$q = 0$

Here is a summary of the work formulation in the different types of thermal processes:

The work done by different process	
Free expansion	$w = 0$
Expansion against constant pressure	$w = -P_{ex} \Delta V$
Reversible expansion	$w = -nRT \ln \frac{P_i}{P_f}$ $w = -nRT \ln \frac{V_f}{V_i}$
The work of gas production	$w = -nRT$
Isochoric work	$w = 0$

Q) A sample of 4.50g of CH₃ expanded isothermally from 12.7 dm³ to 15 dm³ at 310 K. (a) against a constant external pressure of 200 Torr (b) reversibly. Calculate w, q, and ΔU.

(a)

$$p = 200 \text{ torr} \times \frac{133.32 \text{ pa}}{1 \text{ torr}} = 26664.4 \text{ pa} (N \cdot m^{-2})$$

$$\Delta V = V_2 - V_1 = 15 \text{ dm}^3 - 12.7 \text{ dm}^3 = 3.3 \text{ dm}^3 \times \frac{1 \text{ m}^3}{1000 \text{ dm}^3} = 3.3 \times 10^{-3} \text{ m}^3$$

$$w = -p \Delta V = -(26664.4 \text{ N} \cdot \text{m}^{-2})(3.3 \times 10^{-3} \text{ m}^3) = -87.99 \text{ J} \approx 88 \text{ J}$$

$$\Delta U = q + w$$

$\Delta U = 0$ at isothermally process

$$\therefore q = -w = 88 \text{ J}$$

(b)

$$n = \frac{4.5 \text{ g}}{16 \text{ g/mol}} = 0.28 \text{ mol}$$

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

$$w = -(0.28 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(310 \text{ K}) \ln \frac{15}{12.7} = -120.1 \text{ J} \approx -120 \text{ J}$$

$\Delta U = 0$

$$\therefore q = -w = 120 \text{ J}$$

H.W) 1013.25 J of heat energy is supplied to 1 mol of NH_3 (g) which is initially volume is 4L at constant pressure 2 atm. if the process is isothermally expansion, determine its final volume.

Calorimetry

Calorimetry derived from the Latin calor meaning heat, and the Greek metry meaning to measure, is the science of measuring the amount of heat. All calorimetric techniques are therefore based on the measurement of heat that may be generated (exothermic process), consumed (endothermic process) or simply dissipated by a sample.

There are numerous methods to measure such heat, and since calorimetry's advent in the late 18th century, a large number of techniques have been developed. Initially techniques were based on simple thermometric (temperature measurement) methods, but more recently, advances in electronics and control have added a new dimension to

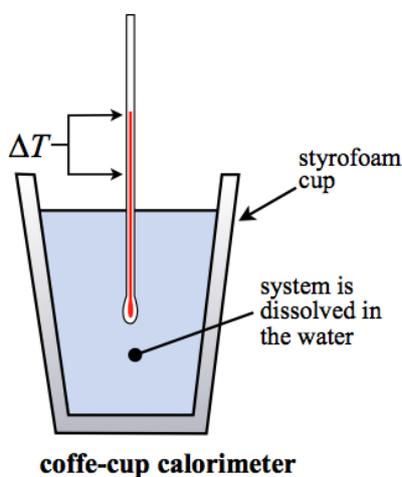
calorimetry, enabling users to collect data and maintain samples under conditions that were previously not possible.

The calorimeter constant

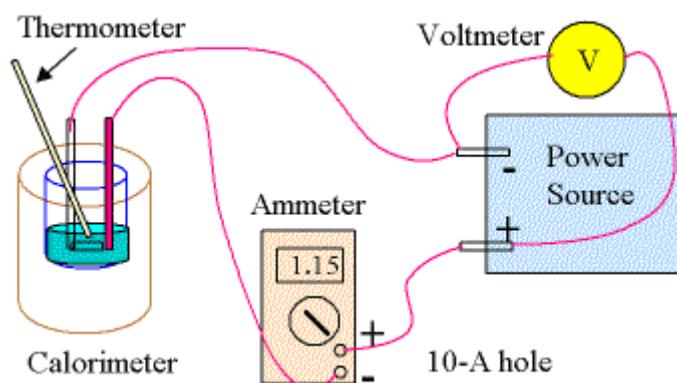
The change in temperature, ΔT , of the calorimeter is proportional to the energy that the reaction releases or absorbs as heat. The conversion of ΔT to q is best achieved by calibrating the calorimeter using a process of known energy output and determining the calorimeter constant, the constant C in the relation:

$$q = C \Delta T$$

The calorimeter constant may be measured electrically by passing a constant current, I , from a source of known potential difference, $\Delta\phi$, through a heater for a known period of time, t , for then



$$q = It \Delta\phi$$



Q) Calculate the calorimeter constant, If pass a current of 10.0 A from a 12 V supply for 300 s, and the observed rise in temperature is 5.5 K.

The energy supplied as heat is

$$q = It \Delta\phi$$

$$q = (10A)(300s)(12V)$$

$$q = 36 \times 10^3 J = 36 kJ$$

Then the calorimeter is

$$q = C \Delta T$$

$$C = \frac{q}{\Delta T}$$

$$C = \frac{36 kJ}{5.5 K}$$

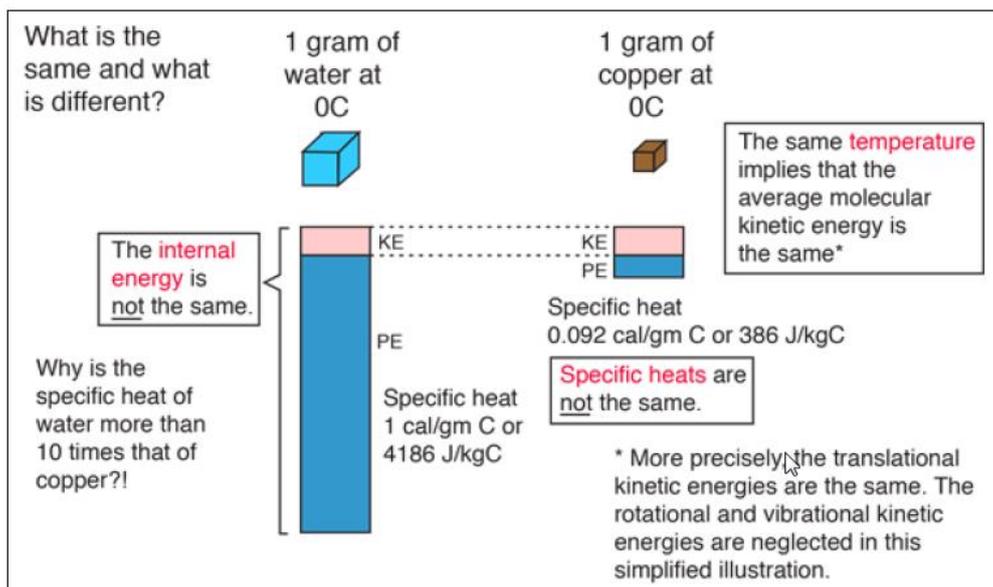
$$C = 6.5 kJ/K$$

Specific Heat

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. The relationship between heat and temperature change is usually expressed in the form shown below where μ is the specific heat.

$$q = m \mu \Delta T$$

The specific heat of water is 1 calorie/gram °C = 4.186 joule/gram °C which is higher than any other common substance. As a result, water plays a very important role in temperature regulation. The specific heat per gram for water is much higher than that for a metal, as described in the water-metal example.



Substance	(μ) at 25°C in J/g °C	Substance	(μ) at 25°C in J/g °C
H ₂ gas	14.267	Potassium	0.75
He gas	5.300	Sulphur	0.73
H ₂ O(l)	4.184	Calcium	0.650
Lithium	3.56	Iron	0.444
Ethyl alcohol	2.460	Nickel	0.440
Ethylene glycol	2.200	Zinc	0.39
Steam @ 100°C	2.010	Copper	0.385
Vegetable oil	2.000	Brass	0.380
Sodium	1.23	Sand	0.290
Air	1.020	Silver	0.240
Magnesium	1.020	Tin	0.21
Aluminium	0.900	Lead	0.160
Concrete	0.880	Mercury	0.14
Glass	0.840	Gold	0.129

Q) Some copper, having a mass of 20 kg, cools from a temperature of 120°C to 70°C. If the specific heat capacity of copper is 385 J/(kg °C), how much heat energy is lost by the copper ?

$$q = m \mu \Delta T$$

$$q = (20 \text{ kg})(385 \text{ J} \cdot \text{kg}^{-1} \cdot ^\circ\text{C}^{-1})(70 - 120^\circ\text{C})$$

$$q = -385000 \text{ J}$$

$$q = -385 \text{ kJ}$$

Group work

H.W) 20.8 kJ of heat energy is required to raise the temperature of 2 kg of lead from 16°C to 96°C. Determine the specific heat capacity of lead.

H.W) 250 kJ of heat energy is supplied to 10 kg of iron which is initially at a temperature of 15°C. If the specific heat capacity of iron is 500 J/ (kg °C) determine its final temperature.

H.W) How much heat energy is needed to raise the temperature by 15°C of: (1) 25 g water ($\mu=4.148 \text{ J/ (g } ^\circ\text{C)}$) (2) 25 g iron ($\mu=0.444 \text{ J/ (g } ^\circ\text{C)}$).