Adsorption from the gas phase

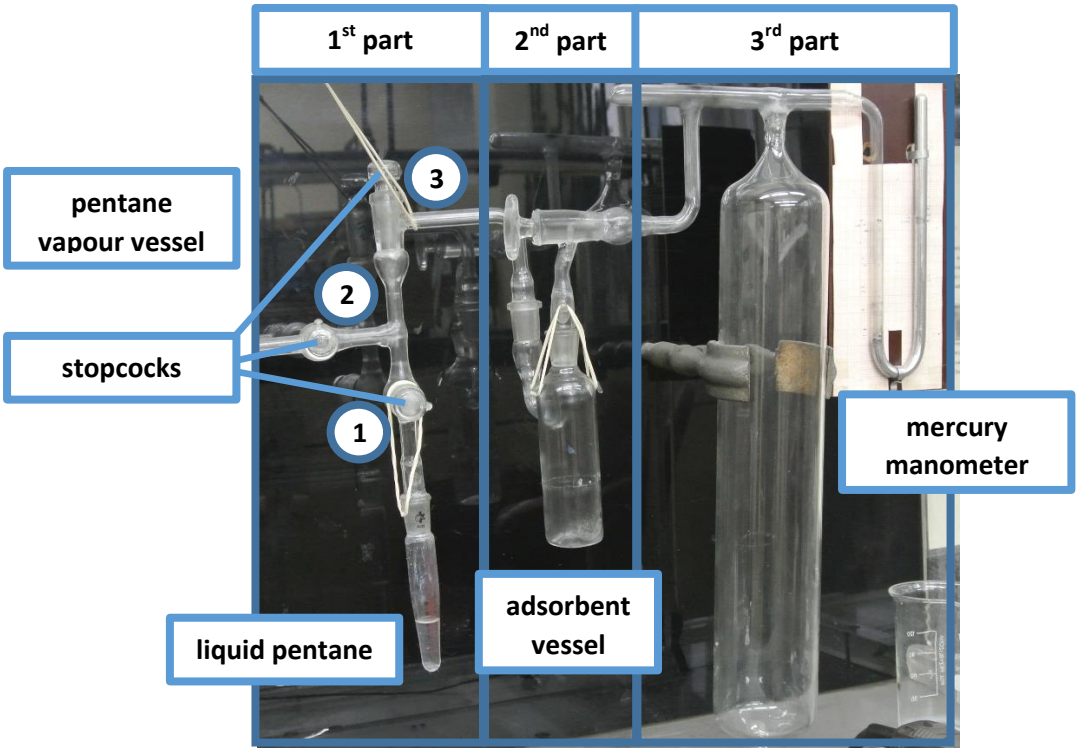
BET Isotherm

Objective

To determine the isotherm for pentane vapour adsorption on activated carbon and to calculate the parameters of the BET isotherm, and the enthalpy of desorption, and the specific surface area of the adsorbent.

Procedure

The apparatus consists of three parts. The first part shown below has a closed space of known volume (23.2 cm^3) that will contain pentane vapour. The second part is a vessel that contains a sample of the adsorbent. The third part is an empty vapour reservoir vessel, the role of which is to damp pressure shocks, and a mercury manometer to measure the vapour pressure in the system.



Weigh ca. 2 g (to 0.01 g) of activated carbon and transfer it quantitatively to the adsorbent vessel. Record the mass of the adsorbent.

Assemble the apparatus as in figure above. Connect the adsorbent vessel to part 3, and part 1 to the vacuum pump and to the adsorbent vessel. At this stage do not connect the test tube containing pentane. Secure the connections using rubber bands.

It is essential that all joints are absolutely airtight.

High vacuum – danger of glass vessel implosion!

Safety glasses should be worn at all times!

Close all the stopcocks in the first part. Start the vacuum pump and cautiously open stopcock 2, then stopcock 3. The stopcock between the adsorbent vessel and the third part should be kept open.

Check the air-tightness of the system by closing stopcock 2 for 60 s and then opening it. Let another person observe the manometer. The mercury level should not move whatsoever. If it does, close stopcock 2, turn off the vacuum pump, aerate it by turning on a special valve, next, slowly open stopcock 1 to cautiously aerate the system, and check the joints and grease them again. Repeat the air-tightness check afterwards.

Place a heating mantle under the adsorbent vessel and connect it to the power supply. Do not overheat! Try keeping the temperature at 130°C ±20°C level. Keep the adsorbent at this temperature under vacuum for 20 min.

Turn off the power supply and cautiously remove the heating mantle. Let the adsorbent cool down to room temperature still under vacuum. You may use a hair-dryer to speed it up. Do not aerate the system!

Check the levels of mercury in the manometer. If they are not even, adjust the apparatus to be in exactly vertical position, so that the mercury levels are even.

Fill the test tube with ca. 5 cm^3 of pentane. Attach the test tube to part 1 of the apparatus. Place a beaker containing water at exactly the room temperature under part 1 so that the part of the test tube filled with pentane is immersed in water.

Measure the room temperature and make sure that water in the beaker has exactly the same temperature. Record the temperature.

Close stopcocks 2 and 3. Stopcock 3 should be kept closed during this stage. Slowly open stopcock 1 to fill the vessel with pentane vapour. Close stopcock 1. Open stopcock 2, to evacuate the vapour vessel. Close stopcock 2 and slowly open stopcock 1 to fill the vessel with vapour. Close stopcock 1, and evacuate the vessel by opening stopcock 2. Repeat it again. Now, you can be sure that over the liquid pentane there are no significant amounts of the air.

All the stopcocks should be closed. At this stage, till the end of the measurements, stopcock 2 (to vacuum) should be kept closed.

- Slowly open stopcock 1 to fill the vessel with pentane vapour.
- Wait at least 10 s to be sure that the vapour pressure attains its equilibrium value.
- Close stopcock 1.
- Slowly open stopcock 3 to let the vapour expand into the adsorbent vessel.
- Wait for ca. 2-4 min for the system to equilibrate. Check the manometer readings. If they remain constant for ca. 30 s, the equilibrium has been attained.
- Measure and record the pressure (the difference in mercury levels in mm)
- Close stopcock 3.

Repeat the above steps 15-20 times.

Close all stopcocks. Turn off the vacuum pump. Aerate the pump using the valve at the front, at the right hand side. Slowly open stopcock 2 to aerate the vapour vessel. Then, slowly open stopcock 3 to aerate the further part of the apparatus. Next, slowly open stopcock 1 to aerate the space above liquid pentane.

Remove the beaker with water, then the test tube containing pentane. Next, disassemble the whole apparatus.

Remove activated carbon from the adsorbent vessel and wash it, first removing grease from the joint with a piece of tissue.

The report

Calculations and data analysis

Basic parameters and constants

Density (pentane) = 0.626 g cm^{-3}

Molecular weight (pentane), MW = 72.15 g mol^{-1}

1 mmHg = 0.133322 kPa

Volume of vapour vessel, V_{vap} = 23.2 cm^3

Volume of the 2nd part of the system, V_2 = 1102 cm^3

The saturated vapour pressure of pentane, p^* in kPa, should be calculated from the Antoine equation:

$$\log p^* = A - \frac{B}{T + C}$$

with the following constants:

A	B	C
5.9892	1070.617	−40.454

at the temperature of measurement.

Temperature, t / °C =

Temperature, T / K =

P^* / kPa =

Mass of activated carbon sample

m_{Cact}/g =

Put the data into Table 1.

Table 1

Measuring point number	mmoles of pentane introduced	Recorded pressure / mmHg	Recorded pressure / kPa	mmoles of pentane in gas phase	mmoles of pentane adsorbed	mmoles of pentane adsorbed per 1 g of activated carbon
1	2	3	4	5	6	7
1						
2						
…						

Method for calculation of the data in the table

2. mmoles of pentane introduced ($n_{introdued}$)

Calculate the amount of pentane vapour in mmoles in the vapour vessel added each time using the perfect gas equation of state (*the compressibility factor for pentane vapour under conditions of the experiment is equal 1.00*). Pentane in the vapour vessel is equal to p^*V_{vap}/RT, and it is divided into two parts, after the measurement, in the vessel remain p(actual value)V_{vap}/RT (mmoles), the rest, equal to

(p^* - p(act value)) V_{vap}/RT

with V_{vap} = 23.2 cm^3

is transferred to the 2nd part of the system.

The amount of mmoles pentane introduced ($n_{introdued}$)is the total amount introduced from the beginning of the experiment.

5. mmoles of pentane in gas phase (n_{gas})

Calculate this amount using the perfect gas equation of state with:

V_2 = 1102 cm^3

p – pressure actually measured in the system

6. mmoles of pentane adsorbed (n'_{ads})

This is equal to the difference between the total amount of pentane introduced and the amount in the gas phase.

$$n'_{ads} = n_{introduced} - n_{gas}$$

7. mmoles of pentane adsorbed per 1 g of activated carbon (n_{ads})

Divide the amount from column 6 by the mass of activated carbon sample.

Adsorption isotherm

- Plot the isotherm from the data of Table 1, the number of mmoles pentane adsorbed (n_{ads}, column 7) as a function of the pressure (p, column 4) (Plot 1). Put only the points, do not draw any line at this stage.
- Prepare Table 2 with data required to draw the plot representing the linear form of the BET isotherm (c and n_{mon} are constants):

$$\frac{1}{\left({p^*}/{p} - 1\right) n_{ads}} = \frac{1}{cn_{mon}} + \frac{(c-1)}{cn_{mon}} \cdot \left(\frac{p}{p^*}\right)$$

- Copy the value of saturated vapour pressure at the experiment temperature:

  p^* / kPa =

Table 2

Measuring point number	$\left(\frac{p}{p^*}\right)$	$\frac{1}{\left(p^*/p - 1\right) n_{ads}}$
1		
2		
…		

- Plot $\frac{1}{\left(p^*/p-1\right)n_{ads}}$ as a function of $\left(\frac{p}{p^*}\right)$. (Plot 2).
  It should be a straight line – if it is not in its full length, reject the points for higher pressures to get the straight line.
- Calculate the values of the slope and y-intercept using the least square regression method.

  The y-intercept = $\frac{1}{cn_{mon}}$

  The slope = $\frac{(c-1)}{c\, n_{mon}}$

- Calculate the values of both constants,

  c =

  n_{mon} =

  from the intercept and the slope.

- Calculate the enthalpy of vaporisation for pentane at the temperature of experiment from the following equation:

$$\Delta_{vap}H = A\,(1 - T_r)^{\beta} \exp(-\alpha T_r)$$

  where: T_r is reduced temperature

$$T_r = \frac{T}{T_c}$$

  Critical temperature (pentane), T_c = 469.6 K

  and the constants: A = 37.01 kJ mol^{-1}; α = −0.1238; β = 0.4121

- Knowing that

$$c = \exp\left(\frac{\Delta_{des}H^{\ominus} - \Delta_{vap}H^{\ominus}}{RT}\right)$$

  Calculate the enthalpy of desorption, $\Delta_{des}H^{\ominus}$.

- Using the calculated values of the BET isotherm constants, c and n_{mon}, calculate ca. 25 points, with 10 points in the range of steeply rising part of the isotherm and the other ones evenly

distributed up to the pressure ca. 20% higher than the last pressure point in the experiment, from the BET isotherm equation :

$$n_{ads} = n_{mon} \frac{c \cdot \frac{p}{p^*}}{\left(1 - \frac{p}{p^*}\right)\left\{1 - (1 - c)\frac{p}{p^*}\right\}}$$

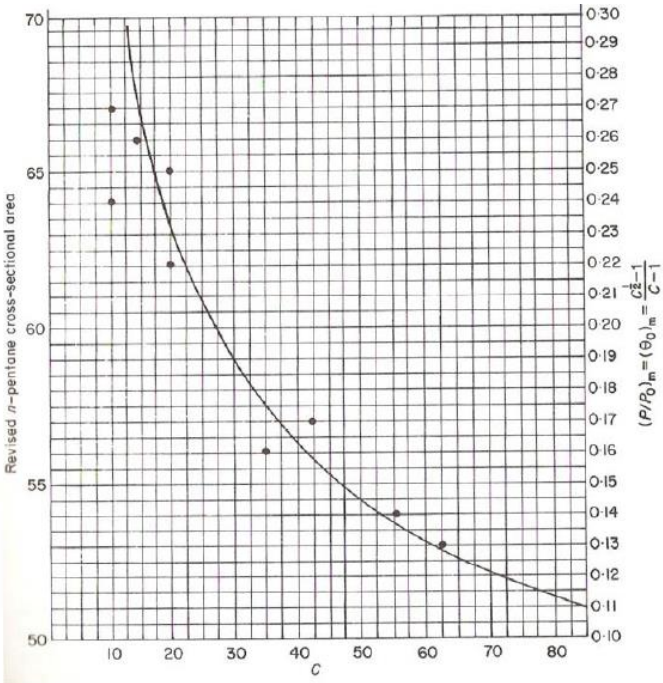
- Add this plot to the isotherm in the form of a line without points to Plot 1, to see how it fits the experimental data.

Calculating the specific surface area

- The specific surface area is the surface area of 1 g of adsorbent.

  It may be calculated from the n_{mon} value once we know the molecular cross-sectional area of the adsorbate.

  For pentane it is a rather complex function of the surface coverage and the *c* parameter value (adsorption enthalpy). It may be retrieved from the diagram below:



  The values are given in square angstroms, Å^2.

  1 Å^2 = 0.01 nm^2

  If the *c* value exceeds 80 then assume the molecular cross-sectional area to be 50 Å^2.

  To get the value of the specific surface area of the adsorbent it is enough to multiply n_{mon} by the cross-sectional area of pentane and the Avogadro constant, N_A = 6.02214129×10^{23}.

  Specific surface area of activated carbon used / m^2/g =