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# Identification of parameters $W_0$ , $n$ , and $D$ of the Dubinin–Radushkevich equation

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**Abstract** This paper considers a cooling system for a thermal engine using heat from exhaust gas. This system uses a physical adsorption process of solid–gas (active carbon and ammonia). An adsorber tubular element of real scale is submitted to heat flux by electrical air heating, simulating exhaust gas. Temperatures and adsorbed mass are measured. Desorption and adsorption phenomena are described by the Dubinin–Radushkevich model equation,  $m = W_0 \rho(T) \exp[-D(T \ln(P_s(T)/P))]n$ , where  $W_0$ ,  $n$ , and  $D$  are parameters characterising the adsorbent–adsorbate couple. These three parameters can be identified from a simple mite method (using data and models) characterising the adsorbent–adsorbate couple chosen.

**Keywords** exhaust gas; physical adsorption process; parameters characterising the adsorbent–adsorbate couple; Dubinin–Radushkevitch model

## Notation

$\rho(T)$	adsorbate density at adsorbent temperature, $\text{kg}\cdot\text{m}^{-3}$
$m$	adsorbate mass per unit mass of adsorbent, $\text{kg}/\text{kg}$
$P_s(T)$	adsorbate saturated vapour pressure at adsorbent temperature, bar
$P$	adsorbate vapour pressure at condenser/evaporator, bar
$M_{\text{bi}}$	initial bottle mass, kg
$M_{\text{bf}}$	final bottle mass, kg
$V_{\text{b}}$	bottle volume, $\text{m}^3$
$\rho_{\text{bpi}}$	nitrogen volume mass at the initial bottle pressure, $\text{kg}\cdot\text{m}^{-3}$
$\rho_{\text{bpf}}$	nitrogen volume mass at the final bottle pressure, $\text{kg}\cdot\text{m}^{-3}$
$\rho_1$	nitrogen volume mass at 1 bar, $\text{kg}\cdot\text{m}^{-3}$
$P_{\text{ib}}$	initial bottle pressure, bar
$P_{\text{fB}}$	final bottle pressure, bar
$Z_{\text{pi}}$	nitrogen compressibility factor at the initial pressure
$Z_{\text{pf}}$	nitrogen compressibility factor at the final pressure
$M_{\text{aZc}}$	nitrogen mass introduced in the circuit, kg
$V_{\text{c}}$	circuit volume, $\text{m}^3$
$\rho_{\text{PC}}$	nitrogen volume mass at PC pressure, $\text{kg}\cdot\text{m}^{-3}$
$M_{\text{is}}$	total ammonia mass introduced in the circuit, kg
$M_0$	empty bottle ammonia mass, kg
$M_{\text{f}}$	bottle ammonia mass after filling, kg
$M_{\text{na}}$	non-adsorbed ammonia vapour mass, kg
$\rho_{\text{ag}}$	gaseous volume of ammonia at filling temperature $T$ , $\text{kg}/\text{m}^{-3}$
$M_{\text{al}}$	mass of ammonia liquid in the tank, $\text{kg}/\text{kg}$

$V_{al}$	ammonia volume in the tank, $m^3$
$\rho_{al}$	ammonia volume mass at filling temperature, $m^3$
$M_s$	maximal mass by adsorbed carbon at temperature $T$ and per unit mass, kg
$M_{ac}$	mass of active carbon in the adsorber, kg
$M$	adsorbed maximal ammonia mass (measured), kg
$W_0$	maximal adsorbable volume, $m^3/kg$
$m_1$	desorbed mass during heating stage, kg
$m_2$	introduced mass in the adsorber during the cooling stage, kg
$T_f$	active carbon temperature at the end of the cooling stage, $^{\circ}C$
$P_e$	evaporation pressure, bar
$P_s(T_f)$	ammonia saturation pressure at temperature $T_f$ , bar
$\Delta G$	potential of adsorption, $kJ/kg$
$f(w)$	function of volume distribution

The thermodynamic phenomenon of adsorption of a gas by a micro-porous absorber represents a bivariate balance. Numerous theories have been developed to determine equations of adsorption isotherms in a micro-porous solid.

The first approach to the adsorption phenomenon consists of describing a molecular model from a kinetic viewpoint [1–3].

A second approach considers the phenomenon of adsorption from a macroscopic viewpoint. The theory of Polanyi [1, 3] is solely thermodynamic, and is thereby liberated from all molecular models: the thickness of the adsorbed layer, interactions between adsorbed molecules and their mobility are not specified. It considers the variation with temperature of the maximal adsorbable quantity.

Dubinin and Radushkevich [4–7], deepening the theory of Polanyi, have developed the concept of the ‘replenishment in volume’ at the time of the adsorption of a gas on a micro-porous absorbent. This theory permits the prediction of isotherms of adsorption, with a unique isotherm for a given gas. The authors [4–7] gave a characteristic curve for all gases on the same adsorbent, with the form:

$$\Delta G = RT \ln \left( \frac{P_s(t)}{p} \right) = \beta f(w)$$

where  $\beta$  is the coefficient of affinity for the adsorbent–adsorbate.

The characteristic Dubinin–Radushkevich equation takes the form:

$$\frac{w}{W_0} = \exp \left[ \frac{k \Delta G^n}{\beta^2} \right]$$

where  $k$  is a characteristic of the adsorbent. This equation may be expressed in linear form:

$$\log(W) = \log(W_0) - D \left( T \ln \frac{P_s(T)}{P} \right)^n$$

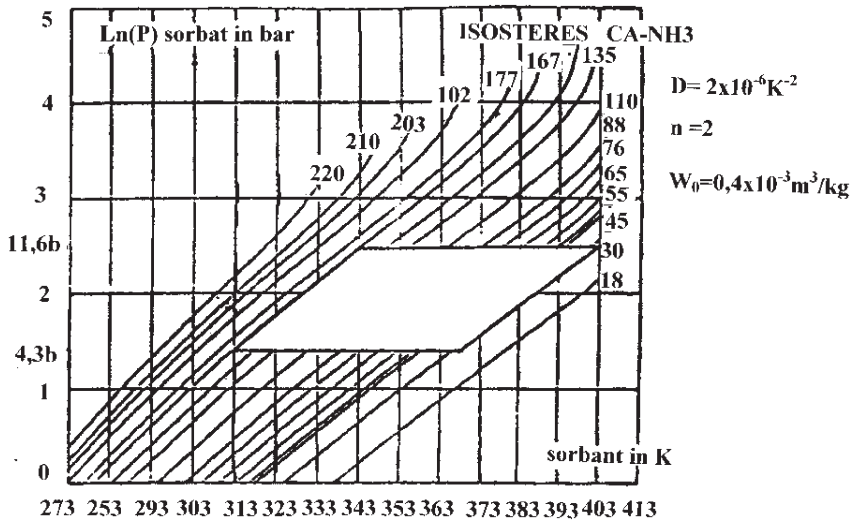


Fig. 1 Isosters for activate carbon – ammonia couple and the thermodynamic cycle.

or

$$m = W_0 \rho(T) \exp \left[ -D \left( T \ln \left( \frac{P_s(T)}{P} \right) \right)^n \right]$$

where  $W_0$ ,  $n$  and  $D$  are characteristics of the adsorbent–adsorbate couple (nature of the adsorbent and the affinity of the adsorbate).

$W_0 \rho(T)$  represents the adsorbable maximal mass by unit of mass of the adsorbent. An alternative version of this equation is:

$$\ln(P) = \ln P_s(T) - 1/T \cdot \left[ -1/D \cdot \ln(m/W_0 \rho(T)) \right]^{1/n}$$

This version allows the isosteres of the adsorbent–adsorbate couple to be established ( $p = f(T)$   $m = \text{constant}$  steady pressure). In a cooling system using the adsorption process [8, 9], the isosteres established and the thermodynamic conditions of the experiment ( $T_c$ ,  $T_{ev}$ ,  $T_{max}$ ,  $T_{min}$ ) allow the determination of the cyclic masses in the system (desorbed and adsorbed).

In order to predict the cyclic masses of an adsorption cooling system under different thermodynamic conditions, it is necessary to know the three parameters,  $W_0$ ,  $n$  and  $D$ , of the adsorbent–adsorbate couple chosen [10, 11] (Fig. 1).

### The proposed experimental system

The set-up of the proposed experiment (Fig. 2a, 2b) includes two interdependent rings. The heating ring is composed of the adsorber, the condenser and the tank. This

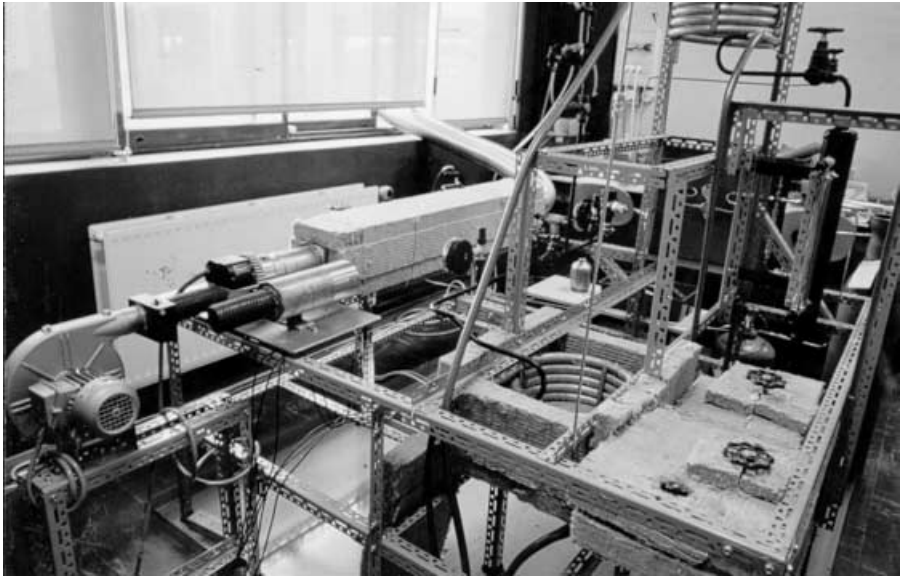


Fig. 2a Photograph of the experimental set-up.

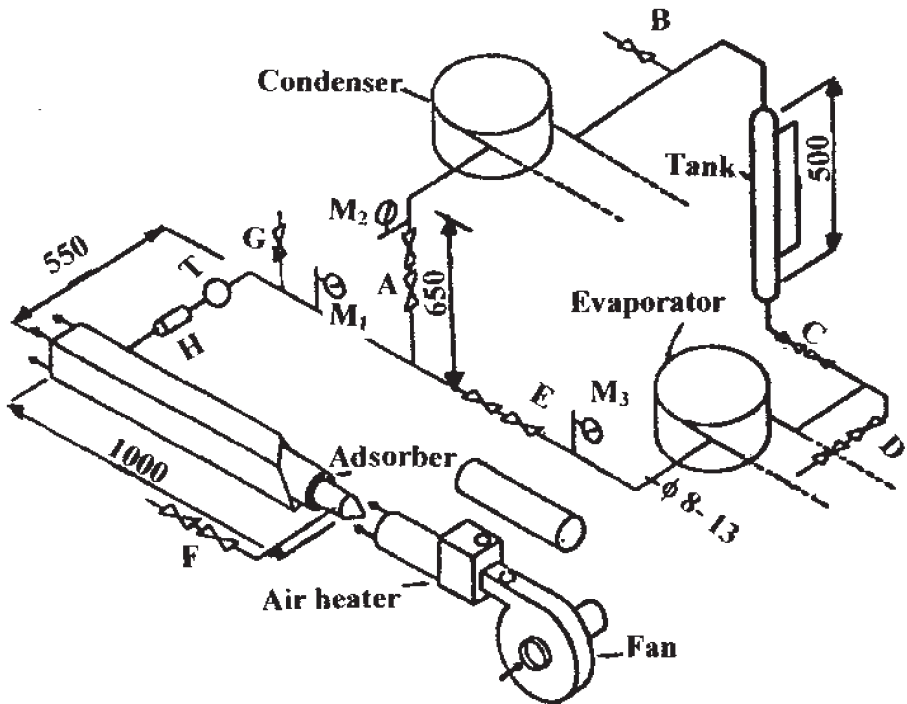


Fig. 2b Schema of the experimental set-up.

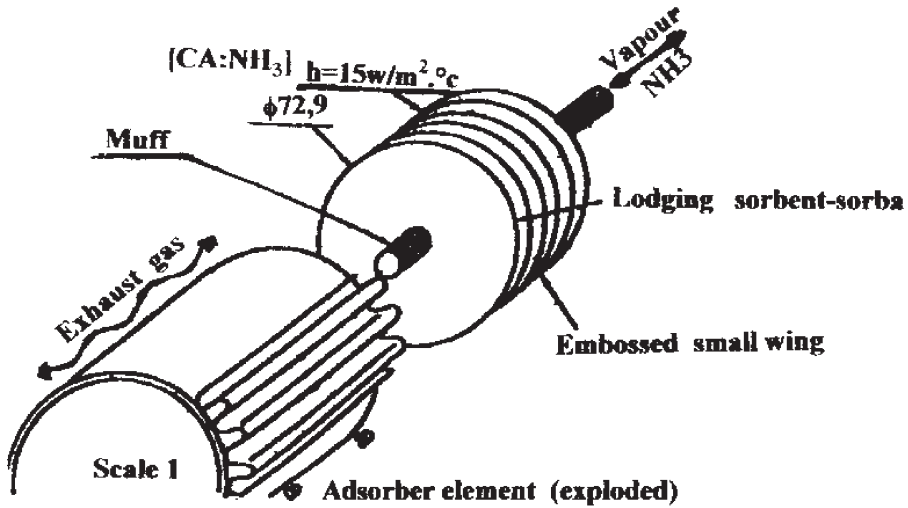


Fig. 3 Detailed representation of the adsorber tube.

ring achieves recycling and condensation of the cooling fluid. The cooling ring is composed of the tank, the evaporator and the adsorber. It achieves cooling by evaporation and the adsorption of the cooling fluid. Exhaust gases are simulated by air heated to high temperatures (20–650 °C).

The adsorber is the principal element of this circuit (Fig. 3). It is a stainless steel tube of 72.9/76.1 mm diameter and 1000 mm length. Sealing is realised by two rounded bottoms with gloved fingers for the thermocouples. Aluminium blades are placed inside the tube every 5 mm, hollowed in the middle to allow gas delivery. The space between the blades is packed with active carbon. A metal fabric tube (200 mm) passes through the blades (in the middle) to gather adsorbed gases and to prevent solid particles of carbon passing through the circuit.

To get good heat transmission, aluminium is placed on the external surface of the adsorber tube. A metal cylinder, 0.5 mm wide, circles the ringlets to allow good thermal contact between them and the tube.

### Preliminary test

Prior to turning the system on and making measurements, we perform the following preliminary test:

- (1) determining the weight of the ammonia introduced in the circuit and determination of the maximal mass adsorbed under standard room temperature, after determining the internal volume of the circuit;
- (2) pressure verification in the adsorber after heating, cooling and noticing the adsorption effect (recycling and adsorption).
- (3) condenser and evaporator circuit verification.

### Determination of the volume of the circuit

The initial vacuum circuit is filled with nitrogen gas, under 22-bar pressure. The weight of the N<sub>2</sub> bottle is determined before and after filling of the circuit, and the difference gives the mass of the N<sub>2</sub> in the circuit. The internal volume of the circuit is then obtained by multiplying this mass by the nitrogen volume mass at 22 bars.

These operations are done at room temperature (27 °C), giving these equations:

$$M_{bi} = V_b \cdot \rho_{bpi}$$

$$M_{bf} = V_b \cdot \rho_{bpf}$$

$\rho_{bpi}$  and  $\rho_{bpf}$  are determined using the compressibility factor of the gas, defined by:

$$\rho_{bpi} = \rho_1 \cdot P_{ib} / Z_{pi}$$

$$\rho_{bpf} = \rho_1 \cdot P_{fb} / Z_{pf}$$

The N<sub>2</sub> mass introduced in the circuit,  $M_{aZc}$ , is:

$$M_{aZc} = M_{bi} - M_{bf}$$

Then the volume of the circuit,  $V_c$ , is:

$$M_{aZc} = M_{bi} - M_{bf}$$

with the  $\rho_{PC}$  density of N<sub>2</sub> under  $P_c$ .

The volume of the circuit is 13.4 litres.

### Determination of maximal adsorbable ammonia

The circuit is under vacuum after evacuation of the nitrogen. We fill the circuit with ammonia gas at room temperature under a pressure of 10.6 bars (vapour saturation pressure at 27 °C). We fill the tank with ammonia to half height, to allow for mass transfers during measurements.

The ammonia bottle is weighed before and after filling, to give the accepted ammonia mass, and we deduce the ammonia mass which is not adsorbed (circuit) and the ammonia liquid mass introduced into tank to obtain the maximal adsorbed mass on the active carbon at room temperature.

The total ammonia mass introduced in the circuit,  $M_{is}$ , is:

$$M_{is} = M_0 - M_f$$

The ammonia mass which is not adsorbed is:

$$M_{na} = VC \cdot \rho_{ag}$$

The liquid ammonia mass in the tank is:

$$M_{al} = V_{al} \cdot \rho_{al}$$

The maximal adsorbed mass by the carbon,  $M_s$ , at temperature  $T$  and per unit mass is:

$$M_s = [(M_0 - M_f) - (M_{al} - M_{na})] M_{ac}$$

The numerical results for  $T = 27\text{ }^{\circ}\text{C}$  are:

$$M_0 = 17.81\text{ kg}$$

$$M_f = 16.47\text{ kg}$$

$$M_{is} = 1.34\text{ kg}$$

$$M_{na} = 0.110\text{ kg}$$

$$M_{ac} = 1.8\text{ kg}$$

$$V_{al} = 1.195 \times 10^{-3}\text{ m}^3$$

$$\rho_{al} = 600\text{ kg/m}^3$$

$$M_{al} = 0.717\text{ kg}$$

$$\rho_{ag} = 8.27\text{ kg/m}^3$$

$$M_s = 0.285\text{ kg/kg}$$

### Measuring test

The active carbon–ammonia couple is introduced into the adsorber (Fig. 3), which is heated with the exhaust gases simulated by the air heater. When the adsorber temperature increases, the vapour pressure of ammonia measured by manometer 1 increases; when it reaches the saturation vapour pressure corresponding to the temperature of the condenser, we open valve A and the recycling starts at the same time as the condensation.

Recycling continues as long as the adsorber is heated. The condensed ammonia is collected in the tank, where mass transfer measurements are made. The condensation continues until the end of the recycling: this represents the end of the heating stage. The temperatures of the adsorber (internal blades) and hot gases are measured instantly by thermocouples linked to an acquisition station.

At the end of the heating stage, we proceed to the contraction of the hot air, to the closing of valve A and we open valve E. The ambient air is sent to the adsorber by a fan, the active carbon temperature decreases, which decreases the evaporation pressure to the evaporator pressure of the ammonia.

We open valve C and evaporation starts; this produces cooling and adsorption by the active carbon of ammonia vapour coming from the evaporator. The evaporation and the adsorption of the ammonia continue to cool the adsorber, to  $40\text{ }^{\circ}\text{C}$ . This is the end of the cooling stage and the end of the cycle. Heating the adsorber again will repeat the cycle. The acquisition station instantly gives the cooling air and the adsorber temperatures. The difference between the volume in the tank during the recycling and adsorption stages gives the cycled ammonia mass.

Several cycles were run under this procedure. The measurements of the transfer mass (cycled masses) were reproducible. Fig. 4 shows the temperature measurement results (gas blades) with the corresponding desorbed and adsorbed mass during one of these cycles. We observe (Fig. 4) that there is an important temperature difference between the input and output of the adsorber, which results in poor mass transfers. We remark also that the temperature difference between the interval blades and the air is practically zero.

**DESORPTION= $78\text{NH}_3/\text{kgCA}$ =ADSORPTION**

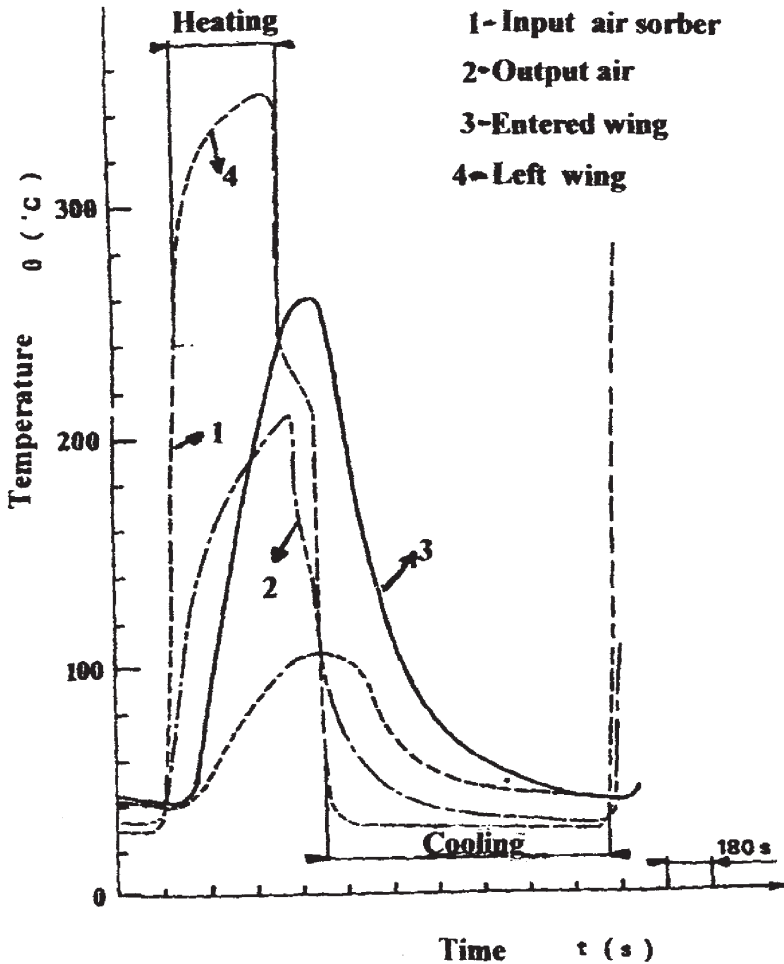


Fig. 4 Temperature of the gases and internal wings with respect to time during an experimental cycle.

### Parameter identification

*Step 1 (point M).* All the system circuit is filled with ammonia at  $30^\circ\text{C}$  and 11.6 bars, until the active carbon is saturated. The maximal adsorbed ammonia mass is measured ( $285\text{ g/kg}$ ) by the weight difference of the ammonia bottle before and after filling.

*Step 2 ( $M \rightarrow B$ ).* The adsorber is heated for 6 minutes and the desorbed and condensed ammonia mass is measured by the volume difference in the tube on the tank

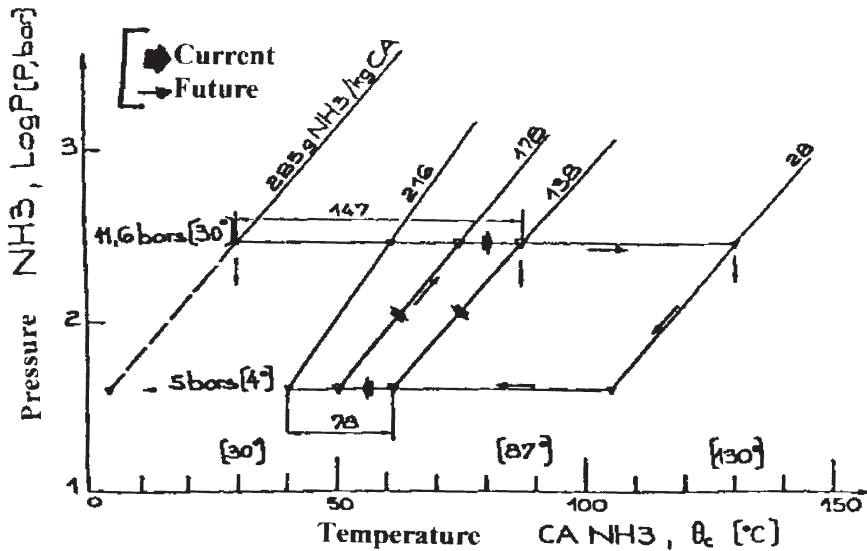


Fig. 5 The experiment which allows us to identify the parameters of the Dubinin–Radushkevich equation.

( $M$  resorbed = 147 g/kg): point B is on the isoster 138 g/kg. So the heating stage is over.

Step 3 ( $B \rightarrow C \rightarrow D$ ). The adsorber is cooled to the evaporation pressure (point C). The ammonia is then directed to the evaporator while the evaporation pressure is kept constant. We continue to cool the adsorber to 40°C (internal blade temperature). Evaporated and adsorbed ammonia mass is 78 g/kg. Point D is on the isoster 216 g/kg. This represents the end of the cooling stage.

The main difficulties in identifying  $W_0$ ,  $n$  and  $D$  result from the fact that we do not have temperature measurements of the active carbon. Nevertheless, we have identified these parameters using a combined simple method (using measurements and models) as follows. From the Dubinin–Radushkevich model,  $n = 2$ .

The maximal adsorbed volume,  $W_0$ , is identified from the maximal adsorbed mass on the active carbon,  $M_s$ , which is determined when filling the adsorber with ammonia (point M). Knowing the ammonia volumic mass at the adsorption temperature,  $T$ , we have:

$$W_0 = M_s / \rho(T)$$

We make the following assumption: at the end of the cooling stage (point D) of Fig. 5, the internal blade temperature is considered equal to the active carbon temperature (we use Kirchoff's assumption, that after a long enough time, independently of the nature of material used, the temperatures of the elements are identical).

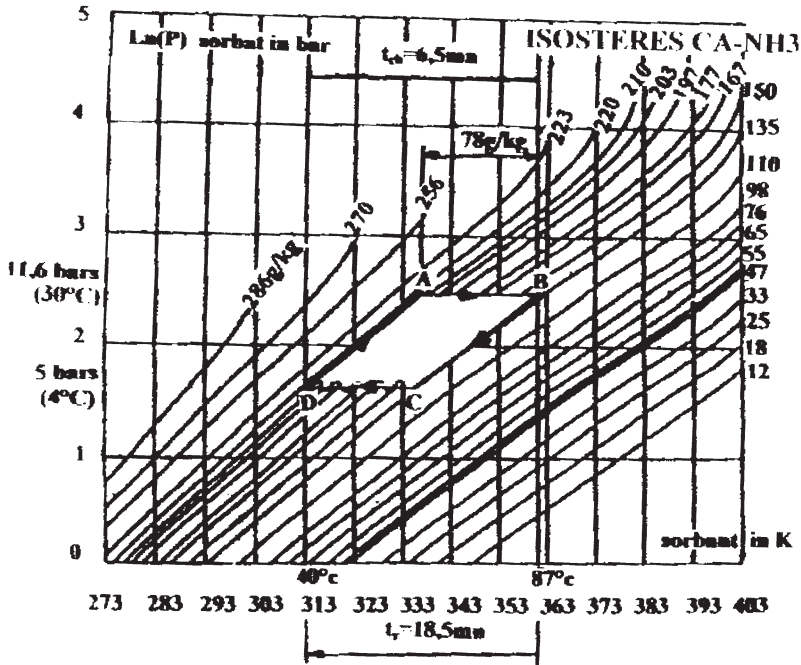


Fig. 6 Representation of a thermodynamic cycle.

From this assumption, knowing  $W_0$  and  $n$ , we identify  $D$  as follows. At the characteristic point  $(m_d, P_e, T_f)$ , using the Dubinin–Radushkevich equation, and with  $m_d(T_f, P_e) = M_s - (m_1 - m_2)$ , the parameters  $W_0$ ,  $n$ , and  $D$  are then identified:

$$D = \frac{-\log \left[ \frac{m_d}{W_0 \rho(T_f)} \right]}{\left[ T_f \cdot \log \frac{P_s(T_f)}{P_e} \right]^2}$$

The experimental results are:

- $M_s = 285 \text{ g/kg}$  of active carbon
- $\rho(T_f) = 581 \text{ kg/m}^3$
- $m_1 = 147 \text{ g/kg}$  of active carbon
- $m_2 = 78 \text{ g/kg}$  of active carbon
- $P_e = 5 \text{ bars}$  ( $4^\circ\text{C}$ )
- $T_f = 40^\circ\text{C}$
- $W_0 = 0.475 \times 10^{-3} \text{ m}^3/\text{kg}$
- $D = 2 \times 10^{-6} \text{ K}^{-2}$

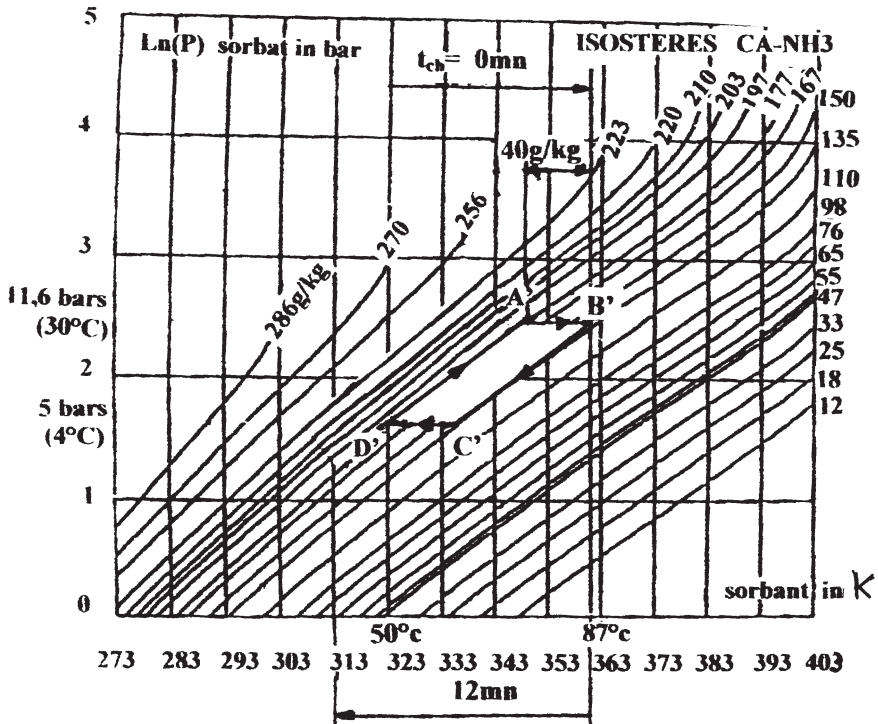


Fig. 7 Thermodynamic cycle leads.

Thus identified, parameters  $W_0$ ,  $n$ ,  $D$  permit, with the help of the Dubinin–Radushkevich model, determination of the network of isotherms of the carbon–ammonia couple and prediction of the cycled masses of refrigerated systems for different thermodynamic conditions. This is shown in Fig. 6. Features of the thermodynamic cycle are:

$$T_{\min} = 40^\circ\text{C} \text{ (point D)}$$

$$T_s = 64^\circ\text{C} \text{ (point A)}$$

$$T_{\max} = 87^\circ\text{C} \text{ (point B)}$$

$$T_{s'} = 62^\circ\text{C} \text{ (point C)}$$

$$\Delta m = 78 \text{ g/kg (cycled mass/unit mass of active carbon)}$$

$$t_{\text{ch}} = 6.5 \text{ min}$$

$$t_{\text{rec}} = 18.5 \text{ min}$$

Otherwise we notice (Fig. 4) that for the specified times (6 minutes for the heating and 12 minutes for the cooling), the temperature of the active carbon (supposed to equal that of the one of small wings) at the end of cooling is  $50^\circ\text{C}$ . These times imply a cycled mass of  $40 \text{ g/kg}$ , which is relatively small (Fig. 7). Characteristics of the thermodynamic cycle for these times are:

$T_{\min} = 50^{\circ}\text{C}$  (point D)  
 $T_s = 75^{\circ}\text{C}$  (point A)  
 $T_{\max} = 87^{\circ}\text{C}$  (point B)  
 $T_s' = 62^{\circ}\text{C}$  (point C)  
 $\Delta m = 40\text{ g/kg}$  (cycled mass/unit mass of active carbon)  
 $t_{\text{ch}} = 6\text{ min}$   
 $t_{\text{rec}} = 12\text{ min}$

Fig. 7 shows that only a third of the mass transfers specified (120 g/kg of active carbon) are achieved by the cycle. This is partly due to the existence of a thermal gradient between the internal small wing and the active carbon ( $= 60^{\circ}\text{C}$ ).

A reduction of the longitudinal temperature gradient of the adsorbent, while achieving a variable radial conductance adapted to the thermal gradients of transfers (reduction of exchange surfaces at the head of the adsorber, increase of exchange surfaces at its tail), would improve the performance of experimental refrigerated systems meaningfully.

## Conclusions

Although we did not measure the temperature of the active carbon, we were able by means of the hypothesis of Kirchhoff to identify parameters of the Dubinin–Radushkevich equation. The results are in agreement with Bougard [10] and Cristoph [11]. These identified parameters, with the help of the Dubinin–Radushkevich model, permit the prediction of cycled masses for a refrigerated system for all thermodynamic conditions imposed on the system. They also determine isotherms and heats of adsorption.

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