USING THE WHEELER-JONAS EQUATION TO DESCRIBE ADSORPTION OF INORGANIC MOLECULES: AMMONIA

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Introduction

Activated carbons can adsorb a wide variety of substances. This is the reason why they are used in canisters to guarantee the safety of the people.
The use of the canisters is dependent on several parameters which makes it interesting if the safety margins of the filter can be predicted.
The Wheeler-Jonas equation is a well-known predictive equation for describing organic vapour breakthrough times of activated carbon beds [1]. The parameters of this equation can be linked to the micropore volume of the carbon and the kinetics of the adsorption process (mass transfers) for physisorped, i.e. organic vapours. Inorganic vapours are usually chemisorbed at the active sites of the carbon surface. Nevertheless, it would be beneficial if a Wheeler-Jonas equivalent equation could be derived for inorganic vapours.
The applicability of the Wheeler equation has been proven earlier for cyanogen chloride [2], but not for other inorganic vapours. This paper investigates the validity of the Wheeler-Jonas equation for the adsorption of inorganic vapours, in particular ammonia.

Theoretical

Contrary to most organic vapours, an inorganic vapour, e.g. ammonia, is chemisorbed when it passes through a carbon filter bed. These two processes, physi- and chemisorption, have some important differences [3].
The forces between adsorbent and adsorbate in Van der Waals adsorption (physisorption) are similar to those acting in condensation phenomena. The adsorption takes place in the micropores of the activated carbon, which involves a heat of the same magnitude as the heat of condensation. The reaction is non-specific and can be either uni- or multimolecular. Contrary to the physisorption, the forces in chemisorption are similar to those acting in chemical reactions and such a chemisorption is associated with a reaction heat. Chemisorption is a specific unimolecular reaction, taking place at the active sites of the carbon surface. Therefore, the activated carbon needs to be impregnated with specific complexes. In the case of ammonia, H_3PO_4 or H_2SO_4 are the appropriate impregnants for the best result [4].

When a model of physisorption is applied to chemisorption, the differences between both processes have to be taken into account.
Different equations, theoretical and semi-empirical, can be applied to predict the breakthrough time. Theoretical equations are the most accurate models, but they are rather complex. The Wheeler-Jonas equation (See Eqn. 1), a semi-empirical equation, proofs to be a good modellisation tool because the number of parameters is limited and because it can be adapted to include the effects of water vapour [5,6]. The parameters are based on the characteristics of the carbon and the vapour and not on the type of adsorption.

$$t_b = \frac{W_e W}{Q C_{in}} - \frac{W_e \rho_b}{k_v C_{in}} \ln\left(\frac{C_{in} - C_{out}}{C_{out}}\right)$$

Eqn. 1: Wheeler-Jonas equation

t_b = breakthrough time [min]
W = weight of the carbon [g]
W_e = static adsorption capacity of this activated carbon for the vapour [g/g_{coal}]
C_{in} = filter inlet concentration of the vapour [g/cm^3]
Q = volumetric flow rate [cm^3/min]
ρ_b = bulk density of the carbon bed [g_{coal}/cm^3]
k_v = overall adsorption rate coefficient [min^{-1}]
C_{out} = chosen breakthrough concentration [g/cm^3]

When Wheeler-Jonas is applicable to an adsorption process (e.g. physisorption), plotting breakthrough time versus inlet/outlet concentration gives a straight line, with equation y = b – ax.

$$t_b = \frac{W_e W}{Q C_{in}} - \frac{W \rho_b}{k_v C_{in}} * \ln\left(\frac{C_{in} - C_{out}}{C_{out}}\right)$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$y = b - a * x$$

A breakthrough test is an experiment determining essential parameters of an adsorption process (e.g. physisorption). The parameters (W, C_{in}, Q, ρ_b, C_{out}) figuring in the Wheeler-Jonas equation are fixed for a specific breakthrough test. During the test, the breakthrough times and the associated outlet concentration are measured at regular intervals. The parameters, W_e and k_v, essential for determining the safety margins of the filter, can then be calculated applying Wheeler-Jonas, more specifically via Eqn. 2 and 3.

$$b = \frac{W_e W}{Q C_{in}} \qquad \text{Eqn. 2}$$

$$a = \frac{W_e \rho}{k_v C_{in}} \qquad \text{Eqn. 3}$$

Experimental

Carbon beds were tested using the parameters given in table 1.

Results and Discussion

Figure 1 shows a typical breakthrough curve of a test with ammonia. The curve presents a steep rise, steeper than the equivalent curve for organic vapours.
Table 2 summarises the results of the breakthrough tests for carbon beds using air contaminated with ammonia (a chemisorption). These tests where executed with test parameters as described in table 1.

Fitting the Wheeler-Jonas equation

If the chemisorption process can be adequately modelled by the semi-empirical Wheeler-Jonas equation, the experimental results of the different breakthrough tests should fit this Wheeler-Jonas equation.
With the results of a set of different breakthrough tests, it becomes possible to plot the influence of a varying C_{in} on the breakthrough time, keeping humidity of the air stream and weight of the carbon bed constant.
Figure 2 illustrates this for three different (humidity, weight carbon bed)-pairs.
Writing Wheeler-Jonas in a somewhat different way:

$$t_b = \frac{1}{C_{in}}\left(a + b \ln \frac{C_{in} - C_{out}}{C_{out}}\right)$$

this curve should fit the experimental results in Fig. 2.
The second term in the equation is negligible with respect to the first term, leading to an equation of the type y = a/x.
When obtaining the equation of the curve fitting the results of Fig. 2, it becomes clear that Wheeler-Jonas is applicable. Indeed, the "best fitting" curves calculated by a computer tend towards the appropriate $y = ax^{-1}$ form.
If the results of a single breakthrough test, i.e. the different breakthrough times that are measured together with the associated outlet concentration, are plotted (see Fig. 3), a straight line is obtained.
From the exploitation of the experimental results of Table 2, it becomes clear that chemisorption can be adequately modelled by the Wheeler-Jonas equation.

Estimation of the parameters W_e and k_v based on Wheeler-Jonas.

Equations 2 and 3 can be used to estimate the parameters W_e and k_v. This can be done for all tested carbon beds and the results are summarised in table 3.
The W_e-values are small, when compared with the values of some organic vapours (10 to 100 times smaller). This is because of the small uptake of ammonia, which is confirmed by the short breakthrough times. These short breakthrough times can be attributed to the activated carbon, because it is not impregnated with H_2SO_4 or H_3PO_4-complexes. The fluctuation of the W_e-value is caused by the experimental error: a small deviation in the straight line causes an important relative error in the W_e-value, even though the absolute error stays small.
This is also true for the k_v-value, where the influence on the error is even bigger (see table 3; test 9, 10 and 16). The k_v-value can also be determined mathematically with equation 4 (See eqn. 4) [7].

$$k_V = 48 * \beta^{0,33} * v_L^{\ 0,75} * d_p^{\ -1,5} \qquad \text{Eqn. 4}$$

k_V = overall adsorption rate coefficient [min^{-1}]
β = affinity (similarity) coefficient of the adsorbate [-]
v_L = linear velocity [cm/s]
d_p = mean diameter of the activated carbon particles [cm]

In order to apply this formula, β has to be known. Wood has reported a β-value of 0.28 for ammonia [8]. When k_v is calculated for both filter sizes (ϕ = 9.5 and ϕ = 10.5), the k_v-value varies between 2824 and 3282 (d_p = 0.12 cm). In other words, looking at table 3, this is in excellent agreement with the experimentally calculated values of k_v. Furthermore, k_v is certainly of the same order of magnitude as for physisorption of organic vapours. Hence we can conclude that the rate controlling step for a chemisorption process is not the adsorption step itself, but the surface diffusion, i.e. the chemisorption of ammonia is preceded by some form of physisorption.

The influence of the humidity

When the breakthrough times of the tests under dry conditions are compared with those of the tests with humid air (no prehumidification), there is no significant difference. This means that the humidity of the air flow does not influence the chemisorption.
When the activated carbon is prewetted, the breakthrough time of the carbon bed rises. This is probably due to the hydrolysation of the ammonia-molecule by the pre-adsorbed water after which it is adsorbed by the carbon bed. The raise of the W_e-values with the degree of pre-humdification confirms the larger uptake of ammonia-molecules. For a very high degree of prehumidification (70 → 90%RH), W_e becomes a constant (See fig. 4).

Comparison of the estimated breakthrough time vs. the experimental breakthrough time.

In figure 5 the experimental results are plotted vs. the breakthrough times calculated with the Wheeler-Jonas equation (ρ= 581 kg/m³). Here, two parameter-pairs are used (70/70 %RH, 70g of carbon) and (0/0 %RH, 70g). The values for W_e and k_v that are used in the Wheeler-Jonas equation are the average values, calculated per parameter-pair.
The breakthrough times calculated with the Wheeler-Jonas equation are a little smaller than the experimental values. But, since the mathematical breakthrough time is an underestimation of the real breakthrough time, the safety of the canisters can be based on the Wheeler-Jonas equation.

Conclusions

- The chemisorption of ammonia, an inorganic vapour, can be modelled by the semi-empirical Wheeler-Jonas equation.
- In this case the adsorption capacity W_e cannot be linked to the micropore volume of the carbon (as for physisorption of organic vapours).
- The adsorption rate coefficient k_v seems to be determined by the surface diffusion of the molecules, similar to the case of physisorption.
- By testing one or two beds of a specific activated carbon, the Wheeler-Jonas equation can be used to predict the breakthrough time of ammonia for respirator filters filled with this particular carbon under variable circumstances.

References

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Table 1: test parameters

filters used:

	weight (g)	diameter (cm)	height (cm)
1	70	9.5	1.9
2	140	10.5	2.9
3	280	9.5	3.9

Carbon: Chemviron ASC-TEDA, (BPL-type carbon impregnated with Cr-, Cu and TEDA-complexes)

250 ppm ≤ inlet concentration ≤ 6000 ppm

0 % RH ≤ pre-humidification ≤ 90 % RH

0 % RH ≤ air stream humidification ≤ 90 % RH

breakthrough time is measured at 25 ml/m³
volumetric flow = 30 ℓ/min

Table 2: Results of the carbon beds tested with ammonia.

weight (g)	concentration (ppm)	RH %	breakthrough time (min)	Nr
280	1000	0-70	98	1
140	237	0-70	164	2
	502		63	3
	744		47	4
	960		21	5
	1882		22	6
	3800		10	7
	5934		4	8
70	573	0-70	20	9
	1079		9	10
	2309		4	11
70	653	0-0	18	12
	1227		10	13
	2353		6	14
70	841	70-70	64	15
	1102		34	16
	2079		20	17
70	1500	90-90	43	18
	1583	80-80	47	19
	1605	80-80	43	20
	1664	70-70	52	21
	1601	50-50	39	22
	1819	40-40	36	23
	1966	30-30	22	24

Table 3: W_e and k_v obtained with the Wheeler-Jonas equation.

Nr	W_e [g/g_{coal}]	k_v [min^{-1}]
1	0.009	1378
2	0.008	1159
3	0.006	1806
4	0.007	1423
5	0.002	3549
6	0.004	3834
7	0.006	2238
8	--	--
9	0.001	9467
10	0.002	7367
11	--	--

Nr	W_e [g/g_{coal}]	k_v [min^{-1}]
12	0.005	2571
13	0.007	2010
14	0.009	1941
15	0.013	2593
16	0.005	11213
17	0.018	3576
18	0.031	2831
19	0.032	3610
20	0.031	3189
21	0.036	3786
22	0.030	2810
23	0.028	3708
24	0.022	3092

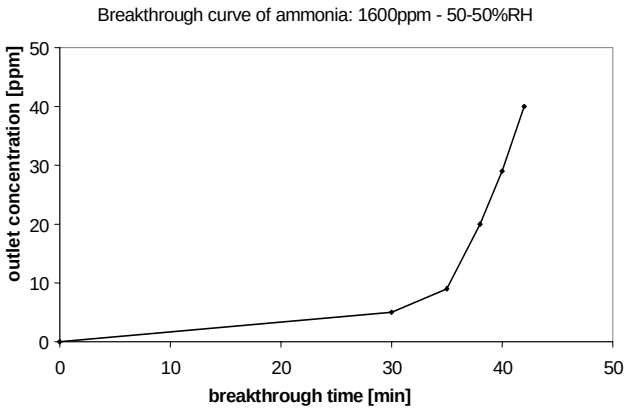

Fig. 1: Breakthrough curve of a carbon bed tested with 1600 ppm ammonia, 50% humid air stream and carbon pre-wetted in equilibrium with 50% RH

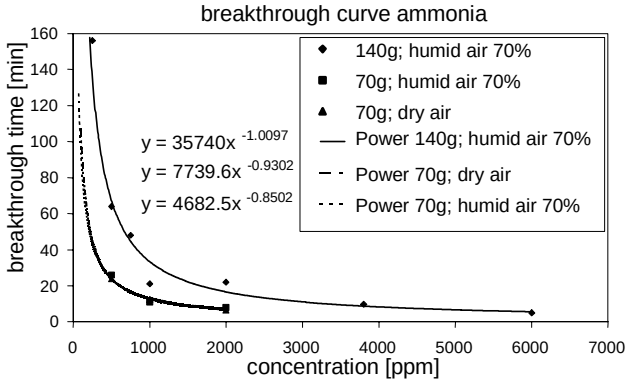

Fig. 2: Plot of the breakthrough time vs. the inlet concentration for a given humidity and weight.

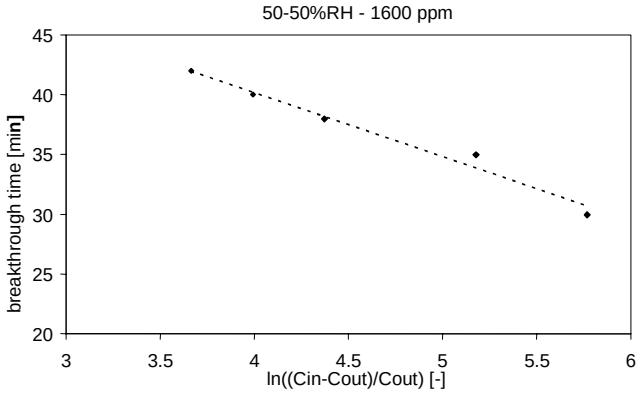

Fig. 3: Breakthrough time vs. $\ln((C_{in}-C_{out})/C_{out})$ for a test with inlet concentration 1600 ppm, prehumidification/ humid air: 50/50%RH

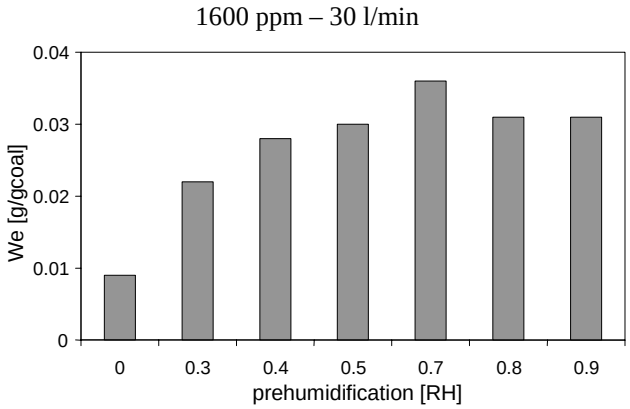

Fig. 4: W_e vs. the degree of prehumidification (RH)

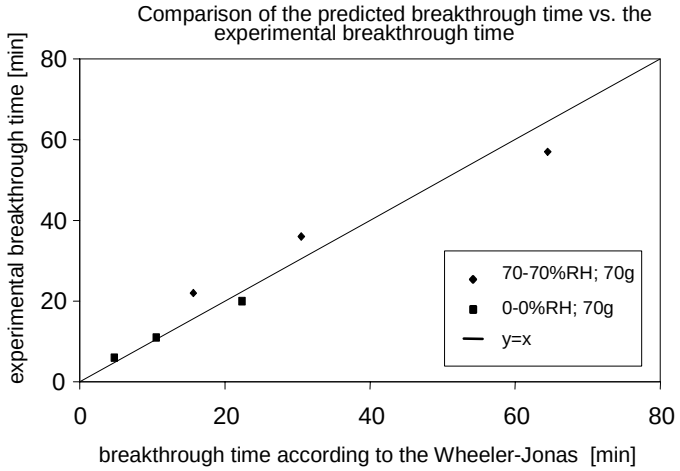

Fig. 5: Comparison of the experimental breakthrough times vs. breakthrough times according to the Wheeler-Jonas equation.