CORRELATION OF MASS TRANSFER DATA FROM LINDE AIR PRODUCTS COMPANY ON THE ADSORPTION OF KRYPTON ON ACTIVATED CHARCOAL

By

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Oak Ridge, Tennessee

Technical Information Service, Oak Ridge, Tennessee
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OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY
POST OFFICE BOX P
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An attempt has been made to correlate the mass transfer data from Linde's adsorption laboratory. Results of these calculations show that the data thus far give an excellent correlation using the mathematical equations presented by Hougen and Marshall, Chemical Eng. Progress 43 197(1947).

The above paper gives an equation for the fraction adsorbable vapor remaining in a gas stream from an adsorption bed as a function of time, flow rate, slope of equilibrium curve, position in bed and $H_{og}$, the height of a transfer unit. This equation is presented in graphical form with the following dimensionless quantities as variables:

$$\frac{Y}{Y_0} = \text{The fraction of the entering stream that has not been adsorbed at position } x \text{ in the bed and time } \tau \text{ after starting operation of the bed.}$$

$$b\tau = \frac{cG x}{\left( \frac{G}{H_{og}} \right)}$$

where:

- $c$ = slope of equilibrium curve gm charcoal / gm carrier gas.
- $G$ = Mass flow rate gm hr cm$^2$
- $\rho$ = Bulk density of charcoal gm/cc
- $H_{og}$ = Height of a transfer unit = cm
- $\tau$ = Time from start of gas flow, hr.
- $ax$ = Number of transfer units = $\frac{x}{H_{og}}$

Where:

- $x$ = length of bed, cm.
The data from Linde Air Products Company were taken in the following manner. Nitrogen containing 1.5% krypton was bled through a bed of charcoal at -183°C. until the concentration of the exit gas showed 100 parts per million of krypton by mass spectrometer analysis. The adsorbed nitrogen and krypton were then stripped from the bed and analyzed. A material balance of the system showed that the data checked quite well except for the lowest flow rate of 180 cc/min. This flow rate is recalculated to check the material balance and becomes 118.4 cc/min for this work.

The Linde data also include a static equilibrium determination of the adsorption of krypton on charcoal. The application of the Freundlich theory to these data give the following formula which fits the data quite well:

\[ v = 256p^{0.110} \quad (^{\circ}C) \]

where:

- \( v \) = adsorbate cc/gm
- \( p \) = pressure over bed in m.m. Hg

The correlation method is as follows:

According to the Hougen and Marshall equation, for \( y/y_0 = 0.00667 \) which is the concentration for this case, the value of \( \alpha \) (number of transfer units) becomes approximately 5.40 at \( br=0 \). The Linde data of time vs. flow rate were then extrapolated on semi log paper (Figure 2) to zero time. The flow rate at which the exit concentration would be 100 p.p.m. at zero time is therefore 420 cc/min. Using the value of 5.4 transfer units, the height of a transfer unit at 420 cc/min becomes 2.036 cm. From this one point and the theory that the \( H_{og} \) varies as the 0.51 power of \( G \), the value of \( H_{og} \) for any flow rate \( G \), may be calculated.

The above theory was checked by actually calculating \( H_{og} \)'s from individual values given in the data. However, Hougen and Marshall assumed a linear equilibrium line for their derivation. For this case, the equilibrium line is far from linear as is shown by the 0.110 exponent in the equilibrium equation. For this calculation, the log mean value of the equilibrium line slope for entrance and exit conditions was used. Next,
for each value of $G$ and $\tau$, the values of $b\tau$ and $ax$ were calculated leaving the value of $H_{og}$ as an unknown. $H_{og}$ was then eliminated by using the ratio $ax/b\tau$. Hougen and Marshall's curves were extrapolated to a value of 0.00667 (Figure 3) and from this curve, another curve was constructed as $ax/b\tau$ vs. $ax$ for the constant $y/y_0 = 0.00667$ (Figure 4).

From this last curve it was possible to find $H_{og}$ from the determined values of $ax/b\tau$. This was done and the calculated values gave excellent agreement (within 16%) with the original method of determining $H_{og}$ (Figure 5).

The above correlation should therefore apply to any bed, at any flow rate, for a temperature of -183°C, and the same grade of activated charcoal (Columbia Grade CXA).

J. M. Holmes

FOSTER WHEELER CORPORATION
CALCULATION OF H$_{og}$ FROM LINDE DATA

A. Velocity when $Br = 0^2 = 200 \text{ cm}^3 \text{ min}^{-1}$

No. of transfer Units $\approx 5.4$ (From Extrapolation)

Height transfer Unit $= \frac{11.0}{5.4} = 2.036 \text{ cm.}$

$\ln H_{og} = 0.710$  

$\ln V = 5.30$

Theory gives $\frac{\ln H_{og}}{\ln F_{og}} = 0.51 \frac{\ln G}{\ln G(2)}$

$\ln H_{og} = \frac{\ln H_{og}}{G(2)} x \frac{\ln V(2)}{\ln V(1)} x 0.51$

(V proportional to G for standard conditions and $N_2$ carrier gas).

B. Calculation of G:

Dimensions of Bed:

Volume = 23.1 cc.

Height = 11 cm.

Area = 2.1 cm$^2$

Diameter = 1.64 cm.

Density of Carbon = $\frac{10 \text{ gm}}{23.1 \text{ cc}} = 0.433 \text{ gm/cc.}$

C. True flow from material balance for observed flow of 180 cc/min.

$\frac{2930 \text{ cc Kr}}{27.5 \times 60 \text{ min}} \times \frac{1}{0.015} = 118.4 \text{ cc/min}$
D. Mass Flow Rate (At Standard Conditions)

\[ G = \text{Flow cc min} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{1}{2.1 \text{ cm}^2} \times \frac{\text{mole}}{22,400 \text{ cc mole}} \times 28 \text{ gms mole} \]

\[ = 0.0358 \times \text{Flow cc min} \]

<table>
<thead>
<tr>
<th>Flow cc/min</th>
<th>( \frac{G}{\text{gms}} ) hr cm²</th>
<th>Velocity through Empty Tube cm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>118.4</td>
<td>4.23</td>
<td>56.4</td>
</tr>
<tr>
<td>230</td>
<td>8.22</td>
<td>109.5</td>
</tr>
<tr>
<td>270</td>
<td>9.64</td>
<td>128.6</td>
</tr>
<tr>
<td>320</td>
<td>11.42</td>
<td>152.4</td>
</tr>
</tbody>
</table>

E. Equilibrium Constant C

\[ C = \text{Slope Equilibrium Line} \]

\[ = \frac{\text{gm Kr/gm Gas}}{\text{gm Kr/gm charcoal}} \]

\[ = \frac{83.7 \times \text{Press. Kr(m.m.)}}{28 \times 760 \frac{\text{cc/gm}}{\text{v}} \times 1.053 \frac{\text{P}}{v}} \]

F. Formula for Kr on Charcoal at -183°C.

\[ v = 256^{0.110} \]

Partial Press. Kr. entering

\[ = 0.015 \times 760 = 11.4 \text{ mm} \]

\[ v = 256(11.4)^{0.110} = 334 \text{ cc/gm.} \]

Partial Press. Kr. leaving at end of run.

\[ = 100 \times 10^{-6} \times 760 = 0.076 \text{ mm} \]

\[ v = 256(0.076)^{0.110} = 193 \text{ cc/gm} \]
\[ c_1 = \frac{1.053 \times 11.4}{334} = 0.03594 \]
\[ c_2 = \frac{1.053 \times 0.076}{193} = 0.000415 \]
\[ \log \text{ mean } C = 0.03594 - 0.00042 = 0.00796 \]
\[ \ln \frac{0.03594}{0.000415} \]

G. Calculation of \( \beta \)

\[ \beta = \frac{CG}{\bar{v} \times H_{og}} \times \text{time} \]
\[ = \frac{0.00796 G \bar{v}}{0.433 \times H_{og}} = 0.0184 G \bar{v} \]
\[ \frac{H_{og}}{H_{og}} \]

\[ \alpha = \frac{11/H_{og}}{\bar{v} \times 0.0184 G/H_{og}} = \frac{598}{G \times \bar{v}} \]
### Determination of $H_{og}$

<table>
<thead>
<tr>
<th>Flow</th>
<th>$G$</th>
<th>Time</th>
<th>$\frac{ax}{bx}$</th>
<th>$ax$</th>
<th>$H_{og}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>118.4</td>
<td>4.23</td>
<td>27.5</td>
<td>5.14</td>
<td>8.90</td>
<td>1.24</td>
</tr>
<tr>
<td>230</td>
<td>8.22</td>
<td>11.0</td>
<td>6.62</td>
<td>7.80</td>
<td>1.41</td>
</tr>
<tr>
<td>270</td>
<td>9.64</td>
<td>8.5</td>
<td>7.30</td>
<td>7.40</td>
<td>1.49</td>
</tr>
<tr>
<td>320</td>
<td>11.42</td>
<td>5.25</td>
<td>9.98</td>
<td>6.26</td>
<td>1.76</td>
</tr>
</tbody>
</table>

### Check of $H_{og}$ with Calculated Value

When $Dx = 0$

$V = 200$

$H_{og} = 2.036 \times \frac{V}{200}^{0.51}$ ($V$ proportional to $G$ for standard conditions and $N_2$ carrier gas).

<table>
<thead>
<tr>
<th>Flow</th>
<th>Velocity</th>
<th>Extrapolated $H_{og}$</th>
<th>Determined $H_{og}$</th>
<th>Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>118.4</td>
<td>56.4</td>
<td>1.07</td>
<td>1.24</td>
<td>16%</td>
</tr>
<tr>
<td>230</td>
<td>109.5</td>
<td>1.50</td>
<td>1.41</td>
<td>6%</td>
</tr>
<tr>
<td>270</td>
<td>128.6</td>
<td>1.62</td>
<td>1.49</td>
<td>8%</td>
</tr>
<tr>
<td>320</td>
<td>152.4</td>
<td>1.77</td>
<td>1.76</td>
<td>1%</td>
</tr>
</tbody>
</table>
Adsorption Mass Transfer Data - Linde Air Products Company

From Report 5/4/51
Central Files 51-5-58

**TABLE I**

<table>
<thead>
<tr>
<th>Input Flow</th>
<th>Time to reach 0.01% Krypton in exit gas</th>
<th>Volume of desorbed gas from trap</th>
<th>Mass spectrometer Analysis of Desorbed Gas</th>
<th>Capacity of trap for Total Gas</th>
<th>Linear Velocity of sample thru empty trap</th>
<th>Time of Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 cc/min</td>
<td>27-1/2 hrs.</td>
<td>3660 cc.</td>
<td>80% Kr.</td>
<td>366 cc/gr.</td>
<td>1.43 cm/sec.</td>
<td>7.7 sec.</td>
</tr>
<tr>
<td>230 °</td>
<td>11 °</td>
<td>3610 cc.</td>
<td>62.5% Kr.</td>
<td>360 °</td>
<td>1.82 °</td>
<td>6.0 °</td>
</tr>
<tr>
<td>270 °</td>
<td>8-1/2 °</td>
<td>3685 cc.</td>
<td>66% Kr.</td>
<td>369 °</td>
<td>2.15 °</td>
<td>5.1 °</td>
</tr>
<tr>
<td>320 °</td>
<td>5-1/4 °</td>
<td>Not measured</td>
<td>-----</td>
<td>-----</td>
<td>2.55 °</td>
<td>4.3 °</td>
</tr>
</tbody>
</table>

**TABLE II**

<table>
<thead>
<tr>
<th>Input Flow</th>
<th>Time to reach 0.01% Kr in Exit Gas</th>
<th>Volume of Kr thru Inlet meter</th>
<th>Volume of Kr in Desorbed trap</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 cc/min (118 corrected)</td>
<td>27-1/2 hrs.</td>
<td>4450 cc.</td>
<td>2930 cc.</td>
</tr>
<tr>
<td>230 cc/min</td>
<td>11 °</td>
<td>2277 cc.</td>
<td>2275 cc.</td>
</tr>
<tr>
<td>270 °</td>
<td>8-1/2 °</td>
<td>2066 cc.</td>
<td>2430 cc.</td>
</tr>
<tr>
<td>320 °</td>
<td>5-1/4 °</td>
<td>1515 cc.</td>
<td>-----</td>
</tr>
</tbody>
</table>
Figure 1

EXTRAPOLATION OF ax TO Br = 0 FOR Y/Yo = 0.00667
Figure 3
Extrapolation of Hougen and Marshall Equation

Data for \(Y/Y_0 = 0.00667\)

<table>
<thead>
<tr>
<th>ax</th>
<th>Br</th>
<th>(ax/Br)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>5.318</td>
<td>17.30</td>
</tr>
<tr>
<td>6.0</td>
<td>5.550</td>
<td>10.91</td>
</tr>
<tr>
<td>7.0</td>
<td>5.820</td>
<td>8.54</td>
</tr>
<tr>
<td>8.0</td>
<td>1.28</td>
<td>6.25</td>
</tr>
<tr>
<td>9.0</td>
<td>1.82</td>
<td>4.95</td>
</tr>
<tr>
<td>10.0</td>
<td>2.42</td>
<td>4.13</td>
</tr>
<tr>
<td>11.0</td>
<td>2.85</td>
<td>3.86</td>
</tr>
<tr>
<td>12.0</td>
<td>3.30</td>
<td>3.64</td>
</tr>
<tr>
<td>13.0</td>
<td>3.70</td>
<td>3.51</td>
</tr>
<tr>
<td>14.0</td>
<td>4.20</td>
<td>3.33</td>
</tr>
<tr>
<td>15.0</td>
<td>4.60</td>
<td>3.26</td>
</tr>
<tr>
<td>20.0</td>
<td>7.24</td>
<td>2.76</td>
</tr>
<tr>
<td>40.0</td>
<td>20.0</td>
<td>2.00</td>
</tr>
<tr>
<td>60.0</td>
<td>36.5</td>
<td>1.64</td>
</tr>
<tr>
<td>80.0</td>
<td>50.0</td>
<td>1.60</td>
</tr>
<tr>
<td>100.0</td>
<td>61.5</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Figure 4

$ax$ vs. $ax/\delta x$

(Number of Transfer Units)

Time Modulus

ax (Number of Transfer Units)
Figure 5

VELOCITY (cm./min.) vs. $H_{og}$ (cm.)

Height Of Transfer Unit $H_{og}$ (cm.)