# On the Methods for the Estimation of Pore-Size Distribution from Sorption Isotherms

Dollimore and Heal (1), in one of their recent articles on the calculation of pore-size distribution from sorption isotherms voiced their opinion critically about the different methods which are mainly being used at the present time. They describe the method of Cranston and Inkley (2) as being accurate, but since it required too much computational effort it was not recommended. As we experienced satisfactory results by using this method to calculate pore-size distributions we studied this method for further possible simplification.

The equation for evaluation of sorption isotherms given by Cranston and Inkley is (in the nomenclature of the original article)

$$V_{12} = R_{12} \left( v_{12} - k_{12} \sum_{d_2+\frac{1}{2}\Delta d}^{d_{max}} \frac{d - 2t_{12}}{d^2} V_d \Delta d \right) \tag{1}$$

The computational effort of this equation is very time-consuming, inasmuch as the summation term has to be recalculated again and again for altogether 13 pore-diameter ranges due to the dependence of the layer thickness $t_{12}$ on the pore diameter. In order to decrease the computational effort it could be considered to add the summation term, which takes into account the coverage of the bigger pores with adsorbate, only at smaller pore diameters. However, this way is not suitable. In unfavorable cases, at pore diameters above 150 Å, the deviation between calculations with and without the summation term already amounts to more than 5%.

Yet, the numerous repetitions of the summation can be circumvented, in analogy to Montarnal (3), by transforming the summation as follows:

$$\sum \frac{d - 2t_{12}}{d^2} V_d \Delta d = \sum \frac{V_d \Delta d}{d}$$
$$- \sum \frac{2t_{12} V_d \Delta d}{d^2} = \sum \frac{V_d \Delta d}{d}$$
$$- 2t_{12} \sum \frac{V_d \Delta d}{d^2} \tag{2}$$

This results in a new overall equation

$$V_{12} = R_{12} \left( v_{12} - k_{12} \sum_{d_2+\frac{1}{2}\Delta d}^{d_{max}} \frac{V_d \Delta d}{d} \right.$$
$$\left. + k_{12} 2t_{12} \sum_{d_2+\frac{1}{2}\Delta d}^{d_{max}} \frac{V_d \Delta d}{d^2} \right) \tag{3}$$

In this equation the summation terms of each step of calculation can simply be formed by adding the term for the new diameter range to the corresponding term of the previous step. This, of course, decreases the computational effort considerably. An additional advantage of this transformation is that now a corresponding value for the layer thickness $(t_{12})$ can be taken for each mean diameter, whereas Cranston and Inkley only use average values over wider diameter ranges. We compute these $t_{12}$ values by using the Halsey (5) equation, which was modified by Lippens (4)

$$t = -3.54 \left( \frac{5}{\ln (p/p_0)} \right)^{1/3} \tag{4}$$

This modification agrees better with numerous data collected from the literature by Cranston and Inkley than the original Halsey equation* (Fig. 1).

* A computer program in ALGOL was written to rationalize the handling of larger amounts of experimental data. This program permits the evaluation of an isotherm within a computing time of 0.5 min by means of a Siemens 2002 computer.
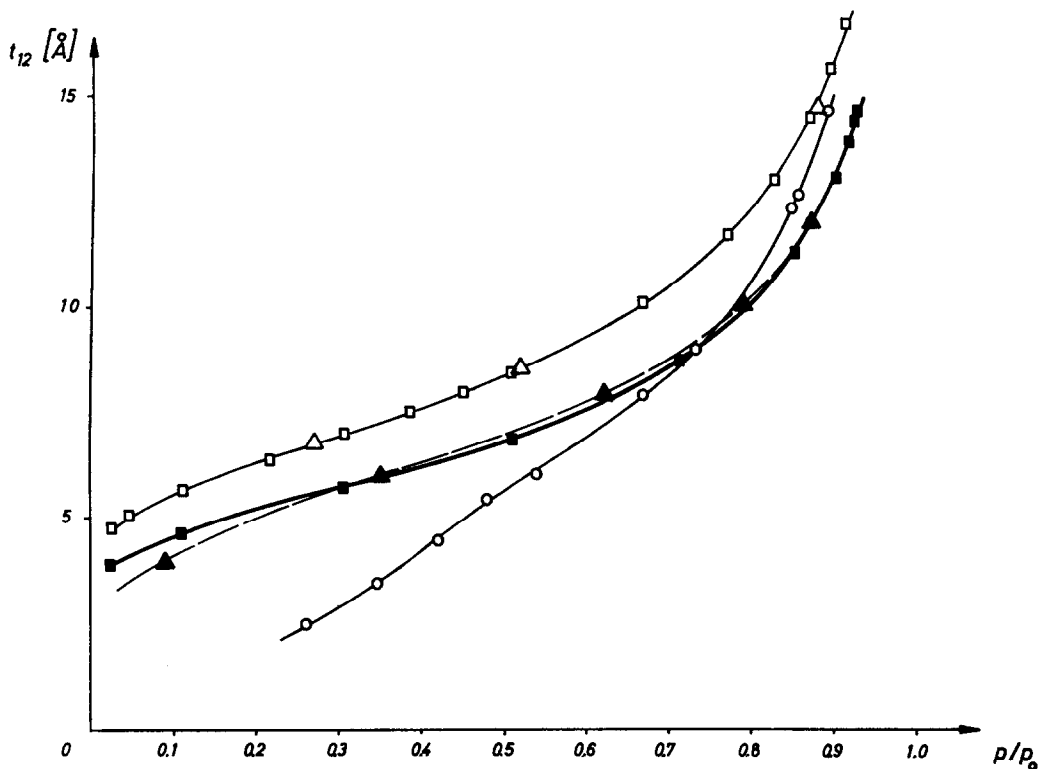
FIG. 1. Thickness of adsorbed layer vs. relative pressure: $\square$, Halsey equation $t_{12} = -4.3$ [5/ln $(p/p_0)]^{1/3}$ (original form) (5); $\blacksquare$, Halsey equation $t_{12} = -3.54$ [5/ln$(p/p_0)]^{1/3}$ (modified form) (4); $\triangle$, curve used by Dollimore and Heal (1); $\blacktriangle$, curve given by Cranston and Inkley (2); $\bigcirc$, curve used by Trambouze et al. (6).

For the determination of pore-volume distribution, based on the cylinder model, three methods are being used most commonly at the present time. In connection with the simplification of Cranston and Inkley's method it is interesting to compare these methods in view of any possible differences and advantages and/or disadvantages, respectively. In their original article, Dollimore and Heal (1) give the equation

$$\Delta V_p = R_n \left( \Delta V_n - \Delta t_n \sum S_p + 2\pi t_n \Delta t_n \sum L_p \right) \quad (5)$$

while Trambouze et al. (6), in a computer program for the modified method of Barret et al. (7) give

$$V(\bar{r}_p)(\Delta r)_p = \left[ \frac{\bar{r}_p}{\bar{r}_k + \frac{1}{2}\Delta t} \right]^2 \left\{ (\Delta V_T) - \Delta t \left[ \sum_{r=r_p}^{\infty} A(r)\Delta r - \bar{t} \sum_{r=r_p}^{\infty} \frac{A(r)\Delta r}{r} \right] \right\} \quad (6)$$

and finally, Cranston and Inkley (2) in the form modified by us, give the equation

$$V_{12} = R_{12} \left( v_{12} - k_{12} \sum \frac{V_d \Delta d}{d} + k_{12} 2 t_{12} \sum \frac{V_d \Delta d}{d^2} \right) \quad (7)$$

All three equations can be written in a single expression of the form

$$V_{12} = R_s \left[ v_{12} - (t_2 - t_1) \sum S_p + t_{12}(t_2 - t_1) \sum \frac{S_p}{r_p} \right] \quad (8)$$

where $V_{12}$ is the volume of the pores with radius between $r_1$ and $r_2$; $v_{12}$ the total volume which is adsorbed or desorbed during one sorption step; $t_{12}$, the layer thickness; $r_p$, the pore radius; and $S_p$, the pore surface area for pores of $r > r_p$. Assuming the respectively chosen layer thickness ($t_{12}$ values) to be the same, the three methods only differ by the prefactor $R_x$. This is given by Dollimore and Heal as

$$R_n = [\bar{r}_p/(\bar{r}_k + \Delta t)]^2 \qquad (9)$$

by Trambouze *et al.* as

$$R = [\bar{r}_p/(\bar{r}_k + \tfrac{1}{2}\Delta t)]^2 \qquad (10)$$

and by Cranston and Inkley as

$$R_{12} = (r_2 - r_1) \bigg/ \int_{r_1}^{r_2} \left[ \frac{(r - t_1)^2}{r^2} \right] dr \qquad (11)$$

Our recalculation of the expression of Dollimore shows that it ought to contain $\tfrac{1}{2}\Delta t$

instead of $\Delta t$. Then it is identical with the expression of Trambouze. The factor given by Cranston and Inkley can be transformed, if $\Delta r$ is small enough, into

$$R_{12} = (r_2 - r_1) \bigg/ \int_{r_1}^{r_2} \left[ \frac{(r - t_1)^2}{r^2} \right] dr$$

$$\approx (r_2 - r_1) \bigg/ \left( \frac{\bar{r} - t_1}{\bar{r}} \right)^2 \int_{r_1}^{r_2} dr$$

$$= \left( \bar{r}_p \bigg/ \left[ \bar{r}_k + \frac{\Delta t}{2} \right] \right)^2 \qquad (12)$$

Hence, it follows that there are no methodical disparities with the exception of the values used by the authors for the layer thickness $t_{12}$. Consequently, the same result should be gained in the evaluation of sorption isotherms regardless of the method used. From this the fundamental importance of the used form of the function $t$ versus $(p/p_0)$ becomes obvious (Fig. 1). Accordingly, for the accuracy of the determination of pore-size distributions an
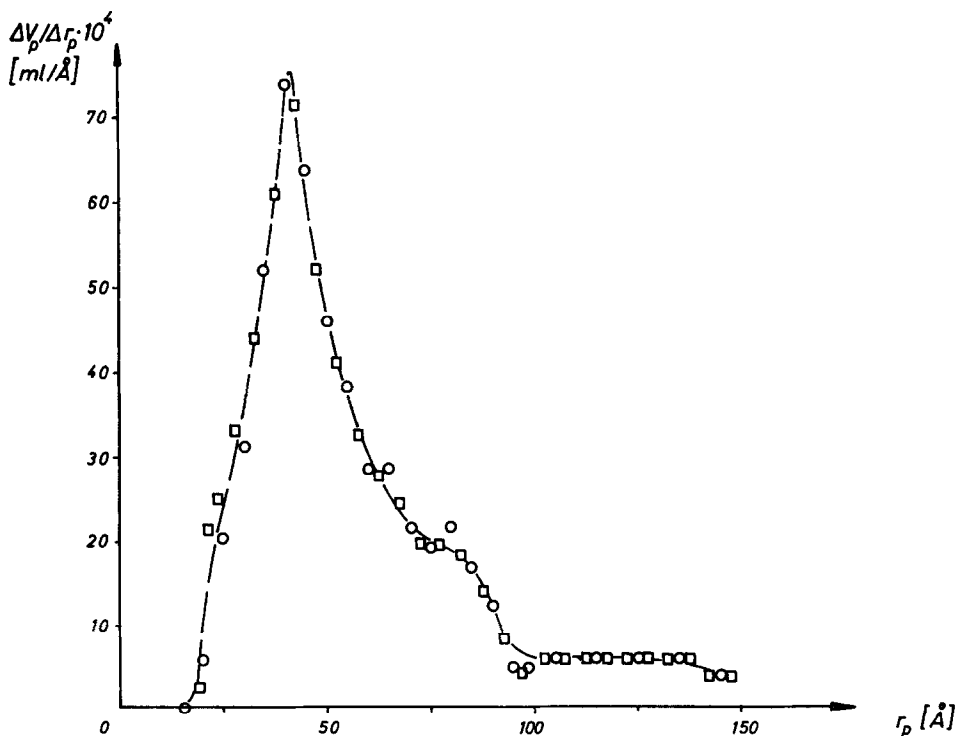


FIG. 2. Pore-volume distribution: ○, distribution calculated by Trambouze *et al.* (*6*); ■, distribution calculated by the modified Cranston and Inkley method for the same data.

important and decisive progress would be made by determination of the absolute value of the layer thicknesses of the adsorbate.

To demonstrate that the different methods really show the same results, computations were made with our modification of Cranston and Inkley's method by using the same sorption data given by the other authors. Figure 2 shows one of the results. The additional calculation of the respective cumulative surface areas and volumes shows good agreement with the corresponding BET values calculated from the isotherms given by the authors. Especially in the case of the Dollimore and Heal data, an improvement relative to the BET value was found, probably on account of the above-mentioned reasons.

REFERENCES

1. DOLLIMORE, D., AND HEAL, G. R., *J. Appl. Chem.* **14**, 109 (1964).
2. CRANSTON, R. W., AND INKLEY, F. A., *Advan. Catalysis* **9**, 143 (1957).
3. MONTARNAL, R., *J. Phys. Radium* **14**, 732–733 (1953).
4. LIPPENS, B. C., M.Sc. Thesis. Technische Hogeschool, Delft, 1961.
5. HALSEY, G., *J. Chem. Phys.* **16**, 931 (1948).
6. CLÉMENT, C., MONTARNAL, R., AND TRAMBOUZE, P., *Rev. Inst. Franc. Petrole Ann. Combustibles Liquides* **17**, 558 (1962).
7. BARRET, E. P., JOYNER, L. G., AND HALENDA, P. P., *J. Am. Chem. Soc.* **73**, 373 (1951).

G. EMIG
H. HOFMANN

*Institut für Technische Chemie*
*Universität Erlangen-Nürnberg, Germany*
    *Received May 9, 1967*

# Author's Note

Vol. 5, No. 1 (1966), in the article entitled, "Determination of Effective Diffusivities of Catalysts by Gas Chromatography," pp. 22–26:

It has been brought to my attention that an error was made in the use of the Weisz-Schwartz formula. I have recalculated the value based on the velocity of nitrogen obtained from the simple kinetic gas relation and obtain a value of $D_p$ of 0.00108 cm²/sec. This is considerably lower than before but not badly out of agreement with experiment. I also calculated the value based on formula (3) and obtain a value of 0.00206 cm²/sec, which is somewhat closer.

AMOS J. LEFFLER
*Villanova University*
*Villanova, Pennsylvania 19085*