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CORRELATION OF ADSORPTION EQUILIBRIA OF CO_2 ON ACTIVATED CARBON

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Abstract — Adsorption isotherms of CO_2 on three types of activated carbon were measured over wide temperature range, from 298°K to 194.5°K. The adsorption equilibria were correlated according to the Dubinin-Radushkevich equation.

The correlations for the carbons in temperature indifferent characteristic curve were yielded by the use of pressure variable density of adsorbed phase in deriving adsorption volume. The pressure variable density, which is the density of saturated liquid CO_2 under given equilibrium adsorption pressure, was determined from reduced density correlation and empirical vapor pressure function of CO_2. Density and vapor pressure of quasi-liquid state CO_2 at below the triple point were evaluated by extrapolation of the correlations.

INTRODUCTION

Adsorption of CO_2 by activated carbon is an interesting technique to separate this gas from other gases. One of the application is the removal of CO_2 from confined room atmosphere. The CO_2 adsorption is also useful method of searching adsoptive properties of activated carbons as has been recommended by Marsh and Wynne-Jones [1]. The adsorption can easily be carried out over wide temperature range from 194.5°K to above the critical temperature of 304.2°K. Equilibrium adsorption of CO_2 on various activated carbons has been measured by numerous authors [2,3,4].

Adsorption equilibria of gases on microporous adsorbents have been usually correlated by means of Polanyi potential theory [5]. The potential theory in principle represents adsorption isotherms at various temperatures in a single characteristic curve. This is very useful way of correlation because adsorptions at many temperatures can be predicted from a single temperature isotherm. The potential theory expresses adsorption in adsorption volume. The adsorption volume is adsorption amount divided by density of adsorbed phase. Proper values of the adsorbed phase density are essential in successful correlation of adsorption equilibria. The correlation by the potential theory should be temperature indifferent characteristic curve.

Adsorption of gases in micropores has been recognized as volume filling and adsorbed phase has generally been assumed as liquid state [6,7]. The knowledge on the state of adsorbed phase is very limited at present. The state of adsorbed phase in micropores, however, whould be quite different from that of ordinary condensed phase. This is because of the influence of adsorption force field which is binding adsobate molecules. With density data of ordinary condensed phase at adsorption temperature, correlations of isotherms into a single characteristic curve have always been unsuccessful. Several correction methods for the adsorbed phase density have been proposed. The validity of the methods is discussed in this paper and a satisfactory correlation method for CO_2 adsorption on activated carbon is described.

THEORETICAL

The adsorption potential ε is the decrease in differential free energy of adsorption,

$$\varepsilon = RT \ln \frac{f_s}{f} \tag{1}$$

where f_s is saturation fugacity of gas at T, and f is fugacity of gas at equilibrium. The potential theory is,

$$\varepsilon = \phi(W). \tag{2}$$

The W is adsorption volume. This equation is characteristic curve of adsorption, which is indifferent of adsorption temperature.

Dubinin and Radushkevich proposed the following adsorption function to correlate adsorption of gases on microporous adsorbents [6,7].

$$\frac{W}{W_o} = \exp[-k(\frac{\varepsilon}{\beta})^2]. \tag{3}$$

In the equation, k is the parameter related to the pore structure of adsorbent, β is the affinity coefficient for different gases, and W_0 is total micropore volume. Equation (3) can be written for a particular adsorption system in linear form as,

$$\log W = \log W_0 - K\varepsilon^2. \qquad (4)$$

Adsorption volume W is derived from adsorption amount by dividing it with appropriate density of adsorbed phase. If adsorbed phase is regarded as ordinary saturated liquid at adsorption temperature T,

$$W = \frac{x}{\rho_T}, \qquad (5)$$

where ρ_T is liquid adsorbate density at T. Usually ρ_T falls very sharply on approaching critical point. Dubinin and coworkers pointed out that the density of adsorbed phase in micropores would differ radically from that of ordinary liquid phase [8]. They posturated constant thermal expansion coefficient of adsorbed phase from normal boiling point to critical point. They proposed a method of determining corrected density ρ^* from the linear interpolation between the density at normal boiling point and criticl density calculated from Van der Waals constant b. In the case of CO_2, which has no normal boiling point, the interpolation should be done between the triple point and the critical point as shown with dashed line in Figure 1. By this method,

$$W = \frac{x}{\rho^*}. \qquad (6)$$

Cook and Basmadjian [9] proposed a similar correction method as Dubinin. In their case, molar volume of adsorbed phase at temperature higher than normal boiling point was expressed by linear extrapolation of logarithmic plot of molar volume versus T. The extrapolation thus starts from normal boiling point.

These methods are empirical in nature. They seem to be lacking in theoretical basis because correction is done only for density values between normal boiling point and critical point. By these methods, isotherms in narrow temperature range might be correlated into a single curve with small deviation. General validity of the methods is doubtful as will be discussed later.

A different approach to the adsorbed phase density was proposed by Lewis et al. [10]. They modified the potential theory as,

$$\frac{\varepsilon}{v_s} = \psi\ (N\ v_s), \qquad (7)$$

where N is adsorption in moles per gram. The v_s is molar volume of saturated liquid adsorbate at equilibrium adsorption pressure p. In this approach adsorption equilibrium is treated as vapor-liquid equilibrium. And the state of adsorbed phase is determined from equlibrium pressure rather than from adsorption temperature. By this approach, adsorption volume is derived by,

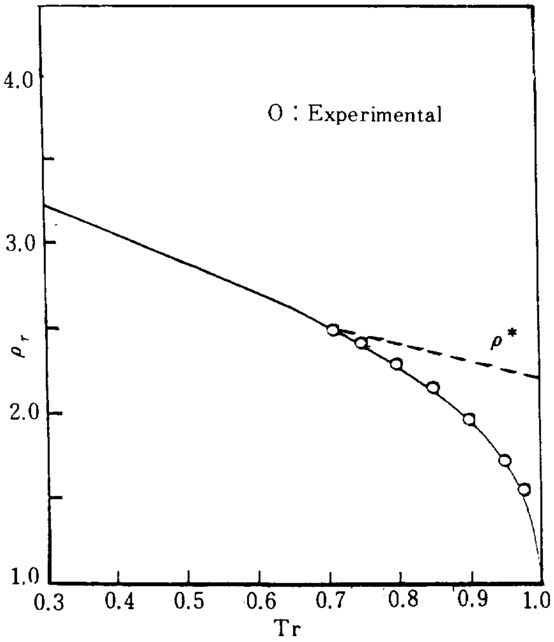

Fig. 1. Reduced density correlation of saturated liquid CO_2.

$$W = \frac{x}{\rho_P} \qquad (8)$$

ρ_p is saturated liquid density of adsorbate under given equilibrium adsorption pressure. ρ_p is pressure variable. The modification of ε with v_s in Equation (7) is similar to the modification of ε with β in Equation (3). The affinity coefficient is very closely proportional to molar volume [11].

The linearity of the DR equation has been extensively studied [12,13,14,15]. It has been concluded that the DR equation is linear for truely microporous adsorbents when their pore volume distributions are Gaussian. However, the DR equation has been widely used for correlations of activated carbon adsorptions. The DR equation presents adsorption in large ε region accurately. Additional parameter is needed for general linear equation [18].

CO_2 is a nonpolar compound which has the critical pressure of 72.85atm at 304.2°K. The criticl density and criticl compressibility factor are 0.467g/cc and 0.275, respectively. Below the triple point of 216.4°K, CO_2 exists as solid and normal sublimation point is 194.5°K. Vapor pressure data of CO_2 are available in literatures. A reliable vapor pressure function for CO_2 has been developed by Kennedy and Thodos as follows [17],

$$\log P_r = 4.2397 - \frac{4.4229}{T_r} - 5.3795 \log T_r + 0.1832 \frac{P_r}{T_r^2} \qquad (9)$$

This equation is capable of evaluating accurate vapor pressure of CO_2 from the triple point to the critical point. Adsorbed CO_2 in micropores has been assumed as liquid state even at below the triple point [18]. Vapor pressure of the quasi-liquid CO_2 can be evaluated from the vapor pressure function. The vapor pressure of 1.76atm was calculated at 194.5°K. This value is smaller than 1.86atm which has been suggested by Lamond and Marsh [18]. Their value was evaluated from the vapor pressure data of Bridgeman [19] by extrapolation. The new value would be more accurate and will be adopted. Fugacity of gas was derived by thermodynamic fugacity coefficient data given in the literature [20]. Saturation vapor pressure and fugacity data at the adsorption temperatures are given in Table 1. When adsorption pressure of CO_2 is limited up to latm, fugacity can be replaced by pressure.

$$\varepsilon = RT \ln \frac{f_s}{p} \qquad (10)$$

Density of CO_2 has been measured by many investigators beginning with Amagat's work [21]. Kennedy and Thodos [17] collected experimental density data and developed a comprehensive reduced density correlation. Density data of saturated liquid CO_2 from the triple point to the critical point are included in the correlation. At below the triple point, density of CO_2 adsorbed as quasi-liquid state have to be evaluated from thermodynamic correlation. The thermodynamic reduced density correlation has also been presented in the literature [20] as tabulated data. Figure 1 is the reduced density correlation constructed from the data for critical compressibility of 0.275(CO_2). Experimental data are included to show that the correlation is sound. Density data of saturated liquid CO_2 at adsorption temperatures are given in Table 1.

The pressure variable density ρ_p can be determined from the reduced density correlation of Figure 1. along with the vapor pressure function of CO_2. For example, for the equilibrium pressure of $100mmH_g$ ($P_r = 1.806 \times 10^{-3}$), T_r is found as 0.52 from Equation (9). For this T_r, ρ_r is read as 2.855 from Figure 1. and ρ_p is 1.335. ρ_p values evaluated by this method are plotted in Figure 2., for the pressure range of $1mmH_g$ to $1000mmH_g$. ρ_p becomes identical to ρ_T when $f = f_s$ at T.

Table 1. Properties of CO_2.

T, °k	P_s, mmHg	f_s, mmHg	ρ_T, g/cc.
194.5	1339*	1316	1.246*
253.0	14781	12653	1.030
273.0	26142	20522	0.924
293.0	42959	30673	0.766

* liquid

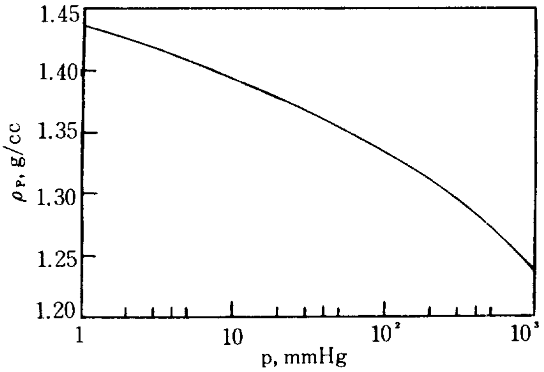

Fig. 2. Equilibrium pressure of CO_2 vs. ρ_P.

EXPERIMENTAL

The adsorption equilibria were measured gravimetically with Cahn RG Electrobalance. The adsorption apparatus was consisted of vacuum system, furnace and temperature programmer, manometers, gas storage and supply lines, recorder, and the balance. CO_2 of high purity was passed through a bed of molecular sieves before introduction to the apparatus. The balance detects 10^{-5}g of weight change. Approximately 130mg of activated carbon sample was used. The sample was degassed at 320°C and 10^{-4}mmHg to constant weight before adsorption. Pressure was measured with three types of manometers, macleod, silicone oil, and mercury, depending on the magnitude of pressure. Equilibria were attained while desorption even though no appreciable adsorption hysteresis was detected. The time to approach to equilibria depended on the temperature and the pressure, ranging from several minutes to several hours.

The activated carbons used were BPL type and CAL type, from the Calgon co., and an activated carbon from Yulim co. of Korea. They are granular carbons. Adsorption temperatures were 194.5°K, 253°K, 273°K, and 293°K with the Calgon carbons and 194.5°K, 273°K, and 293°K with the Yulim carbon. 194.5°K was maintained in dry ice and aceton bath. Constant temperature circulator (Haake FK-2, Refrigerating type) was used for maintaining other temperatures.

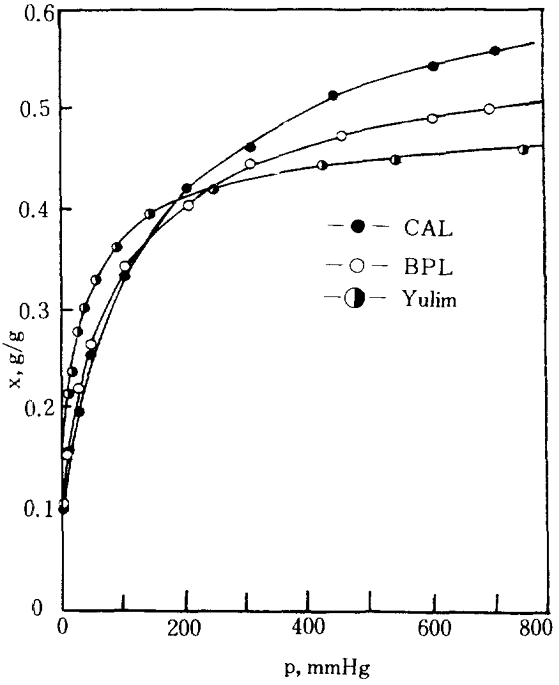

Fig. 3. Adsorption isotherms of CO_2 on activated carbons at 194.5°K.

RESULTS AND DISCUSSION

The adsorption isotherms of CO_2 on the three types of activated carbon at 194.5°K are presented in Figure 3. There are appreciable differences in adsorptive character among the carbons. The CAL type carbon, which was prepared for liquid phase adsorption by the manufacturer, has large adsorption in high pressure region. This indicates wide pore size distribution. Pore volume of the CAL type carbon was reported as 0.94cc/g by the manufacturer. The Yulim carbon has very enhanced adsorption in low pressure region and limited adsorption in high pressure region. This indicates that the included pores are mostly micropores. Pore volume of this carbon was measured as 0.66cc/g by CCl_4 penetration. The BPL type carbon, which was prepared for vapor phase adsorption by the manufacturer, shows intermediate adsorption character between the other two carbons. Pore volume of the BPL carbon was reported as 0.7cc/g by the manufacturer.

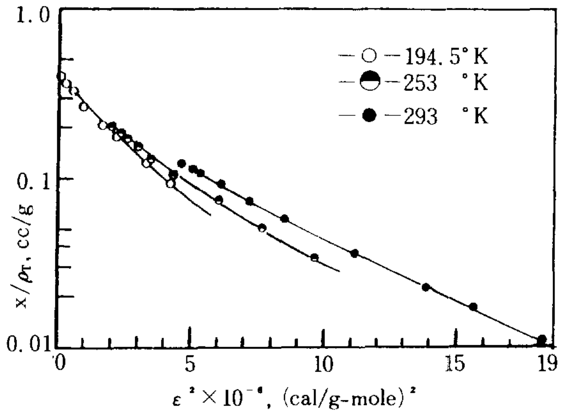

Fig. 4. Correlation of CO_2 adsorption on BPL activated carbon, where adsorption volume was derived by ρ_T.

Correlations of measured adsorption equilibria were done by the DR equation. Firstly, correlation were tried with adsorption volume derived by Equation (5). The result of the correlation for CO_2-BPL activated carbon system is shown in Figure 4. 273°K isotherm was excluded in the Figure to avoid crowd. As was expected, it failed in resulting a single characteristic curve. The separate curves for respective temperatures are also different in their shape or slope. Similar results were obtained when measured isotherms on the other types of carbon were correlated in the same way. The same feature of separate and not paralleled curves for different temperatures were shown in the literatures [22,23], where gases other than CO_2 were adsorbed on activated carbons. It is clear that the DR equation do not yield temperature indifferent characteristic curve when ρ_T is used in deriving adsorption volume.

Figure 4. suggests a significant conclusion. Since the separate curves for the isotherm temperatures are not parallel each other, a single correlation curve will not be yielded by simply shifting the curves by the correction of density for the temperatures. The validity of the density correction methods of either by Dubinin or by Cook is not justified. Any fixed density values at adsorption temperatures would not yield a single curve.

Density values variable of adsorption potential or adsorption pressure is alternate choice for the correlation. Adsorption equilibria measured for each types of activated carbon were correlated by the DR equation with adsorption volume derived from Equation (8). The results are shown in Figures 5, 6, and 7. The equilibria are successfully correlated into temperature indifferent characteristic curves for every systems. For the wide temperature range involved, the correlations are quite satisfactory. The DR curve is by it's nature less sensitive to the variations of W and ε in small ε region. The curve becomes sensitive to the variations of W and ε as ε increases. Adsorption is small for large ε. The DR equation presents therefore adsorption equilibria in small adsorption region accurately. In this region, however, experimental data are usually subject to large

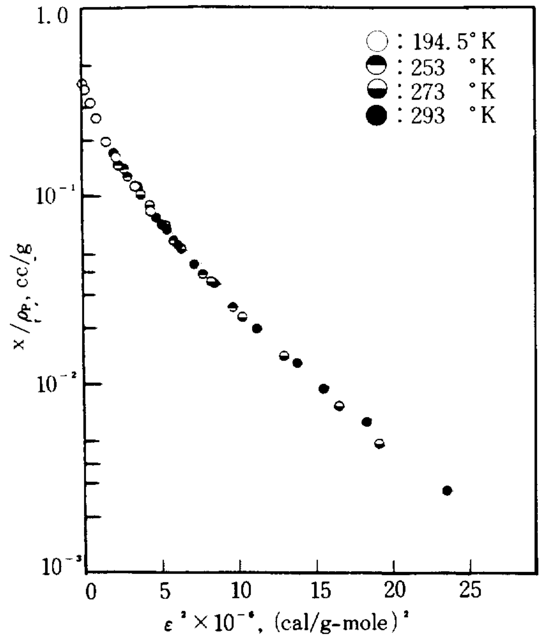

Fig. 5. Adsorption of CO_2 on BPL activated carbon.

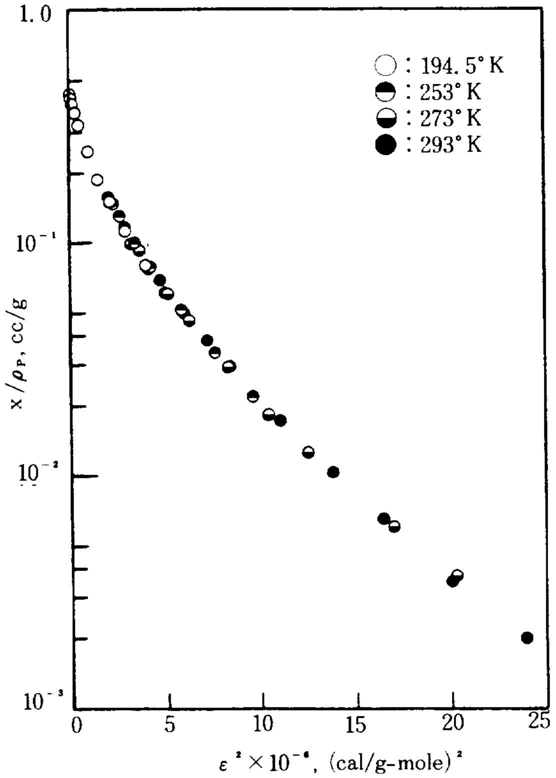

Fig. 6. Adsorption of CO_2 on CAL activated carbon.

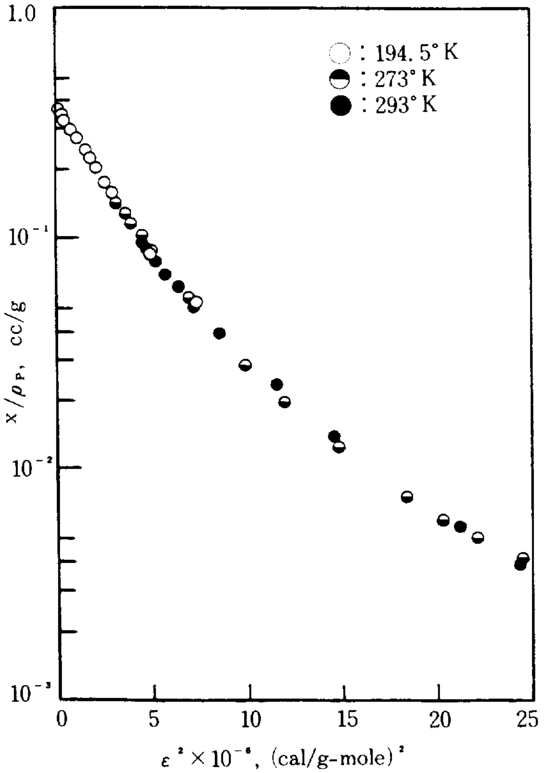

Fig. 7. Adsorption of CO_2 on Yulim activated carbon.

error. Some deviations of data points shown in the large ε region of the Figures are presumably the results of experimental error. The pressure variable density ρ_p increases as adsorption pressure decreases (ε is increasing), as was shown in Figure 2. By this effect, correlation curves were straightened more or less.

The modification of adsorption potential by v_s in Equation (7) did not yield satisfactory results. The affinity coefficient is a shifting factor for different gases. It is doubtful if correction of adsorption potential for adsorption pressure should be neccessary.

CONCLUSION

Adsorption equilibria of CO_2 on activated carbon are correlated into temperature indifferent characteristic curve by the use of density of saturated liquid CO_2 under equilibrium adsorption pressure. The density is pressure variable and is derived from thermodynamic reduced density correlation and vapor pressure function of CO_2.

NOMENCLATURE

f_s : saturation fugacity, mmH_g

f : fugacity of gas, mmH$_g$
K, k : constants
p : equlibrium adsorption pressure, mmH$_g$
P_r : reduced pressure
P_s : saturation pressure, mmH$_g$
T : temperature, °K
T_r : reduced temperature
W : adsorption volume, cc/g
W_0 : adsorption capacity, cc/g
x : adsorption, g/g

Greek Leters
ε : adsorption potential, cal/mole
ρ_T : liquid density at T, g/cc
ρ_P : saturated liquid density under adsorption pressure, p, g/cc
ρ^* : Dubinin's corrected density, g/cc
ρ_r : reduced density

REFERENCES

1. Marsh, H. and Wynne-Jones, W.F.K.: *Carbon*, **1**, 269 (1964).
2. Lamond, T.C. and Marsh, H.: *Carbon*, **1**, 281 (1964).
3. Walker, Jr., P.L. and Shelef, M.: *Carbon*, **5**, 7 (1967).
4. Mahajan, O.P., et al.: *Indian J. Chem.*, **15**A, 35 (1976).
5. Polanyi, M.: *Verhandl. deut. physik. Ges.*, **16**, 1012 (1914).
6. Dubinin, M.M.: *J. Coll. Int. Sci.*, **23**, 487 (1967).
7. Bering, B.P., Dubinin, M.M., and Serpinsky, V.V.: *J. Coll. Int. Sci.*, **21**, 378 (1966).
8. Dubinin, M.M.: Chem Review, **2**, 235 (1960).
9. Cook, W.H. and Basmadjian, D.: *Can. J. Chem. Eng.*, **42**, 146 (1964).
10. Lewis, W.F., et al.: *I & EC*, **42**, 1362 (1950).
11. Young, D.M. and Crowell, A.D.: "Physical Adsorption of Gases" Butterworths, Washington, D.C., 142 (1962).
12. Marsh, H. and Rand, B.: *J. Coll. Int. Sci.*, **33**, 101 (1970).
13. Rand, B.: *J. Coll. Int. Sci.*, **56**, 337 (1976).
14. Biba, Y. and Spitzer, Z.: *J. Coll. Int. Sci.*, **69**, 9 (1979).
15. Huber, U., Stoeckli, F. and Houriet, J.: *J. Coll. Int. Sci.*, **67**, 195 (1978).
16. Dubinin, M.M. and Astakhov, V.A.: *Adv. Chem. Ser., ACS*, No. 102, 69 (1971).
17. Kennedy, J.T. and Thodos, G.: *Chem. Eng. Data*, **5**, 293 (1960).
18. Lamond, T.G. and Marsh, H.: *Carbon*, **1**, 293 (1964).
19. Bridgeman, O.C.: *J. Am. Chem. Soc.*, **49**, 1174 (1927).
20. Hougen, O.A., Watson, K.M., and Raratz, R.A.: "Chemical Process Principle, Part II", Jhon Wiley & Sons, New York, NY, 577 (1947).
21. Amagat, E.H.: *Compt. rend.*, **113**, 446 (1891).
22. Stoeckli, H.F. and Houriet, J.: *Carbon*, **14**, 253 (1976).
23. Freeman, E.M., et al.: *Carbon*, **8**, 7 (1970).