The Determination of the Heat of Adsorption by the Gas Chromatographic Method. I*

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The determination of the heat of adsorption by the gas chromatographic method has been carried out by Greene and Pust.1) In our laboratories, the heats of adsorption of some low-boiling-point hydrocarbons and inorganic gases on active charcoal, alumina, silica gel and synthetic zeolite have also been estimated by the gas chromatographic method by using several carrier gases, such as helium, hydrogen and nitrogen.2-4)

The purpose of this series is to establish the method of the gas chromatographic determination of the heat of adsorption and to compare the results with those obtained by usual static methods.

The heat of adsorption of an eluted gas on an adsorbent is calculated by Eq. 15,6):

$$\frac{R}{R'}=\frac{1}{K_a+1}=\frac{L\cdot A}{F\cdot t_m} \tag{1}$$

where R, is the linear velocity of the sample gas; R', the linear velocity of the carrier gas; K_a, the equilibrium constant for adsorption; L, the packed length of adsorption; t_m, the retention time of the sample gas; A, the interstitial area of the column, and F, the flow rate of the carrier gas.

Then, the equilibrium constant of adsorption (K_a) is expressed by Eq. 2, since $\Delta G=\boldsymbol{R}T_c\ln K_a$:

$$K_a=e^{-\Delta G/\boldsymbol{R}T_c}=e^{-\Delta H_a/\boldsymbol{R}T_c}\cdot e^{\Delta S/\boldsymbol{R}} \tag{2}$$

where T_c, is the column temperature (the gas-solid equilibrium temperature); H_a, the molar differential heat of adsorption; ΔG, the free energy change of adsorption, and ΔS, the entropy change of adsorption.

As ΔS is assumed to be constant when the temperature range is small and when the adsorbent and the adsorbate are the same substance, Eq. 2 is rewritten as Eq. 3:

$$K_a=Be^{-\Delta H_a/RT_c} \tag{3}$$

where B indicates a constant.

Moreover, the apparent retention time (t_m') is expressed by Eq. 4.7)

$$t_m'=t_m-\frac{L\cdot A}{F} \tag{4}$$

Then we have Eq. 5 from the relations of 1, 3 and 4.

$$Ft_m'=LABe^{-\Delta H_a/\boldsymbol{R}T_c} \tag{5}$$

When log Ft'_m is plotted against T_c, the heats of adsorption (ΔH_a) can be estimated from the slope of the (log Ft'_m, $1/T_c$) line according to Eq. 5. In practice, however, a slight pressure drop occurs across the column and the velocity of the sample and carrier gases might change slightly through the column. Therefore, the retention volume (V_m) is usually corrected in such a way that the pressure drop comes to zero, and the flow rate of the

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1) S. A. Greene and H. Pust, *J. Phys. Chem.*, **62**, 55 (1958).

2) Y. Kuge, Y. Yoshikawa and K. Yamasaki, *Science Reports* (*College of General Education, Osaka University*), **12**, 23 (1963).

3) K. Arita, Y. Kuge, Y. Yoshikawa and K. Yamasaki, ibid., **12**, 131 (1963).

4) K. Arita, Y. Kuge, Y. Yoshikawa and K. Yamasaki, ibid., **13**, 15 (1964).

5) A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 1358 (1941).

6) Y. Amenomiya, "Gas Chromatography," Kyoritsu Shuppan, Tokyo (1961), p. 124.

7) "Kiki Gasu Bunsekiho," Kyoritsu Shuppan, Tokyo (1961), p. 182.

carrier gas measured at room temperature is also converted into that at 0°C.

The corrected retention volume (V_o) is expressed by Eq. 6.[8,9]

$$V_o = Ft'_m \cdot \frac{273}{T} \cdot \frac{3}{2} \cdot \frac{(P_i/P_o)^2-1}{(P_i/P_o)^3-1} \qquad (6)$$

where P_i, is the column inlet pressure; P_o, the column outlet pressure, and T_m, the room temperature.

Practically, however, V_m is observed as a function of the column temperature only:

$$V_m = Ft'_m \cdot \frac{273}{T_m} \qquad (7)$$

Therefore, we have Eq. 8 by putting Eq. 5 into Eq. 7:

$$V_m = Ce^{-\Delta H_a/RT_c} \qquad (8)$$

where C is a constant.

Therefore, the heat of adsorption may be estimated by plotting V_m, in place of V_o, against T_c according to Eq. 8.

Experimental

A Yanagimoto gas chromatograph, GCG-2, was employed.

The column is made of a stainless steel U-shaped tube 5 mm. in inner diameter. The length of the column used is 1 m. in the cases of activated charcoal, molecular sieve 5A and a molecular sieve 13X, and 2 m. in the cases of alumina and silica gel. The adsorbents were supplied mostly by Nishio Industry Co., Ltd., and the size of their particles ranged from 40 to 60 mesh, while alumina was supplied by the Wako Chemical Co., Ltd., in sizes from 28 to 48 mesh.

All the sample gases were synthesized except methane, ethane, acetylene and isobutane, and all the gases used were purified.

After the column had been filled with an adsorbent, the adsorbent was activated by heating it up to 200°C and by sweeping with carrier gas with a flow rate of about 50 cc. per minute, the flow rates of the gases being measured by a soap-film flow meter. To avoid error in the determination of the retention time, the experiments were carried out under conditions which would give a symmetrical shape for any peak.

Results

In the case of ethane, the corrected retention volume (V_m) was estimated for five kinds of adsorbents by using nitrogen as the carrier gas. The logarithmic plots of V_m against $1/T_c$ are found to be quite linear, as Fig. 1 shows.

In the adsorption of other sample gases on active charcoal, hydrogen was employed as the carrier gas. In this case, no hydrogenation of

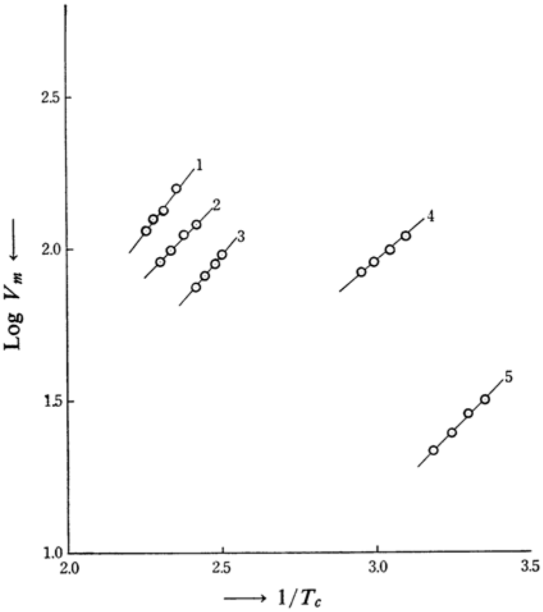

Fig. 1. The retention volume of ethane on five adsorbents. (N_2 carrier gas)
1 Charcoal 2 Molecular sieve 5A
3 Molecular sieve 13X 4 Silica gel
5 Alumina

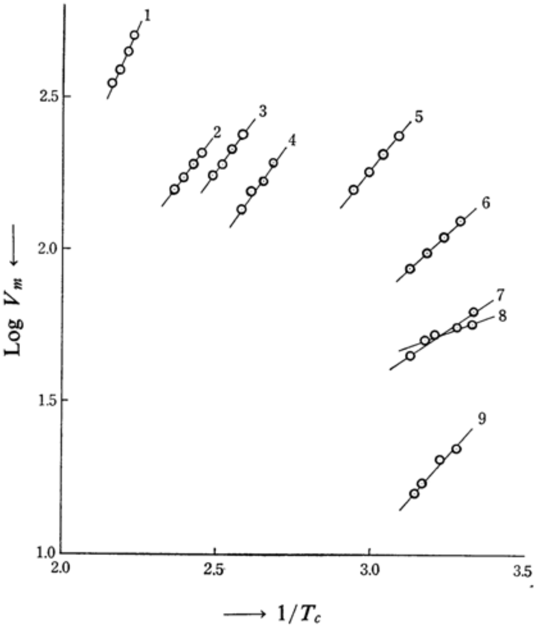

Fig. 2. The retention volume of sample gases on charcoal as a function of temperature. (H_2 carrier gas)
1 C_3H_6, 2 C_2H_6, 3 C_2H_4, 4 C_2H_2,
5 CO_2, 6 CH_4, 7 N_2, 8 Ar, O_2, 9 CO

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[8] A. B. Littlewood, "Gas Chromatography," Academic Press., New York (1962), p. 31.

[9] H. Purnell "Gas Chromatography," John Wiley & Sons, New York (1962), p. 67.

TABLE I. HEATS OF ADSORPTION ON FIVE ADSORBENTS (kcal./mol.)

Adsorbent	Molecular sieve 5A			Molecular sieve 13X			Silica gel			Charcoal			Alumina		
Carrier gas	He	H_2	N_2	He	H_2	N_2	He	H_2	N_2	He	H_2	N_2	He	H_2	N_2
Sample															
Ar	(25—37) 2.5	(26—46) 2.4	(20—40) 2.7	(7.5—17.5) 2.5	(26—46) 2.3	(16—40) 2.0				(19—39) 2.5	(26—46) 2.2	(15—35) 2.5			
O_2	(18—37.5) 2.7	(26—46) 2.6	(20—40) 2.4	(7—17) 2.7	(26—46) 2.4	(16—46) 2.3				(19—39.5) 2.5	(26—46) 2.2	(15—35) 2.4			
N_2	(18—36) 4.2	(26—46) 3.7		(7—17) 4.2	(26—46) 2.8					(19—39.5) 2.5	(26—46) 2.6				
CO	(33—61) 3.4	(26—46) 5.7	(65—85) 4.1	(12.8—41) 4.0	(26—46) 3.8	(17—40) 3.8	(21—41) 4.7	(26—50) 4.4	(20—40) 2.4	(35—63.5) 3.0	(26—46) 3.8	(18—35) 2.7			
CO_2							(65—106) 4.7	(26.5—61) 7.1	(50—70) 5.4	(143—174.5) 4.4	(46—66) 5.8	(91—110) 4.6			
CH_4	(16—49) 3.6	(35—55) 3.7	(41—60) 3.6	(15—99.5) 3.7	(26—46) 3.4	(16—40) 3.4	(34—80) 3.7	(21—41) 3.5	(21—41) 2.8	(88.5—173) 3.1	(26—46) 4.5	(26—45) 4.0	(20—70.5) 1.7	(26—46) 2.7	(30—50) 1.7
C_2H_6	(125—151) 5.2	(130—150) 6.4	(135—161) 6.0	(43—100) 5.9	(71—91) 5.1	(110—140) 5.2	(47—82) 4.7	(22—101) 5.4	(50—70) 3.9	(173.5—210) 6.2	(130—150) 6.3	(150—170) 5.3	(19—69) 3.9	(26—46) 4.5	(21—40) 5.3
C_3H_8							(82.5—116) 6.6	(26—101) 7.1	(100—120) 6.3				(20—68.5) 6.3	(51—71) 6.5	(60—80) 7.1
i-C_4H_{10}							(116—150) 6.4	(100—120) 7.2	(126—145) 6.6				(61.5—85) 6.9	(70—90) 8.3	(90—110) 7.0
C_4H_{10}							(98—133) 7.6	(100—125) 8.7	(120—140) 8.3				(61.5—85) 7.4	(56—76) 7.8	(60—80) 7.6
C_2H_4							(72—99) 6.1	(27.5—61) 6.8	(70—90) 5.7	(108—173) 6.4	(110—130) 6.1	(135—154) 5.0	(19—54) 5.2	(26—46) 3.7	(30—50) 4.3
C_3H_6							(102—132) 7.8	(100—120) 8.9	(130—150) 7.7	(170—190) 8.8	(170—190) 8.5		(45.5—66.5) 7.6	(40—66) 8.7	(60—80) 6.6
C_2H_2										(108—173.5) 5.4	(100—120) 6.7	(110—130) 5.8			

Figures in parentheses show the temperature range covered experimentally.

TABLE II. ORDERS OF PEAK APPEARANCE AND ΔG VALUES OF SAMPLE GASES
ΔG in cal. per deg., per mol., ΔS in cal. per deg., per mol. at 298.16°K

Charcoal

Substance

He carrier gas	$Ar(O_2)$	→	N_2	→	CO	→	CH_4	→	CO_2	→	C_2H_2	→	C_2H_4	→	C_2H_6	→	C_3H_6		
ΔG		38		526		402		531		747		539		97		1283			
ΔS		0		0		−1		2		1		1		−1		4			
H_2 carrier gas	CO	→	O_2	→	N_2	→	Ar	→	CH_4	→	CO_2	→	C_2H_2	→	C_2H_4	→	C_2H_6	→	C_3H_6
ΔG		567		56		0		504		554		774		92		267		1693	
ΔS		4		1		1		6		3		1		−2		0		2	
N_2 carrier gas	O_2	→	Ar	→	CO	→	CH_4	→	CO_2	→	C_2H_4	→	C_2H_2	→	C_2H_6				
ΔG		0		158		522		469		702		49		256					
ΔS		1		0		3		1		−2		3		−3					

Silica gel

He carrier gas	CO	→	CH_4	→	C_2H_6	→	CO_2	→	C_2H_4	→	C_3H_8	→	$i\text{-}C_4H_{10}$	→	C_3H_6	→	C_4H_{10}
ΔG		571		891		349		83		517		416		266		22	
ΔS		−5		1		−1		5		0		−2		4		−1	
H_2 carrier gas	CO	→	CH_4	→	C_2H_6	→	CO_2	→	C_2H_4	→	C_3H_8	→	$i\text{-}C_4H_{10}$	→	C_3H_6	→	C_4H_{10}
ΔG		797		21		1182		57		823		288		219		210	
ΔS		−6		11		−9		6		−3		4		0		−6	
N_2 carrier gas	CO	→	CH_4	→	C_2H_6	→	CO_2	→	C_2H_4	→	C_3H_8	→	$i\text{-}C_4H_{10}$	→	C_3H_6	→	C_4H_{10}
ΔG		183		837		484		91		282		528		319		173	
ΔS		1		1		4		6		1		−1		3		1.5	

Alumina

He carrier gas	CH_4	→	C_2H_6	→	C_2H_4	→	C_3H_8	→	C_3H_6	→	$i\text{-}C_4H_{10}$	→	C_4H_{10}
ΔG		556		112		723		109		321		184	
ΔS		5		4		1		4		−3		1	
H_2 carrier gas	CH_4	→	C_2H_6	→	C_3H_8	→	C_2H_4	→	C_4H_{10}	→	C_3H_6	→	$i\text{-}C_4H_{10}$
ΔG		1292		721		160		866		136		128	
ΔS		2		5		9		11		2		−6	
N_2 carrier gas	CH_4	→	C_2H_6	→	C_2H_4	→	C_3H_8	→	C_3H_6	→	$i\text{-}C_4H_{10}$	→	C_4H_{10}
ΔG		170		450		633		326		273		110	
ΔS		11		−5		7		−3		5		3	

unsaturated hydrocarbons was recognized over the temperature range covered experimentally.

The correlation of V_m with $1/T_c$ is shown in Fig. 2.

On the basis of these data, the differential heats of adsorption on sample gases were calculated. The results are listed in Table I.

The values of the heats of adsorption obtained are in almost the same sequence as those found for the van der Waals constant (a) of the sample gases.

The difference between the values obtained when helium, hydrogen and nitrogen were used as the carrier gases was found to be rather small. The reason for this will be discussed after the experiments using argon as the carrier gas have been carried out.

Next the relation between the order of peak appearance and the free energy change was investigated.

The relation between the retention time (t'_m) and the free energy change (ΔG) has been obtained by Cremer[10] as follows:

$$\Delta G = G_1 - G_2 = \boldsymbol{R}\boldsymbol{T}\ \ln t'_m(1)/t'_m(2) \tag{9}$$

The numbers in parentheses ((1),(2)) show the kind of adsorbate.

Since the apparent retention volume (V_m) can be written as $V_m = Ft'_m$, ΔG is expressed as Eq. 10:

$$\Delta G = \boldsymbol{R}\boldsymbol{T}\ \ln \frac{V_m(1)}{V_m(2)} \tag{10}$$

The free energy change of the adsorption of several sample gases on the same adsorbent was calculated according to Eq. 10. The results obtained are listed in Table II, where the values are converted into those at 25°C. As is shown in Table II, the smaller the value of

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[10] E. Cremer, *Z. anal. Chem.*, **170**, 219 (1959).

the free energy change of adsorption ($-\Delta G$), the greater the velocity of the adsorption of sample gases.

The discussion of the results will appear in the next report.

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