METHANE FORMATION AND RETENTION IN COAL

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OBJECTIVE

The methane content of coal seams in Utah and Colorado are measured in situ as well as in the laboratory and correlated with the geological and geochemical history of the seams and surrounding strata. Chemical and physical properties are measured in the laboratory for coals that contain methane and coals of similar rank which do not contain methane. Methane yields on pyrolysis are used to measure the propensity of coals to form additional methane. Methane formation and retention will be interpreted in terms of the physical and chemical properties of the coal and the chemical and geological history of the coal seam.

PROJECT STATUS

A gas chromatographic technique has been used to determine adsorption characteristics of various gases on coals. This report consists of three sections, the derivation of the theory used to calculate adsorption from gas chromatographic elution times, the results of adsorption studies on Castlegate Sub 3 coal, and the results of high pressure studies.

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THE CONSERVATION EQUATION OF A GAS ADSORPTION COLUMN

List of the symbols:

a_A :	adsorption quantity of species A on a unit mass of coal, mol/g
C_A :	concentration of adsorbed species A in the mobile phase, mol/cm ³
F_c :	volumetric flow rate across the column, cm ³ /sec.
$K_{c,A}$:	adsorption coefficient of concentration of species A, cm ³ /g
$K_{p,A}$:	adsorption coefficient of pressure of species A, mol/(Pa)(g)
L :	column length, cm
m :	total mass of coal in the column, g/cm
m_L :	mass of coal in a unit length of the column, g/cm
t_M :	retention time of unsorbed gas (gas hold-up time), sec.
t_R :	retention time, sec.
u_A :	linear migration velocity of species A at concentration C_A moving along the column in the mobile phase, cm/sec.
V :	total volume of the mobile phase or total free volume in the column, cm ³ /cm
V_{column} :	volume of the column, cm ³
V_{GC} :	dead volume in gas chromatography, cm ³
V_L :	volume of the mobile phase or free volume in a unit length of the column, cm ³ /cm
V_M :	retention volume of unsorbed gas (gas holdup volume), cm ³
V_N :	net unit retention volume, cm ³ /g-adsorbent
V_R :	retention volume, cm ³
x :	distance from the inlet to any point of the column, cm
ϵ :	packed-column porosity, cm ³ /cm ³
ρ_{coal} :	density of coal

Basic relationships:

$$\epsilon = \frac{V}{V_{column}} ,$$

$$V = L \times V_L ,$$

$$m = L \times m_L ,$$

$$\rho_{coal} = \frac{m}{(1-\epsilon) V_{column}} ,$$

$$u_A = \left(\frac{\partial x}{\partial t} \right)_{C_A} ,$$

$$V_M = V_{GC} + V ,$$

$$K_{p,A} = \frac{K_{c,A}}{RT} .$$

Derivation:

$$C_A = f(t, x). \quad (1)$$

If the accumulation of species A in the column increment dx is dn_A (Figure 1),

$$\begin{aligned} dn_A &= \text{inlet}_A - \text{outlet}_A \\ &= -F_c dC_A, \end{aligned} \quad (2)$$

i.e.

$$(dn_A)_{x,t} = -F_c \left(\frac{\partial C_A}{\partial x} \right)_t dx. \quad (3)$$

This accumulated quantity of species A in the column increment dx is distributed between the mobile phase and the stationary phase. Thus, the quantity of adsorbate A in a unit length of column is:

$$V_L C_A + m_L a_A.$$

According to mass conservation law,

$$\begin{aligned} -F_c \left(\frac{\partial C_A}{\partial x} \right)_t dx &= \left[\frac{\partial}{\partial t} (V_L C_A + m_L a_A) \right]_x dx, \\ -F_c \left(\frac{\partial C_A}{\partial x} \right)_t &= V_L \left(\frac{\partial C_A}{\partial t} \right)_x + m_L \left(\frac{\partial a_A}{\partial t} \right)_x, \end{aligned}$$

or

$$F_c \left(\frac{\partial C_A}{\partial x} \right)_t + V_L \left(\frac{\partial C_A}{\partial t} \right)_x + m_L \left(\frac{\partial a_A}{\partial t} \right)_x = 0. \quad (4)$$

Since

$$\left(\frac{\partial a_A}{\partial t} \right)_x = \left(\frac{\partial a_A}{\partial C_A} \right)_x \left(\frac{\partial C_A}{\partial t} \right)_x, \quad (5)$$

$$\left(\frac{\partial a_A}{\partial C_A} \right)_x = \frac{da_A^*}{dC_A}, \quad (6)$$

* The derivative $(\partial a_A / \partial C_A)_x$ represents the dependence of the adsorbed quantity of species A on its concentration in the mobile phase, C_A , at a given temperature; it thus represents the adsorption isotherm.

$$dC_A = \left(\frac{\partial C_A}{\partial t}\right)_x dt + \left(\frac{\partial C_A}{\partial x}\right)_t dx, \quad (7)$$

and

$$\left(\frac{\partial C_A}{\partial t}\right)_x = -\left(\frac{\partial C_A}{\partial x}\right)_t \left(\frac{\partial x}{\partial t}\right)_{C_A}, \quad (8)$$

substituting Equations 5, 6, and 8 in Equation 4 gives:

$$\begin{aligned} F_c \left(\frac{\partial C_A}{\partial x}\right)_t + (V_L + m_L \frac{da_A}{dC_A}) \left(\frac{\partial C_A}{\partial t}\right)_x &= 0, \\ F_c \left(\frac{\partial C_A}{\partial x}\right)_t - (V_L + m_L \frac{da_A}{dC_A}) \left(\frac{\partial C_A}{\partial x}\right)_t \left(\frac{\partial x}{\partial t}\right)_{C_A} &= 0, \\ F_c - (V_L + m_L \frac{da_A}{dC_A}) \left(\frac{\partial x}{\partial t}\right)_{C_A} &= 0, \end{aligned} \quad (9)$$

or

$$F_c - (V_L + m_L \frac{da_A}{dC_A}) u_A = 0. \quad (10)$$

Solution for the linear isotherm adsorption:

When an infinite dilution* of gas sample is used, for all proposed isotherm types (Figure 2), the adsorption isotherms are linear, i.e.

$$\lim_{C_A \rightarrow 0} \left[\frac{da_A}{dC_A} \right] = K_{C,A}. \quad (11)$$

Based on conservation Equation 10, for an ideal packed-column (no pressure drop along the column, i.e. $F_c = \text{constant}$), it is obtained that

$$u_A = \frac{L}{t_R}, \quad (12)$$

$$V + mK_{C,A} = F_c t_R, \quad (13)$$

* The range of infinite dilution of sample size is: < 0.01 - 1 ml, which depends on the properties of adsorbed species.

$$\begin{aligned}
 K_{C,A} &= \frac{1}{m} (F_c t_R - V) \\
 &= \frac{1}{m} (V_R - V) .
 \end{aligned}
 \tag{14}$$

By considering the dead volume in gas chromatography (V_{GC}), the retention volume of unsorbed gas is

$$\begin{aligned}
 V_M &= V + V_{GC} \\
 &= F_c t_M ,
 \end{aligned}
 \tag{15}$$

and

$$\begin{aligned}
 K_{C,A} &= \frac{1}{m} (V_R - V_M) \\
 &= \frac{F_c}{m} (t_R - t_M) .
 \end{aligned}
 \tag{16}$$

Pressure and Temperature correction

For a real packed-column, there is a significant pressure drop along the column. The pressure gradient of the carrier gas depends on:

$$\begin{aligned}
 \frac{dp}{dx} &= - \frac{\eta}{\kappa} u \\
 &= - \frac{\eta}{\kappa A_{column}} F_c \\
 &= C_1 F_c ,
 \end{aligned}
 \tag{17}$$

where, η is gas viscosity, κ column permeability, A_{column} cross-area of the column, and u_c linear velocity of the carrier gas, and

$$C_1 = - \frac{\eta}{\kappa A_{column}} .
 \tag{18}$$

If the carrier gas is assumed to be an ideal gas under the experimental conditions,

$$\begin{aligned}
 \frac{p F_c}{T_c} &= \frac{P_o F_{c,o}}{T_o} , \\
 F_c &= \frac{T_o P_o F_{c,o}}{T_c p} ,
 \end{aligned}
 \tag{19}$$

where 'o' means at measuring conditions, and T_c is column temperature. Substituting Equation 19 into Equation 17 gives:

$$\begin{aligned}\frac{dp}{dx} &= c_1 P_o F_{c,o} \frac{T_c}{T_o} \frac{1}{p}, \\ \frac{1}{2} p^2 &= c_1 P_o F_{c,o} \frac{T_c}{T_o} x + c_2.\end{aligned}\quad (20)$$

The constants, c_1 and c_2 , in Equation 20 can be determined by following boundary conditions:

$$\begin{aligned}x = 0, \quad p &= P_i; \\ x = L, \quad p &= P_o.\end{aligned}\quad (21)$$

Applying boundary conditions (Equation 21) to Equation 20 gives:

$$\begin{aligned}c_1 &= \frac{T_o}{2 T_c P_o F_{c,o} L} \frac{1}{P_o^2 - P_i^2}, \\ c_2 &= \frac{1}{2} P_i^2.\end{aligned}\quad (22)$$

Substituting Equation 22 in Equation 20 gives:

$$x = \frac{P^2 - P_i^2}{P_o^2 - P_i^2} L. \quad (23)$$

The plots of the pressure and volumetric velocity gradient along the column are shown in Figure 3.

Differentiation of Equation 23, gives:

$$dx = \frac{2L}{P_o^2 - P_i^2} p dp. \quad (24)$$

Applying conservation Equation 10 to the carrier gas gives:

$$F_c - V_L u_c = 0^*. \quad (25)$$

Substituting Equation 19 and Equation 24 into Equation 25 gives:

$$\frac{2L}{P_o^2 - P_i^2} p \frac{dp}{dt} = \frac{P_o F_{c,o}}{V_L} \frac{T_c}{T_o} \frac{1}{p}. \quad (26)$$

* For the unsorbed carrier gas, $K_{c,A} = 0$.

The boundary conditions for Equation 26 are:

$$\begin{aligned} t &= 0, \quad p = P_i; \\ t &= t_M, \quad p = P_o. \end{aligned} \quad (27)$$

$$\int_{P_i}^{P_o} \frac{2L}{P_o^2 - P_i^2} p^2 dp = \int_0^{t_M} \frac{P_o F_{c,o}}{V_L} \frac{T_c}{T_o} dt. \quad (28)$$

Integrating, rearranging, and substituting V by V_M^* ,

$$\begin{aligned} V_M &= \frac{3}{2} \frac{T_c}{T_o} \frac{1 - \left(\frac{P_i}{P_o}\right)^2}{1 - \left(\frac{P_i}{P_o}\right)^3} F_{c,o} t_M \\ &= J_{p,T} F_{c,o} t_M, \end{aligned} \quad (29)$$

where $J_{p,T}$ is a pressure and temperature correction factor, and

$$J_{p,T} = \frac{3}{2} \frac{T_c}{T_o} \frac{1 - \left(\frac{P_i}{P_o}\right)^2}{1 - \left(\frac{P_i}{P_o}\right)^3}. \quad (30)$$

Comparing Equation 29 with Equation 15 gives:

$$F_c = J_{p,T} F_{c,o}. \quad (31)$$

Substituting Equation 31 in Equation 16 gives:

$$K_{c,A} = \frac{1}{m} J_{p,T} F_{c,o} (t_R - t_M). \quad (32)$$

Let us define net unit retention volume as:

$$V_N = \frac{1}{m} J_{p,T} F_{c,o} (t_R - t_M). \quad (33)$$

Thus,

$$\begin{aligned} K_{c,A} &= V_N, \\ K_{p,A} &= \frac{V_N}{RT}. \end{aligned} \quad (34)$$

* By considering the dead volume in gas chromatography.

2. How to determine t_R

The most convenient way to determine t_R is by peak retention time, t_R . However, it can not characterize a non-ideal elution process very well. In this circumstance, it is better to use average retention time, $\bar{t}_R$, rather than peak retention time, t_R .

The relationship between the peak retention time, t_R , and the average retention time, $\bar{t}_R$ is shown in Figure 4, i.e.

$t_R = \bar{t}_R$, *symmetric peak;*

$t_R > \bar{t}_R$, *peak distorted with front profile spread;*

$t_R < \bar{t}_R$, *peak distorted with tailing line spread.*

There are two types of average retention time. One is weighted arithmetic mean of retention time, $t_{r,m}$. It is calculated by

$$t_{r,m} = \frac{\int_0^{\infty} h t dt}{\int_0^{\infty} h dt} \quad (35)$$

Another one is half elution-out retention time, $t_{r,e}$. It is determined by following derivations:

For reversible adsorption, it gives:

$$n_a(t_R) = \int_0^{t_R} k h dt \quad (36)$$

where, n_a (mol) is eluted amount of adsorbed species A at t_R ; k (mol/(V)(sec.)) is detector constant; and h (V) is height of the peak at t_R . Substituting $t_R \rightarrow \infty$ into Equation 36 gives:

$$\begin{aligned} n_{a,o} &= \int_0^{\infty} k h dt \\ &= k S_{peak} \end{aligned} \quad (37)$$

where $n_{a,o}$ is the total injected amount of species A. If $\bar{t}_{r,m}$ is defined as the t_R at which a half amount of species A is eluted from the column, we have:

$$t_{r,m} = n_a^{-1} \left(\frac{n_{a,o}}{2} \right) \quad (38)$$

GAS CHROMATOGRAPHIC ADSORPTION STUDIES

The equipment for gas chromatography adsorption studies is shown in Figure 5. The chromatograph column is packed with the coal sample. The characteristics of the column are as follows:

coal sample	Castlegate Mine, Sub 3 seam
particle	-200 mesh
sample size	4.0126 g
length	38.1 cm
o.d.	6.35 mm
i.d.	3.97 mm

The operating conditions are as follows:

flowrate	0.25 - 0.30 cm ³ (STP)/s
detector temperature	40 °C
bridge current	220 mA
column temperature	273 K

The gas chromatograph peaks for each of nine gases are shown in Figures 6, 8, and 10. The peak for methane is repeated on each figure. The cumulative signal is shown in Figures 7, 9, and 11. The peak retention time of many of the gases are similar. The cumulative curves give a better idea of the asymmetry of the peaks. Retention times, mean retention times, and weighted retention times are listed in table 1. Retention times for helium, nitrogen, oxygen, argon, carbon monoxide and methane are similar. Those for carbon dioxide, ethane, propane, and propylene are higher and show some differences. The weighted retention times reflect the asymmetry of the adsorption peaks. The order of the weighted retention times compares with the adsorption of the various gases reported in the previous quarterly report. The results for the hydrocarbon gases are interesting and bear further studies. The implications of the adsorption properties on methane recovery from coalbeds are important.

The adsorption conditions for each of the gases are listed in Tables 2 and 3.

HIGH PRESSURE ADSORPTION/DESORPTION SYSTEM

Basic Information

The high pressure adsorption system is shown in Figure 12. About 17 grams of coal was used for each test. Pressure signals from the pressure transducer, flowrate signals from mass flow monitor, and temperature signals from thermocouple were recorded by the PC Data Acquisition system. The temperature of the isothermal bath was controlled by a temperature controller, and set at 25 °C (298 K). The temperature fluctuation was ± 0.3 °C.

CO₂ Adsorption/Desorption

After CO₂ adsorption at an intermediate pressure (< 1000 psi) reached equilibrium, the CO₂ desorption was measured. During the desorption process, the pressure and flow rate was continuously recorded. Therefore,

$$\text{Cumulative flow-out gas: } n_{\text{out}}(t) = \int_0^t f dt$$

If

$$\text{Total flow-out gas: } n_{\text{total}} = \int_0^{\infty} f dt,$$

$$\text{gas left in the adsorption chamber: } n_{\text{left}}(t) = n_{\text{total}} - n_{\text{out}}$$

On the other hand, based on the results of Helium calibration of the free volume, V_f , in the adsorption chamber, we have:

$$\text{Free gas in the adsorption chamber: } n_{\text{free}}(t) = \frac{p(t) V_f}{z(p) RT}$$

where $z(p)$ (since $T = \text{constant}$) was calculated by the equation¹:

$$z = z^{(0)}(T_r, P_r) + \omega z^{(1)}(T_r, P_r)$$

Finally, we have:

$$\text{Gas adsorption: } n_{\text{ads}} = \frac{n_{\text{left}} - n_{\text{free}}}{m}$$

where m is the mass of coal used in adsorption chamber.

BET Method to Determine the Surface Area of Coal Samples

The quantity of CO₂ (or other species) needed to cover the adsorbent (coal) surface with a monolayer is given by the BET equation:

$$\alpha_p = \frac{p}{p_s} \quad (\alpha_p = 0.05 \text{ to } 0.35^*)$$

$$\frac{\alpha_p}{a(1-\alpha_p)} = \frac{1}{a_m C} + \frac{C-1}{A_m C} \alpha_p,$$

where a_m is the amount of species needed to cover completely a surface with a monolayer (mol/g), p the equilibrium pressure of the adsorbate, p_s the saturated vapor pressure of adsorbate at the experimental temperature, and C a constant depending on the adsorption energy and temperature. The constants C and a_m can be determined by plotting of $\alpha_p/[a(1-\alpha_p)]$ against α_p .

The specific surface area of the adsorbent (coal), S , can be determined if the magnitude of a_m and the area occupied by a molecule of adsorbate in the monolayer, σ , are known.

$$S = a_m N_A \sigma,$$

where N_A is the Avogadro number, $\sigma = 0.235 \text{ nm}^2/\text{molecule}$ for CO₂ at 298 K².

EXPERIMENTAL RESULTS

The high pressure adsorption system was used to measure gas adsorption during depressurization. The flow valve was used to reduce the pressure at the mass flow meter. Under these conditions, the mass flow meter was used to measure the flow of methane. The dead volume of the cell was calibrated using helium, which is assumed to not adsorb on the coal. The carbon dioxide flow data were used to calculate the volume of carbon dioxide in the cell at any time. The flow and the pressure are both recorded continuously, hence the total volume of methane in the cell and the volume of carbon dioxide occupying the dead volume of the cell can be determined at any time or pressure. The results for Sub 3 seam coal at -100/+115 mesh is shown in Figure 13. The solid line is the total carbon dioxide and the dashed line is the gaseous carbon dioxide. The difference is the adsorbed dioxide as shown in Figure 14, plotted versus cell pressure.

To understand the time required for equilibrium adsorption of carbon dioxide, the cell was exposed to a pressure of 231 psi for different periods of time. At each exposure time, the depressurization experiment was performed to determine the total volume of carbon dioxide adsorbed versus time. The results are shown in Figure 15 and expanded for short times in Figure 16. It is

clear that over one hour is required for equilibrium under these conditions. This is less than the time required for equilibrium with methane, but still relatively long.

The carbon dioxide adsorption is plotted versus the relative saturation pressure in Figure 17. The solid line represents the data determined from the depressurization plots of Figures 13 and 14. The open circles represent equilibrium adsorption points determined from data of Figure 15. Multiple measurements at the same conditions give high reproducibility. The continuous data obtained from one depressurization experiment agree very well with the many experiments of equilibrium adsorption measured by depressurization after different exposure times. The shape of the curve fits that expected for the BET isotherm. The equilibrium adsorption points from Figure 15 are plotted in a BET adsorption isotherm format in Figure 18. A very good fit is obtained using relative saturation pressures of from 0.1 to 0.3. A surface area of 69.9 m²/g was determined. The depressurization data of Figure 13 is plotted in a similar format in Figure 19. The fit is not as good as the adsorption data, but is still quite good. The surface area is 69.8 m²/g, in good agreement with that obtained from Figure 18. Figure 20 is a similar plot for the same coal, but of smaller mesh size. The surface area of 71.0 m²/g indicates that particle size does not have a big effect of surface area and it is mostly internal area.

The continuous depressurization technique offers a relatively simple method of obtaining surface area measurements at higher pressures, from continuous data.

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3. Gregg S. J. and Sing K. S. W., Adsorption, Surface Area and Porosity, 2nd Edition, Academic Press, 1982.

* The appropriate range of relative pressure, a_p , is 0.05 - 0.35 for the determination of specific surface area by the BET method.

Table 1 GC Adsorption Parameters of Castlegate Sub 3
(-200 mesh) at 273 K.

Species	S_p (V) (sec)	S_r (V) (sec) ²	R.T. _m sec	R.T. _e sec	R.T. _p sec	h_p V
He	49.79	7.23E+03	145.31	136	138	2.7149
N ₂	83.11	1.11E+04	133.82	125	122	4.8086
O ₂	78.60	1.15E+04	146.32	129	124	3.6518
Ar	91.13	1.34E+04	147.18	126	122	4.6645
CO	86.75	1.35E+04	155.61	127	123	4.3555
CH ₄	73.83	1.17E+04	157.93	128	122	3.1821
C ₃ H ₈	129.39	4.67E+04	361.01	149	127	3.9394
C ₂ H ₆	212.11	8.80E+04	414.99	193	134	2.7422
CO ₂	465.91	4.30E+05	923.30	520	302	0.9497
C ₃ H ₆	430.04	9.67E+05	2249.70	1152	241	0.4224

S_p : Peak area,

$$S_p = \int_0^{\infty} h dt$$

S_r : Retention area,

$$S_r = \int_0^{\infty} h t dt$$

R.T._m: Weighted arithmetic mean of retention time,

$$\begin{aligned}
 R.T._m &= \frac{\int_0^{\infty} h t dt}{\int_0^{\infty} h dt} \\
 &= \frac{S_r}{S_p}
 \end{aligned}$$

R.T._e: Retention time at half elution of injected gas

R.T._p: Peak retention time

h_p : Peak height

Table 2 GC Adsorption Conditions of Castlegate Sub 3
(-200 mesh) at 273 K.

Species i	C_i mol/ml	P_i psia	f ml/sec	P_{in} psia	P_{in}/P_{out}	$J_{p,T}$
He	2.22E-06	0.730	0.2482	35.30	2.40	0.557
N ₂	2.05E-06	0.674	0.2852	34.96	2.38	0.561
O ₂	1.63E-06	0.535	0.2882	35.10	2.39	0.559
Ar	1.79E-06	0.588	0.2902	34.86	2.37	0.562
CO	1.78E-06	0.585	0.2850	34.99	2.38	0.561
CH ₄	1.50E-06	0.494	0.2897	34.68	2.36	0.565
C ₃ H ₈	1.07E-06	0.353	0.2866	34.97	2.38	0.561
C ₂ H ₆	4.59E-07	0.151	0.2841	35.17	2.39	0.558
CO ₂	7.09E-08	0.023	0.2898	34.73	2.36	0.564
C ₃ H ₆	3.50E-08	0.012	0.2834	35.18	2.39	0.558

C_i : Concentration of species i in the adsorption column,

$$C_i = kh_p$$

where k is the TCD detector constant ((μ mol)/(ml)(V)), and $k = n_{a0}/(fS_p)$, and the amount of injected gas $n_{a0} = 10.1 \mu$ mol, i.e., 0.25 ml at $p_a = 14.5$ psia, and $T_a = 298$ K.

P_i : Partial pressure of species i in the adsorption column,

$$P_i = C_i RT$$

f: Flow rate of carrier gas

P_{in} : Inlet pressure of the adsorption column

P_{out} : Outlet pressure of the adsorption column

$J_{p,T}$: Temperature and pressure correction factor,

$$J_{p,T} = \frac{3}{2} \frac{T_c}{T_o} \frac{1 - (\frac{P_i}{P_o})^2}{1 - (\frac{P_i}{P_o})^3}$$

where T_o , and P_o are temperature and pressure at the measuring point

Table 3 GC Adsorption Results of Castlegate Sub 3
(-200 mesh) at 273 K.

Species	V_r ml	$V_{r,c}$ ml	V_N ml/g	K_c ml/g	K_p (mol)/(g)(psia)	(ml(STP))/(g)(psia)
He	36.07	20.07	-	-	-	-
N ₂	38.17	21.41	0.33	0.33	1.01E-06	0.023
O ₂	42.17	23.58	0.87	0.87	2.65E-06	0.059
Ar	42.71	24.01	0.98	0.98	2.98E-06	0.067
CO	44.35	24.86	1.19	1.19	3.62E-06	0.081
CH ₄	45.75	25.83	1.44	1.44	4.36E-06	0.098
C ₃ H ₈	103.47	58.02	9.46	9.46	2.87E-05	0.644
C ₂ H ₆	117.90	65.81	11.40	11.40	3.46E-05	0.776
CO ₂	267.57	150.90	32.60	32.60	9.90E-05	2.218
C ₃ H ₆	637.56	355.80	83.67	83.67	2.54E-04	5.693

V_r : Measured retention volume,

$$V_r = (f)(R.T._m)$$

$V_{r,c}$: Corrected measured retention volume,

$$V_{r,c} = J_{P,T} V_r$$

V_N : Net unit retention volume,

$$V_N = \frac{V_{r,c} - V_M}{m}$$

where V_M is the retention volume by unsorbed gas, and m the amount of coal packed in the column

K_c : Adsorption coefficient for concentrations

K_p : Adsorption coefficient for pressures

**Diagram of an Ideal Elution Process of Species A
through a Permeably Packed Column**

**The Change in the Concentration of Species A
across a Chromatographic Column**

Figure 1

The Five Types of Adsorption Isotherm, I to V,
in the Classification of S. Brunauer, L. S. Deming, W. S. Deming and E. Teller,
J. Amer. Chem. Soc. 62, 1723 (1940).
together with Type VI, the Stepped Isotherm.

Figure 2

The Pressure and Volumetric Velocity Gradient
along the Chromatographic Column

Figure 3

The Relationship
between Peak Retention
Time, t_R , and Average
Retention Time, $\bar{t}_R$, in
an Ideal or Non-ideal
Adsorption Column.

Figure 4

Diagram of Apparatus for Determining the Adsorption Isotherm of Gases

Figure 5. Equipment for gas chromatography adsorption studies.

Figure 6. Elution peaks for nitrogen, argon, oxygen, and methane.

Figure 7. Cumulative elution for nitrogen, argon, oxygen, and methane.

Figure 8. Elution peaks for carbon monoxide, carbon dioxide, and methane.

Figure 9. Cumulative elution for carbon monoxide, carbon dioxide, and methane.

Figure 10. Elution peaks for methane, ethane, propane, and propylene.

Figure 11. Cumulative elution for methane, ethane, propane, and propylene.

High Pressure Adsorption/Desorption System

Figure 12. High pressure adsorption and desorption equipment.

Figure 13. Carbon dioxide in high pressure cell during slow depressurization.

Figure 14. Carbon dioxide adsorbed versus pressure.

Figure 15. Carbon dioxide uptake by high pressure absorption cell.

Figure 16. Carbon dioxide uptake by high pressure cell at short times.

Figure 17. Methane adsorption versus relative saturation pressure.

Figure 18. BET plot of methane adsorption.

Figure 19. BET plot of continuous depressurization data.

Figure 20. BET plot from continuous depressurization data.

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