

SOME ASPECTS OF THE CONSTITUTION OF COAL

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The last ten years have witnessed rapid strides in our knowledge of the complex nature and constitution of coal. The recent contributions from the physical techniques e.g. infra-red, nuclear magnetic resonance, X-ray and van Krevelen et al's statistical approaches have given a new impetus to the study of coal science as a result of which various models^{1,2} of the structural 'unit' of coal have been suggested from time to time. However, the problem of coal constitution is ultimately a chemical one and in the long run sanction of chemical approaches have to be sought for any structure proposed for coal, irrespective of the technique employed in formulating the model. In the past, extensive studies on the oxidation, reduction, halogenation, pyrolysis etc. of coal had been carried out but the data, though informative, failed to unravel the intricate chemical structure of coal in the orthodox chemical sense, nor did they yield any significant information on the structural parameters of coal, an essential prerequisite for hypothesizing a model structure. However, as a result of recent studies an attempt may now possibly be made to make tentative proposals based on the information on the state of carbon, hydrogen and oxygen in coal³⁻¹³.

Oxygen in Coal

Though there is still divergence of opinion regarding the actual values of hydroxyl, carbonyl and carboxyl oxygen groups in coal, a fair order of estimate particularly for hydroxyl is now available¹⁴. 50-60 per cent of the total oxygen in coal, at least in lower ranks ($C < 85-86\%$) is found to be in the form of hydroxyl groups, and the rest appears to be present in small amounts as carbonyl, carboxyl and ether and/or heterocyclic oxygen groups. In higher rank coals ($C > 86\%$) few of the functional oxygen groups are believed to be present, but the major part of oxygen remains unaccounted for.

State of Carbon and Hydrogen in Coal:

Oxidation & Dehydrogenation Studies: The work of Bone, Wheeler and their collaborators¹⁵ in the early twenties and of Horton¹⁶ and others established that aromaticity of coals increased with increase of the rank. But, for precise determination of aromaticity obviously a method of controlled oxidation was needed which would selectively oxidise the non-aromatic part of the coal structure. Such a method of oxidation was recently advanced⁴ by the present writers. It was shown that prolonged oxidation of coal in air at 170°C was chiefly restricted to the non-aromatic structures of coal, leaving the aromatic carbon skeleton practically intact. Such an approach, supported by further work^{7,17} led to a number of deductions regarding aromaticity, forms of hydrogen, the size of the aromatic nucleus, and an assessment of the dimensions of the aliphatic side-chains in a coal unit. These deductions are presented in Tables 1 and 2.

The recent studies on dehydrogenation^{10,11,12,13} of coals have thrown some fresh light on the problem. The non-aromatic carbon structure of coal has so far been assumed to be only aliphatic in nature. Dehydrogenation studies by Vesterberg's technique and with halogens¹⁸, appear to indicate that the non-aromatic part may be largely constituted of alicyclic carbon. Similar indications have since been obtained by Ergun¹⁹ from X-ray studies.

The presence of hydroaromatic or alicyclic structure was, however, first suggested by Weiler²⁰ on the score of the dehydrohalogenation phenomenon (which he called "spitting").

Quantitative measurement of alicyclic carbon and hydrogen from dehydrogenation studies show that a considerable proportion of carbon in bituminous coal is in alicyclic form (10-25%) and also that the alicyclicity progressively diminishes with increase in the rank of coal. Anthracite does not contain any alicyclic carbon nor does it undergo any dehydrogenation.

The chief objection²¹ to this technique (Vesterberg's) for quantitative measurement of alicyclicity of coals has been that the method may not selectively dehydrogenate alicyclic carbon alone and that aromatic carbon may also be affected to some degree. Further studies¹³ have, however, shown that only a minor part of dehydrogenation may be due to some side-reactions (possibly cross-linking) with aromatic positions and there does not appear to be any doubt, that the method is fairly reliable (as far as coal is concerned). Corrections have now been made for such possible stray side-reactions and the new set of values for alicyclicity of coal derived, are presented in Table 3.

It may appear strange, but statistical and experimental facts seem to indicate that the sum of aromatic and alicyclic carbon percentage is virtually constant (0.87 ± 0.03) as will be seen from Table 4.

If this be true, then obviously the value for the percentage of aliphatic carbon can be deduced from experimentally determined values of aromaticity and alicyclicity, and naturally the value for aliphatic carbon percentage in coals will also be nearly constant. This value is between 10-15%: it may, however, be somewhat on the higher side, as it is likely that the values for alicyclicity presented here is likely to err on the minimum side. Be that as it may, the constant nature of the aliphatic carbon in coal (if this be the case) would appear to be a remarkable fact, for which no explanation can be offered at this stage.

It was suggested⁹ earlier that the aliphatic side-chains present in coal should be small and even as small as in methyl group, and certainly not longer than in an ethyl group. The estimation of C-methyl content by Kunn and Koth's reaction^{22,23,24} yielded a value of 2 to 4% of the carbon present as methyl group in coal. It is possible that this value is also on the lower side, as the aromatically linked methyl group may not be estimated quantitatively by this technique²⁵. Exhaustive chlorination²⁶ on the other hand gave a higher estimate of C-methyl content i.e., 6-7% of the carbon. The agreement between the experimental values and those theoretically deduced as far as the order is concerned may or may not be significant. Further refinement in the techniques of determination of aliphaticity in coals should prove to be of great value.

The Alicyclic Structure in Coals

The formation of tar is completely inhibited when a dehydrogenated coal is carbonized. There is, also, a proportionate increase in the yield of char. The additional carbon 'fixed' in the char is apparently proportional and almost equal in value to the alicyclic carbon estimated directly^{10,11,13}. Therefore, it may not be illogical to conclude that tar has its origin in the alicyclic structures of coal¹². The complete inhibition of tar formation by any method of dehydrogenation (even by air/oxygen)²⁷ is also significant.

van Krevelen and Fitzgerald recently concluded²³ that "that part of coal structure which yields tar must be weakly linked or not at all bonded to the remainder". A study on the extent of the inhibition of tar formation with varying degrees of dehydrogenation (Fig.1) also leads to a similar conclusion¹³. The complete inhibition of tar formation, however, does not appear to depend on the completeness of the dehydrogenation but a minimum quantity of the dehydrogenating agent (sulphur) is apparently needed for the maximum inhibition (Fig.1). It appears probable that simultaneously with dehydrogenation, a condensation reaction (possibly by cyclo-dehydrogenation) between the alicyclic part and the rest of the coal structure is possibly initiated. The action of sulphuric and

phosphoric acids²⁹, phosphoryl oxychloride³⁰, even Scholl's reagent³¹ also appear to have similar effects on inhibition of tar formation and probably through a similar mechanism of condensation reaction, leading to fixation of the alicyclic carbon in the char.

Another significant fact is that on dehydrogenation or even in condensation reactions mentioned above, nearly 92% of the total carbon in coal is found to be retained in the char (600°C) on carbonization, irrespective of the rank of coal so treated from lignite upto the high rank bituminous coals. Normally, in carbonization only 70-80% of the carbon is fixed in the coke or char at 600°C. Thus, the 'extra' carbon retained in char is of the order of 10-22% of the total carbon in coal, which corresponds to the values of alicyclic carbon determined directly by dehydrogenation reactions. The proportion of carbon normally fixed in coke and char on carbonization at 600°C corresponds to the aromatic carbon in coal³². The additional carbon fixed on treatments mentioned above and the constancy of the value at about 92%, again, appears to correspond to the sum of aromatic and alicyclic carbon, irrespective of the rank of coal.

This would indicate that in course of coalification enrichment of aromatic carbon takes place at the expense of alicyclic carbon (and possibly derived from it), the sum total of the two being constant.

Stages in Coalification :

The progressive increase in aromaticity in coal (at the expense of alicyclic carbon) during coalification must be a very slow process and a gradual one. One may, therefore, envisage a 'parent' coal unit at any particular stage of evolution which will vary in aromaticity, alicyclic carbon and ring size. This concept of the evolution of coal with increasing rank may be hypothetically illustrated in terms of the structural models shown in Fig. 2.

The model I, C = 68%, may be arbitrarily assumed to be the 'parent' structural unit of coal, existing in the lignitic stage (there may be other structural units, but the model I may be conceived to be as the predominant species at this level). Decarboxylation and partial dehydroxylation (which are believed to be the major reactions in the evolution of coal in the lower ranks) of model I can lead to the stage of model II, C = 79%. The model IIIA, C = 91% is envisaged to be the transitional stage marked by the completion of the decarboxylation, dehydroxylation and dehydrogenation of the alicyclic ring and its fusion with the aromatic nucleus. Partial demethylation may also occur between the stage II and IIIA.

The transitory nature of these structures is to be emphasised at any particular stage of the rank evolution of coal. Decarboxylation may be largely completed at or near about 80% carbon coal but the process may continue well after this stage is reached. Small amounts of carboxylic oxygen can still be detected even in 84-85% carbon coal. Dehydrogenation of the alicyclic ring and ring-closure by cyclodehydrogenation (model II & IIIA) may constitute the major steps in the bituminous coal range.

The properties of the three hypothetical structures designed to portray the three important transition steps in rank-evolution may be depicted as in Table 5.

The analysis of structure IIIA (Table 5) broadly represents a typical high rank bituminous coal (C = 91%) having 91% aromatic carbon. This 'unit' given in the model is presumed to be the most predominant one present at 91% carbon level. At any intermediate stage of coalification between lignite and this high rank bituminous coal, a certain fraction of the 'unit' of model I may undergo metamorphosis into the 'unit' of model II which in its turn, under the prevailing geo-chemical condition may undergo further progressive transformation into the model IIIA. The final stage (model IIIA) is, thus, a result of the sum total of decarboxylation, dehydroxylation, dehydrogenation and partial demethylation of the 'parent' unit (model I). The incipient initiation of stage II to IIIA reaction in

the earlier stages is also not precluded. As a result, any transitory stage in rank-evolution may contain a mixture of one or two or all of the above types of units, though one or the other model species may predominate, depending upon the level of geochemical metamorphosis attained in the natural state.

No coal can, therefore, be homogeneous in respect of their unit structures. As an example, a proportion of 10:70:20 of the three structures may represent the typical analysis, both chemical and structural, of a 80% carbon coal (Table 5). Such a plausible structural analysis of a 80% carbon coal would indicate that it has undergone substantial decarboxylation. It would also indicate that dehydroxylation, dehydrogenation, (including cyclo-dehydrogenation) and demethylation processes had been initiated in varying degrees. All the transformations are consistent with the known properties of coal of such a rank. A partial conversion of model II to IIIA (say to the extent of 22% as suggested in the proportion of the units) will lead to an increase in aromaticity and also to the growth of the aromatic nucleus at the expense of alicyclic carbon.

The possibility of a number of model species (units) occurring together at any stage of coalification (though one or the other may be the dominant one) may also explain some of the following observations: (1) the assortment of ring sizes in any coal, (2) the constant trend of the sum of aromaticity and alicyclicity in any rank of coal (lignites and bituminous coal), (3) the constancy of carbon per cent retained in the char of dehydrogenated coal samples of any rank, as well as several other apparently perplexing facts observed in course of our studies on dehydrogenation and cyclo-condensations.

Whereas the transition of stage I to stage IIIA depicts the evolution of normal coals upto the highest rank in the bituminous range occurring under a set of geochemical conditions, the transition of stage III to stage IV (anthracite stage) must, by all accounts, be an abrupt and drastic one, involving a completely new set of geochemical conditions. The evolution of a typical anthracite may be conceived as shown in Fig. 3.

The structural models given here are not intended to actually represent any coal but has merely been used to illustrate the concept of the heterogeneity of the coal structure at any particular stage, and to emphasise the predominant chemical transmutation that may take place in response to geochemical forces in nature at any given level of metamorphic history of coal.

Studies in rank classification of coal have led to the formulation of the well-known coal band, which by itself, emphasises the transitory nature of the metamorphic changes in coal. Whether there are distinct and discretely separate zones of chemical reactions in course of rank-evolution is yet to be established, though the predominance of one set of reactions over another at any stage can not be disputed.

Admittedly, the models, the reactions, and the concept of co-existence of several models may explain many experimentally determined properties of coal, but we do not submit them here as pure "models" of any 'unit' coal; that stage may yet be far off. The number of rings assumed or other structural feature shown in the models (e.g. the disposition of unaccounted oxygen) may be different and still fit into the general picture of evolution of rank, but what is emphasised is that rarely any reaction in nature is ever complete, though the ideal is always towards perfection.

References

1. Dryden I.G.C., J. Inst. Fuel, (1957), 193.
2. Given, P.H., Fuel 39(1960), 147
3. (a) Mazumdar, B.K., Bhangale, P.H. & Lahiri, A., J. Sci. industr. Res., 15B (1956)
(b) Mazumdar, B.K., Bhangale, P.H. & Lahiri, A., Fuel (Lond.), 36(1957), 254.
4. Mazumdar, B.K., Anand, K.S., Roy, S.N. & Lahiri, A., Brennst-Chemie, 19/20, 38(1957), 305.
5. Mazumdar, B.K., Chakrabartty, S.K., (Mrs.) Saha, M., Anand, K.S. & Lahiri, A., Fuel, 38, 4 (1959), 469.
6. Mazumdar, B.K., Chakrabartty, S.K., & Lahiri, A., J. sci. industr. Res, 16B (1957), 275.
7. Mazumdar, B.K., & Lahiri, A., Fuel, 37 (1958), 495.
8. Chakrabartty, S.K., Mazumdar, B.K., & Lahiri, A., Fuel, 37(1958), 498.
9. Chakrabartty, S.K., Mazumdar, B.K., Roy, S.N., & Lahiri, A., Brennst-Chemie, (in press).
10. Mazumdar, B.K., Chowdhury, S.S., Chakrabartty, S.K., & Lahiri, A., J. sci. industr. Res., 17B (1958), 509.
11. Mazumdar, B.K., Chakrabartty, S.K., Chowdhury, S.S., & Lahiri, A., Proc. Symp. on the "Nature of Coal" Central Fuel Research Institute (India), February, 1959, 219-229.
12. Mazumdar, B.K., Chakrabartty, S.K., & Lahiri, A., Fuel, 38 (1959), 112.
13. Mazumdar, B.K., Chakrabartty, S.K., De, N.G., Ganguly, S, & Lahiri, A., Fuel, (in press).
- 14(a) Halleux, A., Delavarenne, S., Tschamler, H., Fuel (1959), 283.
- 14(b) Brooks, J.D., Proc. Symp. on the "Nature of Coal" Central Fuel Research Institute (India), February, 1959, p. 167-172.
- 15(a) Tidswell, F.V. and Wheeler, R.V., J. Chem. Soc., 1922, 121, 2345.
(b) Francis, W. and Wheeler, R.V., J. Chem. Soc, 1927, 2958.
(c) Fischer, F. and Schröder, H., Gas Abh. Kennt. der Kohle, 1919, 4, 342.
(d) Bone, W.A. and Quarendon, R., Proc. Roy. Soc. A 1926, 110, 537.
16. Horton, L., Fuel, Lond. 1955, 34, S 14.
17. Mazumdar, B.K., Chakrabartty, S.K., Lahiri, A., "Determination of Aromaticity of Coal" - Submitted to the Conference at brussels to be held in Nov., 1960.
18. Mazumdar, B.K., Choudhury, S.S. & Lahiri, A., Fuel, 39 (1960), 179.
19. Ergun, S, & Tiensuu, V.H., Nature, June 13, 1959, 1668.
20. Wieler, J.F., Fuel, 14, 190-6 (1935).
21. van Krevelen, D.H. et al, Fuel, 38(1959), 256.

22. Kinney, C.R., J. Amer. Chem. Soc., 69 (1947), 284.
23. Brooks, J.D., Durie, R.A., Sternhell, S., Aust. J. Appl. Sci., 9, 3, (1958), 303.
24. (Mrs.) Kaiser, F., Rao, H.S., & Lahiri, A., Proc. Symp. on the "Nature of Coal", Central Fuel Research Institute, February, (1959), 245.
25. Kuhn, R. and L'Orsa, F., Angew. Chem., 44 (1931), 847.
26. Bhowmik, J.N., Mukherjee, P.N., Mukherjee, A.K., & Lahiri, A., Proc. Symp. on the "Nature of Coal", Central Fuel Research Institute, February (1959), 242.
27. Chakrabartty, S.K., Mazumdar, B.K. and Lahiri, A., Nature (in press).
28. Fitzgerald, D. and van Krevelen, D.W., Fuel, 38(1959), 17.
29. Mazumdar, B.K., Ganguly, S., De, N.G., & Lahiri, A., Fuel (in press).
30. De, N.G., Mazumdar, B.K., & Lahiri, A., Unpublished work.
31. Mookherjee, S.K., Mazumdar, B.K., & Lahiri, A., Unpublished work.
32. Mazumdar, B.K., Chakrabartty, S.K. & Lahiri, A., Proc. Symp. on "Nature of Coal", Central Fuel Research Institute, February (1959).
33. Mazumdar, B.K., Chakrabartty, S.K. and Lahiri, A., J. sci. industr. Res, 168, 11, (1957), 509.

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Table 1 - Calculation of Aromaticity in Coal from Oxidation Studies
(based on oxidation of 100 gm. of coal substance)

[Reproduced from Unkrabarty, S.K., Mazumdar, B.K., Roy, S.N., Lahiri, A., Brennst-Chemie, in press]

Sample	C		H %	Gain/ loss in wt. %	Oxygenated groups in oxy-coal			Carbon input gm.	Carbon output gm.	COOH (in oxy- coal) gm.	W aromatic (C _{ar})	C _{ar}	
	g	%			COOH %	OH %	COO %					COO %	W aromatic (C _{ar})
Lignite	71.53	4.66		-26.4	17.5	7.4	4.0	71.53	45.23	4.83	40.40	0.56	
Overall (1)	80.69	5.33		-3.0	14.3	2.3	6.5	80.69	62.38	4.93	57.45	0.71	
Vitrain (1)	81.46	5.40		-7.0	16.0	4.0	6.5	81.46	60.82	5.58	55.24	0.68	
Vitrain (2)	84.35	5.72		-7.6	16.0	2.6	7.9	84.35	60.56	5.52	55.04	0.65	
Overall (2)	85.15	5.70		-5.0	14.3	4.0	5.3	85.15	63.86	5.10	58.76	0.69	
Vitrain (3)	87.25	5.27		+0.8	14.0	2.2	8.9	87.25	68.08	5.28	62.80	0.72	
Vitrain (5)	89.56	4.93		+8.0	11.2	1.5	11.0	89.56	75.60	4.56	71.04	0.79	
Overall (3)	90.31	4.86		-2.9	10.3	3.0	4.4	90.31	73.79	3.75	70.04	0.73	
Anthracite	93.20	3.50		+4.0	2.1	2.1	2.4	93.20	91.60	0.83	90.77	0.97	

Table 2 - Forms of Hydrogen and Average Ring-size of Coal Units from Oxidation Studies
 (based on oxidation of 100 gm. coal-substance, d.a.f.)

[Reproduced from Chakrabarty, S.K., Mazumdar, B.K., Roy, S.N., & Lahiri, A., Brennst-Chemie, in press]

Sample	Rank	Atomic H/C.	Hydrogen input gm.	Hydrogen output gm.	Correction for		H _{ar} ⁺ gm.	H _{ar} /H	atomic H/C oxycoal	Atomic H/C (hypothetical hydrocarbon corresponding to the oxy-coal)	*** No. of rings condensed	*** No. of rings pericond.
					H _{alip} [*] gm.	H _{arom} ^{**} gm.						
Lignite	71.53	0.78	4.66	1.77	-0.40	Nil	1.36	0.29	0.71	0.75	-	5
Overall (1)	80.69	0.79	5.33	1.93	-0.41	+0.27	1.79	0.32	0.67	0.60	7	5
Vitrain (1)	81.46	0.79	5.40	2.10	-0.47	+0.26	1.89	0.35	0.65	0.63	5	4
Vitrain (2)	84.35	0.81	5.72	2.09	-0.46	+0.43	2.06	0.36	0.64	0.62	6	4
Overall (2)	85.15	0.80	5.70	2.25	-0.43	+0.30	2.12	0.37	0.63	0.63	5	4
Vitrain (3)	87.25	0.72	5.27	2.20	-0.44	+0.50	2.26	0.43	0.57	0.60	7	5
Vitrain (5)	89.56	0.63	4.98	2.41	-0.38	+0.74	2.77	0.55	0.44	0.60	7	5
Overall (3)	90.31	0.65	4.86	2.33	-0.31	+0.25	2.27	0.47	0.53	0.49	7	7
Anthracite	93.20	0.47	3.50	2.70	-0.07	+0.016	2.79	0.80	0.20	0.39	-	12

* H Corresponding to COOH, See Table 1.

** H replaced by quinone gr., see Table 1.

+ This includes the hydrogen of the phenolic hydroxyl group.

*** Calculated from the hypothetical atomic H/C ratio corresponding to the 'hydrocarbon' model of the oxidised coal.

Table 3 - Values of alicyclicly determined by dehydrogenation studies
 (Based on dehydrogenation of 100 gm. coal substance by sulphur)^{10,11,13}
 [Data mostly reproduced from 'Further Studies on Dehydrogenation of Coal'¹³, Fuel, in press]

Sample	C		H		H ₂ dehydrogenated from alicyclic positions*	Total alicyclic (Hha)/gm		Total alicyclic (Cha)/gm.		Cha = alicyclic city	% of carbon retained in 600°C		Cha
	%		%			Hha	H	Cha	U		Normal coal	dehydrogenated coal	
lignite	71.53		4.66		-	-	-	-	-	-	68	91.0	0.23
Overall (a)	80.10		5.44		23.5	2.55	0.47	15.30	0.19	0.19	75	92.0	0.17
Overall (1)	80.69		5.33		22	2.35	0.44	13.50	0.17	0.17	75	95.0	0.20
Vitrain (1)	81.46		5.40		20	2.16	0.40	12.96	0.16	0.16	74	92.0	0.18
Vitrain (2)	84.35		5.72		16	1.83	0.32	10.98	0.13	0.13	70	87.0	0.17
Overall (2)	85.15		5.70		16.5	1.88	0.33	11.28	0.13	0.13	71	87.0	0.16
Vitrain (3)	87.25		5.27		12	1.27	0.24	7.62	0.09	0.09	78	92.0	0.14
Vitrain (5)	89.56		4.98		10	1.00	0.21	6.00	0.07	0.07	86	92.0	0.06
Overall (3)	90.31		4.86		14.5	1.43	0.29	8.58	0.10	0.10	82	95.0	0.13
Anthracite	93.20		3.50		nil	nil	nil	nil	nil	nil	98	98.0	nil

* After correcting for "side-reactions" with aromatic positions shown elsewhere¹³. The corrections may be on the higher side and the values of alicyclicly presented here should be treated as the minimum estimate.

** Taken from earlier papers^{10,11}

Table 4 - Structural Parameters from Oxidation⁹, Dehydrogenation³² and Pyrolysis³²
(Typical values of aromaticity, alicyclicity and aliphaticity)

Sample	C %	H %	Distribution of Carbon			Distribution of Hydrogen		
			** Aromaticity $\frac{C_{ar}}{C}$	Alicyclicity $\frac{C_{ha}}{C}$	Aliphaticity $\frac{C_{al}}{C}$ (by diff.)	$\frac{H_{ar}}{H}$	$\frac{H_{ha}}{H}$	$\frac{H_{al}}{H}$ (by diff.)
Lignite	71.53	4.66	0.62	0.22	0.16	0.30	0.50	0.20
Overall (1)	80.69	5.35	0.72	0.18	0.10	0.35	0.45	0.20
Vitrain (1)	81.46	5.40	0.71	0.17	0.12	0.35	0.43	0.22
Vitrain (2)	84.35	5.72	0.68	0.15	0.17	0.34	0.36	0.30
Overall (2)	85.15	5.70	0.70	0.15	0.15	0.35	0.36	0.29
Vitrain (3)	87.25	5.27	0.75	0.11	0.14	0.43	0.30	0.27
Vitrain (5)	89.56	4.98	0.82	0.07	0.11	0.50	0.20	0.30
Overall (3)	90.31	4.86	0.83	0.05	0.12	0.49	0.13	0.38
Anthracite	92.20	3.90	0.97	nil	0.03	0.82	nil	0.18

** Average values on the basis of oxidation⁹ and pyrolysis³² studies.

Table 5 - Comparison of the Chemical and Structural properties of the suggested Structural Pattern with those of a typical Coal

Analysis	Model I	Model II	Model IIIA	Assembly of structure with 10% of Model I, 70% of Model II, 20% of Model IIIA	Coal (Typical value)
Empirical formula	C ₂₄ H ₂₄ O _{6.7} N _{0.5}	C ₂₃ H ₂₂ O _{2.7} N _{0.5}	C ₂₂ H ₁₂ O _{0.5} N _{0.5}	-	-
Unit wt.	426.2	348.2	291	80.4	80.2
C%	67.6	79.3	90.7	5.7	5.4
H%	5.6	6.4	4.1	2.0	1.9
N%	1.6	2.0	2.4	11.9	12.5
O%	25.2	12.3	2.8	0.8	0.9
COOH%	7.5	Nil	Nil	4.4	6.0
OH%	11.3	4.6	Nil	3.6	1.8
CO%	3.8	4.6	Nil	3.1	3.8
*OC-O-%	2.6	3.1	2.8	0.67	0.68
f _a (aromaticity)	0.58	0.61	0.91	0.24	0.18
** f _{ha} (alicyclicity)	0.29	0.30	Nil	0.09	0.14
f _{al} (aliphaticity)	0.13	0.09	0.09	0.26	0.35
*** har	0.21	0.17	0.60	0.44	0.45
H _{ha}	0.50	0.55	-	0.30	0.20
H	0.29	0.28	0.40	-	-
H _{al}	-	-	-	3.5	4
H	-	-	-	-	-
Average No. of aromatic Rings	3	3	5	4	4

* In the models, the unaccounted oxygen usually found in coals have been represented as ether linkages: this may not be true. On the other hand, the possibility of the heterocyclic oxygen in coal in the form of flavone structure or similar configuration can not be ruled out (unpublished work : Mazumdar, D.K. et al). No attempt is made now to represent this in the models.

** This includes the bridge methylene group.

*** This includes the hydrogen of the phenolic hydroxyl group.

+ Proportion of nitrogen assumed; its disposition in the models has not been shown.

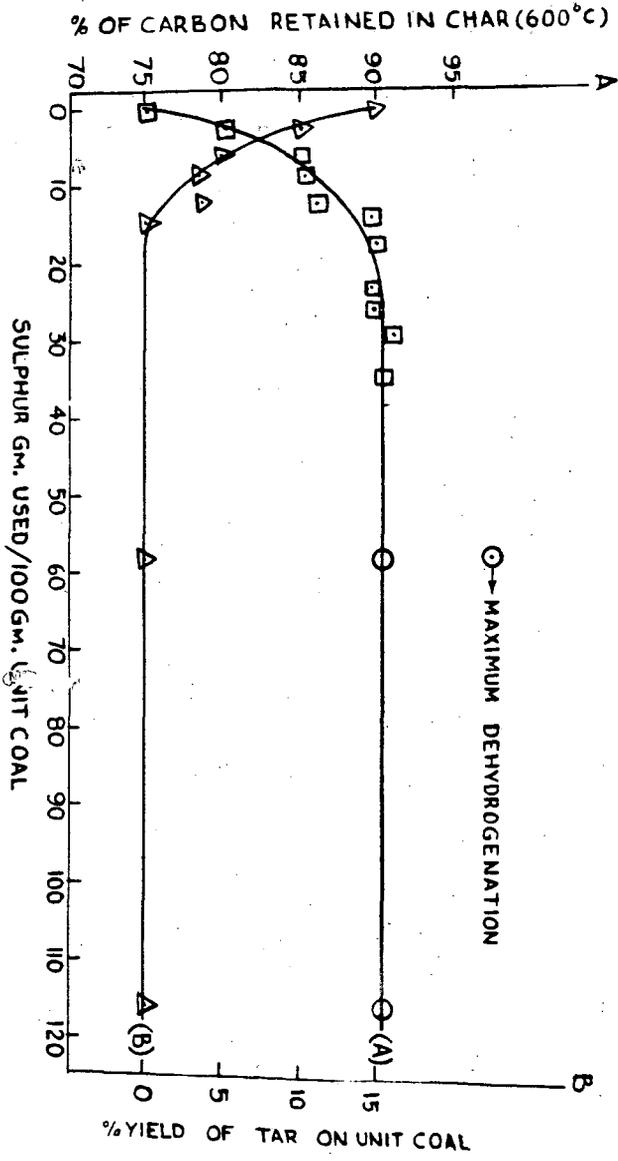
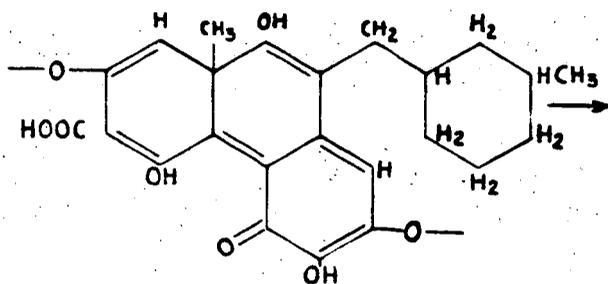
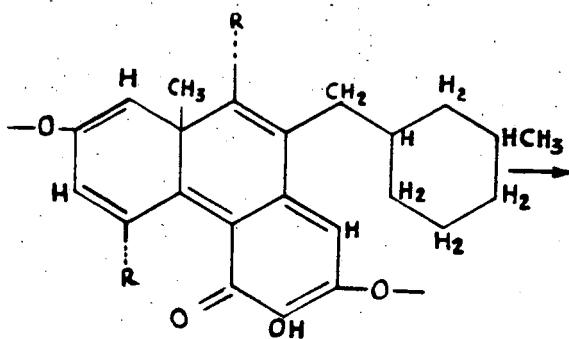


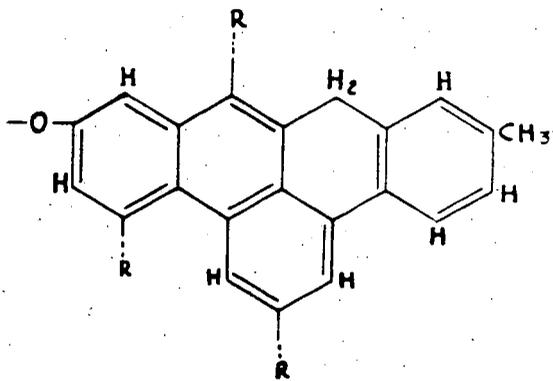
Fig. 1 Inhibition of Tar Formation and Fixation of Additional Carbon in Char consequent on Varying Degrees of Dehydrogenation.



I
C=67.6%



II
C=79.3%



III A
C=91.0%

Fig. 2

Hypothetical model Unit illustrating its Transition from the stage of Lignites to High Rank Bituminous Coal.

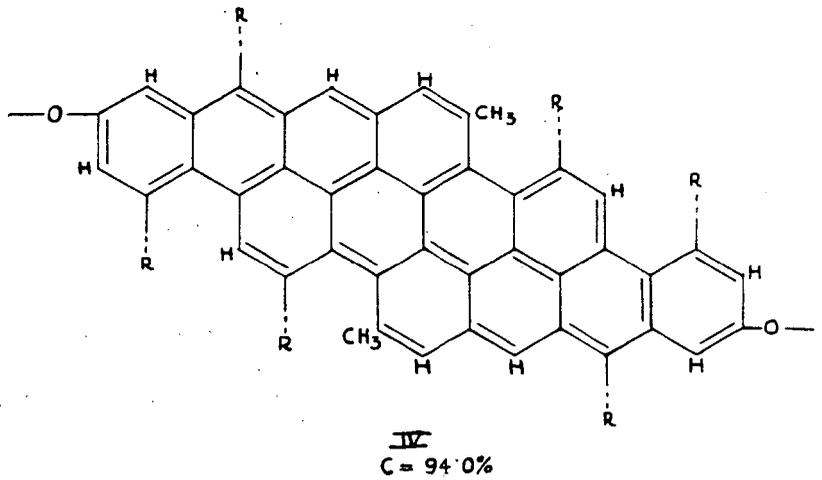
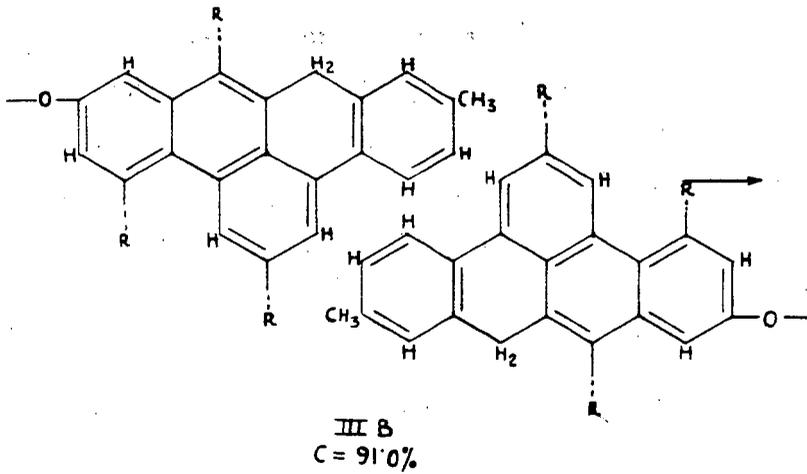


Fig. 3 Hypothetical Model Units depicting the Formation of Anthracite from the Stage of High Rank Bituminous Coal.

Model IV : Empirical formula : $C_{44}H_{16}O_{0.7}N_{0.5}$
Unit wt. = 562.2, C = 94.0, H = 2.8
N = 1.2, O = 2.0, $f_a = 0.95$.

Typical analysis of anthracite, C = 94.3, H = 3.0, N = 1.0,
O = 1.7

Molecular Weights of Humic Acids in Sulfolane

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INTRODUCTION

Recent viscosimetric studies by Mukherjee and Lahiri (1) and by Rajalakshmi et al. (2) offer convincing evidence that humic acids behave as polyelectrolytes. Since this behaviour is fundamentally inconsistent with previously reported molecular weights - which range from 160 to 700 when measured cryoscopically in catechol or acetamide (3, 4) - re-examination of the molecular weight of humic acids appears to be fully warranted.

The difficulties inherent in such a study are formidable and have been discussed by several investigators (1, 2, 3, 5, 6, 7). For example, Yokokawa (7) notes that molecular weight determinations on solutions of humic acids in acetamide amount to little more than an estimate of the proportion of functional groups. From conductivity measurements and parallel cryoscopic determinations on potassium humates in aqueous solutions, he concluded that some of his preparations had molecular weights in the thousands rather than in the hundreds. Osmotic pressure techniques (8) have likewise yielded molecular weights estimated in the range of 1200-2200. And Dryden (9), using semi-quantitative diffusion measurements, concluded that some 90% of the ethylene diamine extract of coal* has a molecular weight in excess of 6000.

Some of the specific problems associated with cryoscopic measurements on humic acids emerge from an analysis of published data, e.g. those of Polansky and Kinney (4). A particularly noteworthy feature of these data is the variation of the cryoscopic constant K with solute concentration, which suggests some form of molecular association, dissociation or solvation in acetamide. Fig. 1, which reproduces typical results obtained in this laboratory with 1, 2, 4, 5 - benzene tetracarboxylic acid in acetamide, may serve to illustrate the general effect: the curvilinear shape of the graph suggests complex behaviour including probable ionization at low molality and solvation at higher molalities (10). A second difficulty to be overcome in molecular weight determinations by cryoscopic means relates to the removal of water without simultaneous chemical change and loss of solubility. Finally, it should be recognized that humic acid preparations, particularly those obtained by oxidative degradation of coal, may show a wide distribution of molecular weights. In order to attach real significance to a number-average molecular weight of such materials, and permit a meaningful comparison of M_n with weight-average molecular weights obtained by other methods, it is, therefore, important to undertake appropriate fractionation of the sample.

To a considerable degree, however, it appears that most of these difficulties can now be eliminated. Burwell and Langford (11) recently suggested that tetramethylene sulfone (sulfolane) because of its low latent heat of fusion and resulting high cryoscopic constant (K) might represent a good medium for the cryoscopic determination of molecular weights, and this suggestion seems to have real merit. It has been found that sulfolane is not only a reasonably good solvent for humic acids, but that it behaves as an essentially ideal solvent for a variety of solids with normally quite distinct associative and dissociative tendencies. The detailed findings are reported below.

*While humic acids need not necessarily have similar molecular weights, some preparations or fractions of humic acids prepared from coal might be expected to be in such a range.

EXPERIMENTAL

Materials

Acetamide used was Fisher certified reagent dried in an oven at 60°C/20 mm. for 24 hours and stored in a desiccator over phosphorous pentoxide until used.

Sulfolane was the product of Shell Development Co., Emeryville, California. This material was distilled from powdered sodium hydroxide under reduced pressure and the portion boiling at about 100°C/0.01 mm. retained for use.

1, 2, 4, 5 - Benzene tetracarboxylic acid (mp. 177-8°C) was obtained from Aldrich Chemical Co., dried and stored in the same manner as the acetamide.

β -Naphthalene sulfonic acid was recrystallized from an alcohol-benzene mixture as the hydrate, but no attempt was made to dry it as this was accomplished in the course of its use (see below).

Humic acids were derived from two sources. One was commercially available Baroid Carbonox, a naturally oxidized (i.e. weathered) North Dakota Lignite, and the other a weathered sub-bituminous coal from the upper seam at Sheerness, Alberta. Each was extracted with sodium hydroxide solution, filtered, precipitated with hydrochloric acid, washed until nearly free of salts, and finally electro-dialyzed until the current had fallen to a minimum.

Cryoscopic Procedure

Cryoscopic measurements were carried out in an apparatus similar to that employed by Smith and Howard (3) and Polansky and Kinney (4) and flooded with purified nitrogen to exclude moisture. Measurements in acetamide were performed following the procedure of Polansky and Kinney (4). When sulfolane (mp. 28.2°C) was used, the bath was slightly cooled by a cold water-coil in order to permit operation of the heater-controller.

Materials such as biphenyl and benzoic acid, which did not present a significant drying problem, were weighed out and directly dissolved in sulfolane for cryoscopic constant determinations. In the case of β -naphthalene sulfonic acid, it was found more convenient to dissolve a roughly weighed sample in more sulfolane than actually required and subsequently to distill off part of the solvent (and all water) at 100°C/0.01 mm. The acid concentration was then determined by titrating an aliquot of the solution with standard alkali.

Molecular Weight Determinations

Since humic acids did not dissolve rapidly in sulfolane, and since it was also necessary to use a drying technique on the resultant solution, it was found most convenient to dissolve the sample (300-500 mg.) in 20-30 ml. of a 3:1 acetone-water mixture, add this to 55-60 ml. sulfolane, filter the mixture repeatedly (5-8 times) through a Seitz bacterial (sterilizing) filter (previously found adequate to render the filtrates optically void) and remove the acetone, water and some sulfolane under reduced pressure (with the final conditions not exceeding 100°C/0.01 mm.). After determination of the freezing point depression, the weighed sulfolane solution was diluted with sufficient benzene to precipitate the humic acid, which was then removed by centrifugation, washed free of sulfolane with more benzene, dried and weighed. In the case of lower molecular weight humic acids, a significant amount of material remained in solution in the mother liquor after the first precipitation; this was recovered by concentrating the solution to a very small

volume under reduced pressure and further dilution with benzene. The precipitate was then treated like the first one and added to it.

The techniques described above for sample drying eliminate the water problem entirely. Because of the large difference in the boiling points of sulfolane (278°C/700 mm.; 100°C/0.01 mm.), and water it was possible to remove water entirely by vacuum distillation prior to the freezing point determination. Caution is, however, necessary in the case of humic acid solutions, whose exposure to temperatures much in excess of 100°C results in the formation of anhydrides with consequent changes in solubility. This aspect will be discussed in another paper.

The Cryoscopic Constant of Sulfolane

The average cryoscopic constant of sulfolane ($K = 65.5^\circ\text{C}/\text{mole}/\text{kg.}$), which agreed well with the figure of $66.2 \pm 0.6^\circ\text{C}/\text{mole}/\text{kg.}$ quoted by Burwell and Langford (11), was established by measuring the freezing point depression (ΔT) for various concentrations of benzoic acid, biphenyl and β -naphthalene sulfonic acid. The results are shown in Fig. 2 and indicate that the constant is valid for use with materials of vastly differing dissociative and associative potentialities.

Fractionation

Humic acids were prepared for molecular weight determination by two fractionation techniques, one involving successive extractions with an alcohol-benzene mixture and the other precipitation from sulfolane solution with benzene as the non-solvent. In the former case, 14.18 g. of Carbonox humic acid (average m.w. 1570) was extracted in a soxhlet apparatus with the azeotrope of alcohol and benzene for 25 days; the results are set out in Table I. Infrared spectra were obtained for each fraction, typical ones being shown in Fig. 3. Apart from small variations in the carbonyl band, which are listed in Table I, all spectra were similar.

In the second method, a 10 g. sample of Sheerness, Alberta, humic acid (average m.w. 4600) was dissolved in 200 ml. of sulfolane by the acetone-water technique described above, filtered through a Seitz (sterilizing) filter until optically void and then diluted with 130 ml. of benzene. The resultant precipitate was removed in the centrifuge, washed with benzene and dried at 60°C/20 mm.

The remaining solution was treated with more benzene to produce a second precipitate and so on. The general procedure is summarized in Table II.

DISCUSSION

A number of factors combine to make sulfolane a peculiarly attractive solvent for cryoscopic measurements. Its cryoscopic constant (65.5 degrees per mole) is very much higher than those of other readily available solvents (thus permitting accurate measurements of freezing point depressions at low solute concentrations). It has good solvent properties for humic acids and a wide variety of simpler materials. It permits effective drying of hygroscopic materials and also allows their concentration to be determined quantitatively after drying. And most important, sulfolane appears to eliminate disturbing effects arising from association or dissociation of solute molecules.

Fig. 2 supports this last contention by showing that sulfolane exhibits ideal cryoscopic behaviour - cf. Spauschus (10) - with K values independent of concentration for benzoic acid, β -naphthalene sulfonic acid and biphenyl. It should be emphasized that this constancy of K

Table I
 Fractionation of Carbonox Humic Acid with Alcohol-Benzene
 (Average molecular weight of starting material 1570)

Fraction	Incremental Extraction Time	Extract (% of original sample)	%C*	%H	E ^{0.4%} ** 0.09 cm.	Molecular Weight
1	2 hours	8.21			19.4	600
2	3 hours	6.77	56.98	4.39	23.9	970
3	12 hours	24.75	57.46	4.26	21.0	1546
4	48 hours	6.19	58.30	4.30	18.2	
5	12 hours	1.61	57.84	3.95		
6	24 hours	1.01	57.32	4.40	18.3	
7	24 hours	0.95	57.76	4.19	19.9	
8	4 days	5.39	58.40	4.02	18.3	5370
9	7 days	1.07	58.96	4.04	19.1	
10	7 days	1.01	58.78	4.15	19.3	
Residue		45.46	57.91	3.19	13.4	
Total		102.42				

* Carbon and hydrogen analyses were performed by Micro-Tech Laboratories, 8000 Lincoln Avenue, Skokie, Illinois.

** E^{0.4%}_{0.09 cm.} = extinction coefficient of carbonyl band (1720 cm.⁻¹)
 (determined in KBr)

Table II
 Fractionation of Sheerness Humic Acids by Precipitation from Sulfolane (200 ml.)
 (Average molecular weight of starting material 4600)

Fraction	Incremental Volume of Benzene added	Precipitate (% of original sample)	%C	%H	Molecular Weight
1	130	66.13			See note A
2	100	9.98	56.8	4.58	
3	100	3.77	58.6	4.43	1, 260
4	400	0.64	57.95	4.90	
5	material remaining in solution	2.21	59.37	4.66	460
Total		82.72*			

* A material balance shows that some 17% of this initial sample were lost during fractionation. We are inclined to the view that this loss accrues from partial peptization of this humic acid and elimination of the peptized material with the washings.

Note A

Fraction 1 was dissolved in 200 ml. of sulfolane and 100 ml. benzene added. The fraction which precipitated (3.55 g.) had molecular weight 8,500, and contained 52.1% C, 4.00% H.

would not be observed if the carboxylic or sulfonic acid groups were to ionize or associate in sulfolane solution. Burwell and Langford (11) cite three other examples of this ideality in sulfolane solution, the most interesting from the standpoint of the present study being acetic acid, which they describe as behaving as a monomer when dissolved in sulfolane.

That sulfolane solutions of humic acid also yield concentration-independent results is illustrated by the fact that the observed molecular weights of a humic acid preparation over the 0.01-0.005 molal range varied only between 1520 and 1560. This variation is considered to lie within the normal experimental error incurred in the measurement.

On the assumption that association would be at a maximum in the solid state and at a minimum in dilute solution, further evidence for the absence of association in sulfolane solution can be derived from infrared data, in particular from analysis of the carbonyl stretching frequency between 1733 and 1695 cm.^{-1} and from the -OH stretching frequency between 3700 and 2500 cm.^{-1} .

When benzoic acid is examined in a Nujol mull, the carbonyl absorption band appears at 1695 cm.^{-1} , while a 0.5% solution in sulfolane shows this band at 1733 cm.^{-1} . Since such a shift is known to be associated with a change from the dimeric to the monomeric form of the acid (12), molecular association in sulfolane solution would imply a progressive shift of the carbonyl band towards 1695 cm.^{-1} or the appearance of a second band there (12) as the solute concentration increases. This does not occur: even for a 5% solution of benzoic acid in sulfolane, the carbonyl absorption was found to remain at 1733 cm.^{-1} .

The same conclusion can be derived from the position of the -OH stretching band. According to Bellamy (13) and Flett (12) absorption between 2700 and 2500 cm.^{-1} is commonly taken as evidence for the existence of dimeric carboxylic acid groups. This is observed in the solid state spectrum of benzoic acid, but is absent in spectra of sulfolane solutions. The -OH band which did appear occurred at 3226 cm.^{-1} . This is too low for completely free -OH (3700-3500 cm.^{-1}) but is in the region of weak hydrogen bonding. Since the cryoscopic results showed no variation with concentration, and since the carbonyl absorption showed no indication of dimerization of the benzoic acid molecules, this shift does not appear to be caused by inter-action between the acid molecules. It is possible that the -OH group is hydrogen-bonded to an oxygen atom of the sulfolane, cf. Jones (14). This would remove some of the solvent molecules from that role and make them in effect part of the solute. However, over the concentration range here studied this has been calculated to exert a negligible influence on the effective concentration.

The unsuitability of acetamide as a cryoscopic solvent is borne out by the variation of its cryoscopic constant (determined with 1, 2, 4, 5 - benzene tetracarboxylic acid solute) with solute concentration (Fig. 1). Spauschus (10) reported similar behaviour for high molecular weight esters in benzene and discussed the large departure from ideality in the region of low concentration. Assuming that a similar behaviour to that seen here for benzene tetracarboxylic acid would be exhibited by humic acids in acetamide solution, it is likely that previously reported measurements were carried out in the region of large deviations from ideality (below 0.03 molal), since the materials used probably had number average molecular weights in excess of 1000.

Further evidence for the unsuitability of acetamide for cryoscopic work is offered by Magne and Skau (15) who note that the molar depressions of closely related fatty acids in acetamide vary widely. They suggest that differing degrees of dissociation of the molar complexes of these materials with acetamide may explain this phenomenon.

Considerable errors would also be introduced if insufficiently dried humic acids were used. For example, 1% water in a material of m.w. 1500 would double ΔT . The same impurity would result in a 3-fold increase in ΔT if the molecular weight were 5000.

In order to show that the humic acids here studied were also subject to these uncertainties in acetamide, a sample of molecular weight 970 (determined in sulfolane) was found to give a value of 230 in acetamide (using $K = 3.58$).

The fractionation procedures described above provided samples which, from several stand-points, are more appropriate for molecular weight studies than an aggregate, unfractionated sample. For example, in order to compare values obtained by number and weight average techniques, as small a range of molecular sizes as possible is desirable.

There is reason to believe that further fractionation is possible and that the molecular weights of humic acids may extend well beyond the upper limit reported here. The method adopted in this study is limited by the fact that acids of high equivalent weight and/or very high molecular weight are difficultly soluble in sulfolane.

In the case of fractionation by extraction with an alcohol-benzene mixture, attempts to determine the molecular weight of the residue encountered difficulties. The sample would only incompletely dissolve in either acetone-water or in this mixture plus sulfolane, and each attempted molecular weight determination accordingly resulted in different ΔT 's with calculated molecular weights ranging from 985 to 1510. We venture to suggest that this behaviour is intimately connected with particular properties of the residue. While a residue fraction with an apparent molecular weight of 985 was shown by sodium aminoethoxide titration to have an equivalent weight of 240, previously separated alcohol-benzene soluble fractions, irrespective of their molecular weights, had equivalent weights of about 140. It is, therefore, reasoned that the residual material includes both high and low molecular weight fractions characterized by a relative lack of polarity. This view is consistent with the low carbonyl extinction coefficient of $E_{0.09}^{0.4\%} = 13.4$ for the whole residue as compared with an average of $E_{0.09}^{0.4\%} = 19.6$ for the soluble fractions.

It has thus been shown that the molecular weights of humic acids dissolved in sulfolane, and thoroughly freed from water, can be determined satisfactorily by the cryoscopic method. The resultant measurements appear to have resolved the apparent inconsistencies between previously determined cryoscopic values and those obtained by other methods.

Acknowledgment

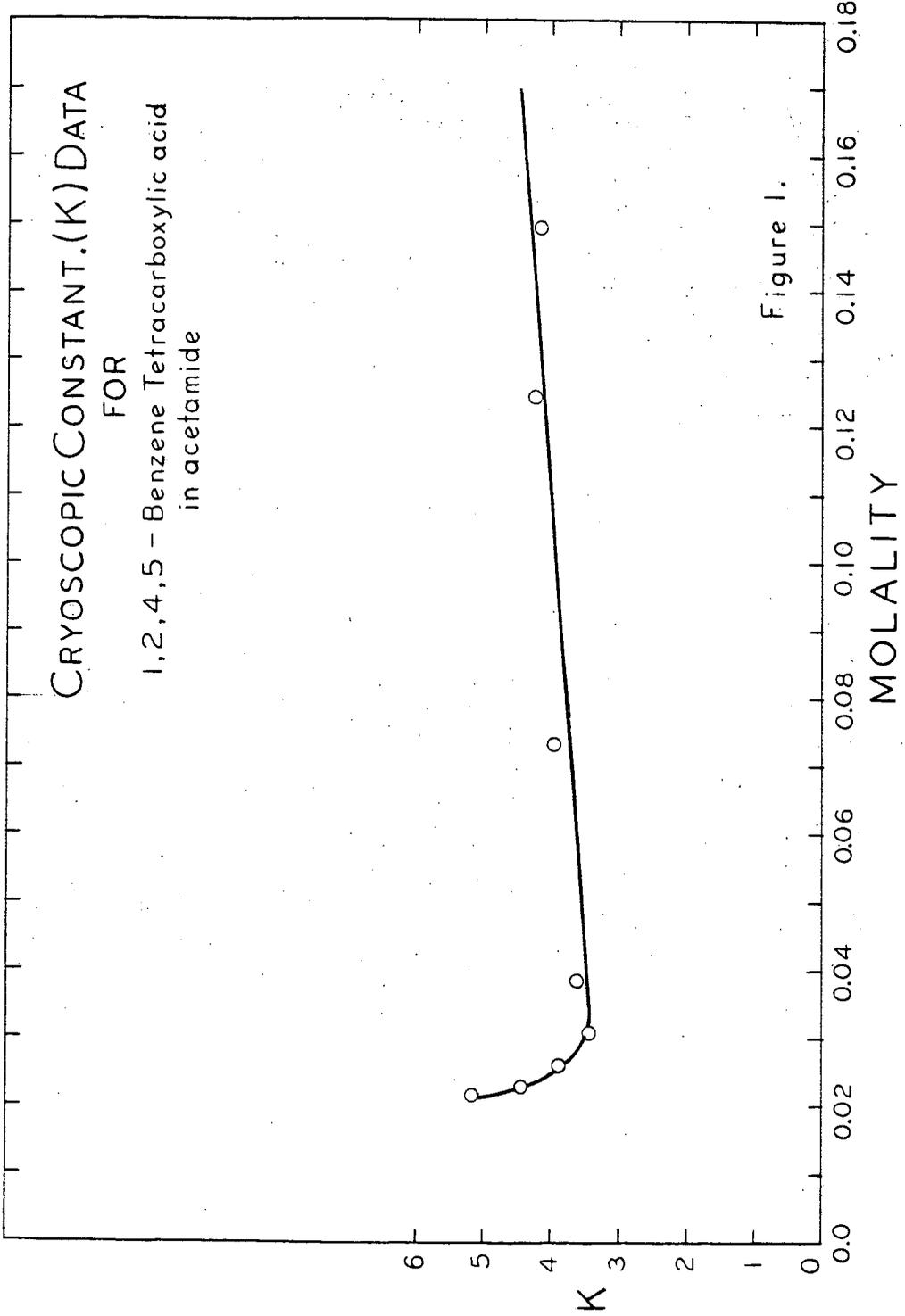
The authors wish to express their thanks to Drs. H. W. Habgood and N. Berkowitz for their assistance and encouragement throughout this work.

Thanks are also extended to the Shell Development Co. of Emeryville, California, for samples of sulfolane, with which this work was begun.

References

- (1) Mukherjee, P.N., Lahiri, A., *J. Colloid Sci.*, 11, 240 (1956).
- (2) Rajalakshmi, N., Sivarajan, S.R., Vold, R.D., *J. Colloid Sci.*, 14, 419 (1959).
- (3) Smith, R.C., Howear, H.C., *J. Am. Chem. Soc.*, 57, 512 (1935); *ibid.* 58, 740 (1936).
- (4) Polansky, T.S., Kinney, C.R., *Fuel*, 31, 409 (1952).

- (5) Howard, H. C., "Chemistry of Coal Utilization", H. H. Lowry, ed., Vol. I, John Wiley & Sons, Inc., New York, 1945, p. 352.
- (6) Yohe, G. R., Illinois State Geol. Survey, Rep. Invest. No. 207, 21 (1953).
- (7) Yokokawa, C., "Chemical Constitution of Coal", Dept. of Fuel Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, 1958, p. 10.
- (8) Wynne-Jones, W. F. K., Blayden, H. E., Shaw, F., Brennstoff Chem. 32, 201 (1952).
- (9) Dryden, I. G. C., Fuel, 31, 176 (1952).
- (10) Spauschus, H. O., J. Chem. and Eng. Data 5, 201 (1960).
- (11) Burwell, R. L. Jr., Langford, C. H., J. Am. Chem. Soc., 81, 3799 (1959).
- (12) Flett, M. St. C., J. Chem. Soc., 962 (1951).
- (13) Bellamy, L. J., "The Infrared Spectra of Complex Molecules", John Wiley & Sons, Inc., New York, 1954, p. 142.
- (14) Jones, R.N., "Chemical Applications of Spectroscopy", W. West, ed., Interscience Publishers, Inc., New York, 1956, p. 427.
- (15) Magne, F. C., Skau, E. L., J. Am. Chem. Soc., 74, 2628 (1952).



CRYOSCOPIC CONSTANT.(K) DATA FOR

- Benzoic Acid O
- Biphenyl..... x
- Naphthalene Sulfonic Acid.Δ
- in sulfolane

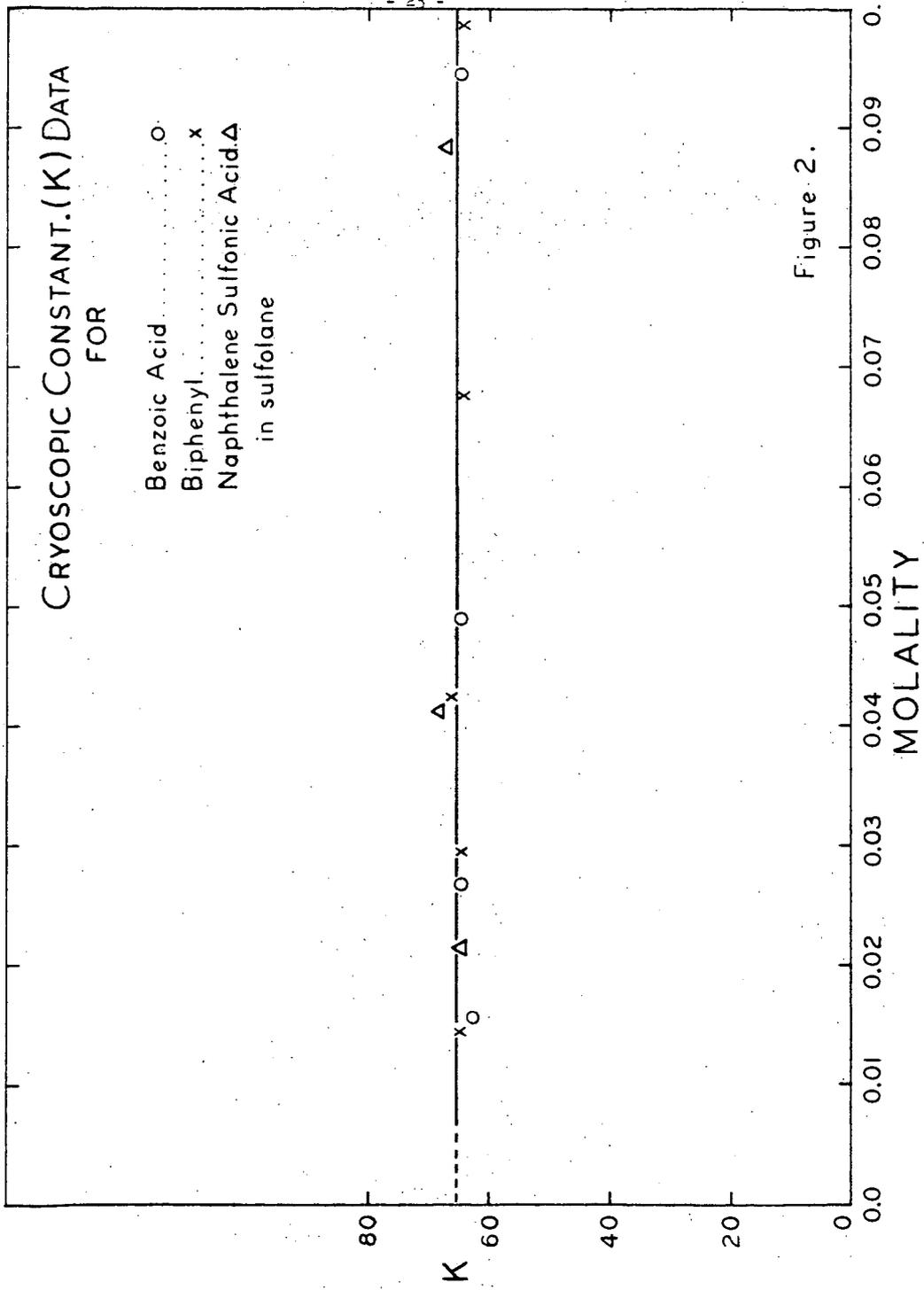
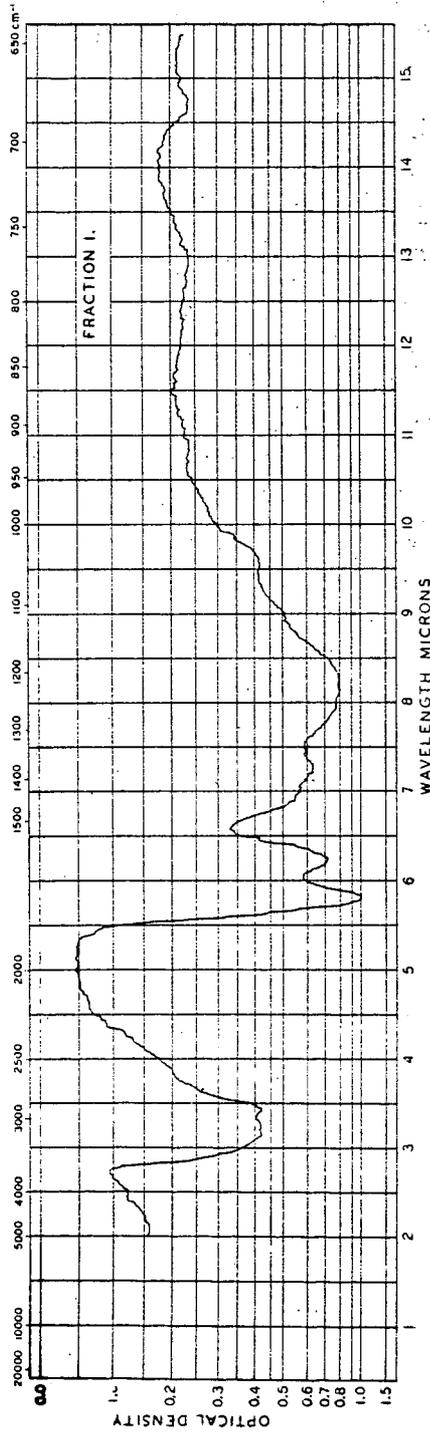
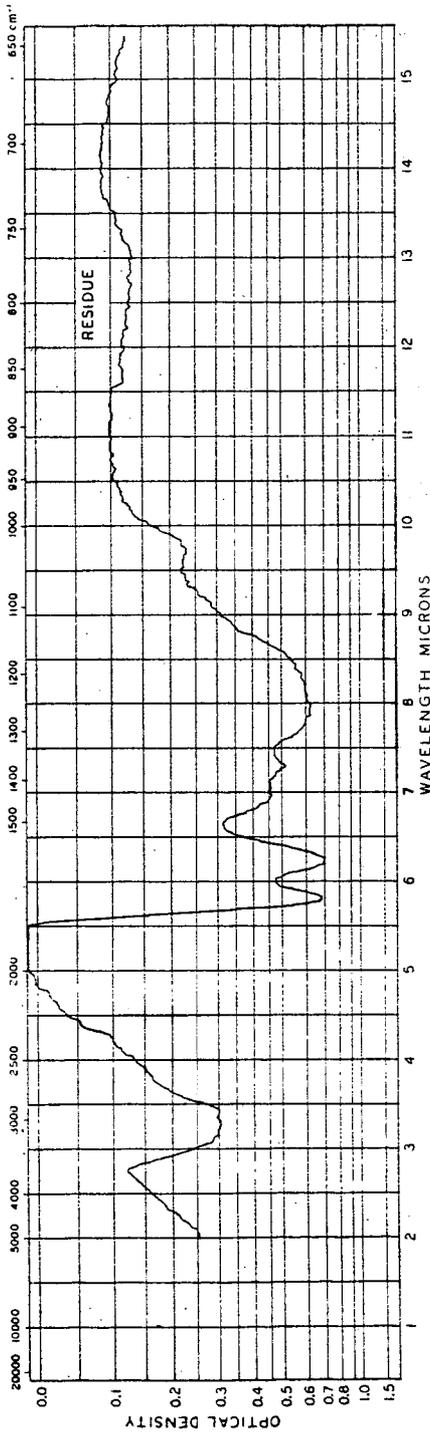


Figure 2.

Figure 3.



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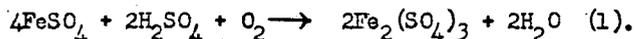
THE ELIMINATION OF SULFUR FROM COAL BY MICROBIAL ACTION

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INTRODUCTION

The sulfur present in coals in the form of iron pyrites is of interest for at least three reasons: (1) as a contaminant in coals used for the preparation of metallurgical coke, (2) as a contaminant in coal used for power purposes, and (3) as the ultimate source of the sulfur appearing as sulfuric acid in the effluents of mines producing acid waters. Certain bacteria are known which, when grown in the presence of pyrites, copper sulfides, or molybdenum sulfides, catalyze the formation of sulfuric acid with concurrent release of the metallic cation in a soluble form (1-3). Microbiological studies have thus far shown that one of these organisms, Ferrobacillus ferrooxidans, catalyzes the reaction:



Experimentally, it has been demonstrated that iron- and/or sulfur-oxidizing organisms catalyze the production of acid and soluble iron from coal sulfur ball material (1) or from the sulfidic constituents of finely ground coal (2). It is therefore believed that a thorough microbiological study of the oxidation of pyrites would not only clarify the role microorganisms play in the process but conceivably, through strain selection, determination of nutritional requirements, and control of the physical environment, a method for the removal of pyritic sulfur from coal by a microbial process might be devised. Such a study would also clarify the role of microorganisms in the formation of acid mine waters. A related problem, the treatment of acid waters by a microbial process utilizing the unique abilities of the bacterium Desulfovibrio desulfuricans to reduce sulfates to elemental sulfur and/or sulfide, might possibly be carried out by extension of the aforementioned line of attack.

There is very little known concerning the activities and abilities of microbes which may attack organic sulfur-containing compounds other than the naturally-occurring amino acids and vitamins. A study of the oxidation of aromatic sulfur compounds by microorganisms has been initiated in the hope of finding a way of eliminating organic sulfur from coal.

EXPERIMENTAL

A. Materials and Methods

1. Stock Cultures. Stock cultures of the following autotrophic strains of bacteria have been obtained from the Syracuse University Culture Collection. (a) Ferrobacillus ferrooxidans - Culture capable of oxidizing ferrous iron to ferric state. Maintained on medium 9K (see below) containing FeSO_4 as energy source. (b) Thiobacillus thiooxidans - Culture capable of oxidizing elemental sulfur to sulfate. Maintained on medium 9KS^o and ThS. Strains of the heterotrophic Pseudomonas aeruginosa were those reported previously (4).

2. Media Used. The following media are used for the routine culture of the above bacteria and/or were used in the screening studies with the acid mine water samples:

(a) Medium 9K (5) for iron bacteria: Solution A - Basal Salts - $(\text{NH}_4)_2\text{SO}_4$, 3.00 g.; KCl, 0.10 g.; K_2HPO_4 , .50 g.; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, .50 g.; $\text{Ca}(\text{NO}_3)_2$, .01 g.; $10\text{NH}_2\text{SO}_4$, .10 ml.; distilled water, 700 ml. Solution B - Energy Source - $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 300 ml. of a 14.74% (w/v) solution is added to 700 ml. of the basal salts solution to make one liter of medium. The pH is 3.0 to 3.6 without further adjustment.

(b) Medium 9KS 0 - For sulfur oxidizers. As in (a) with 1-2% elemental sulfur (sterilized separately by autoclaving at 100° C. for 3 hours) replacing the iron salt as source of energy; pH adjusted to 3.5.

(c) Medium 9KS - For sulfur oxidizers. As in (a) with 1.0% Na_2S as $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) as source of energy.

(d) Medium 9KP - For iron or sulfur oxidizers. As in (a) with 5% pyrite (Sample No. PS-34-6008 obtained in a pulverized form from Bituminous Coal Research, Inc.) as source of energy. This medium was prepared at two pH levels: 3.5 and 7.0.

(e) Medium ThS - For sulfur oxidizers (6).

(f) Medium SS-1 - For sulfate reducers (6).

3. Bacteriological Methods

Standard plate count methods for numbers of heterotrophs were used with nutrient agar (Difco) or Czapek's medium in Petri plates. Tubes of media for determination of autotrophs were examined visually or subjected to microscopic examination. Liquid media for isolation of sulfate-reducing bacteria were prepared in Virtis anaerobic tubes. Agar media were prepared as deep tubes or drawn into foot lengths of 4 mm. OD pyrex tubing. The ends of the latter were sealed with paraffin wax. Growth in these tubes is recognized visually by the production of a black precipitate of iron sulfide.

4. Cultures for Manometric Experiments

Preparations of resting cells of iron and sulfur oxidizers were made according to the methods of Silverman and Lundgren (5,7); heterotrophs were grown as previously noted (4). The Warburg apparatus was used in the conventional manner to measure oxygen uptake (8). Description of the flask contents for any particular experiment is found in the figure legend.

5. Determinations of iron were made by the colorimetric o-phenanthroline method, as described in ASTM methods. A standard curve for concentrations between 20 to 240 μ of iron was prepared, reading optical density at 500 m μ in a Beckman Spectronic 20 spectrophotometer-colorimeter.

6. The source, description, and analyses of the pyritic materials is shown in Table I. The material was used as originally received (passing 65 mesh) or ground in an agate mortar to pass a 325-mesh screen. The crystalline form of the sulfuritic material in these samples was verified as pyrite by X-ray diffraction. In addition, samples of museum-grade pyrite and marcasite ground to -325 mesh were used.

Table I. Analyses of pyritic material

Sample No.	Description and source	Percent pyrite
29	Waste material—pyrite concentrate from coal from Tabo bed, Power Mine, Montrose, Henry County, Missouri.	77.0
30	Waste material—pyrite concentrate from Illinois #6 coal, Peabody #10 Mine; Christian County, Illinois.	60.0
34	Pyrite concretion (sulfur ball) from Pittsburgh bed, Osage #3 Mine, Monongalia County, West Virginia.	54.4 ^a
35	Pyrite concretion (sulfur ball) from Meigs Creek #9 coal, Bradford #1 Mine, Harrison County, Ohio.	74.5

a Contained 13.8% CaCO₃ in the form of calcite.

B. Procedures and Results

Samples of acid mine muds were obtained from shafts of the Hutchinson Mine near Irwin, Pa., and waters and bottom muds from the point of exit of the mine waters, and the acid swamp these waters form (Marchand Pool). The pool empties into Sewickley Creek, from which samples were obtained upstream from the pool entry. The samples collected are listed in Table II.

Table II. Samples of acid mine waters and related materials

Sample No.	Source	Description	pH
1	Hutchinson Mine	Acid gob (yellow mud)	2.9
2	Hutchinson Mine	Alkaline gob (orange mud)	6.3
3	Sewickley Creek,	Surface water	3.8
4	upstream from	Bottom mud	4.1
5	Marchand Pool	Green algal streamer	too small
6	Exit point of	Surface water (clear)	5.3
7	acid waters	Bottom water (clear)	5.5
8	from mine	Bottom mud (orange)	4.9
9	Junction of mine water and Marchand Pool	Bottom water (clear)	5.7
10	Marchand Pool	Top scum (oily)	4.6
11	Marchand Pool	Surface water (orange)	5.7
12	Marchand Pool	Bottom mud (orange)	5.8
13	Marchand Pool	Bottom water (green-brown)	4.9
14	Marchand Pool	Bottom water (green)	5.0
15	Pool spillway to Sewickley Creek	Bottom water (green)	5.0

After collection, the samples, were examined microscopically. The presence of viable bacteria was noted in samples 1, 2, 4, and 12. Sample 5 contained not only bacteria but green streamers recognizable as algae; numerous protozoa and planarians were present. The samples were used to inoculate duplicate tubes of culture media.

The various media were incubated at room temperature with the exception of 4 mm. OD pyrex tubes of agar medium SS-1, which were incubated at 30°C. Tubes of medium 9KS^o were incubated on the shaker. The subcultures to the various media were observed daily and examined microscopically as required.

Observations made on the various media after one week of incubation at room temperature are summarized in Table III. Microscopic observations were made on the pyrite and iron media (9KP and 9K), although in some cases, simple visual examination was sufficient to recognize the deep red-orange precipitate formed by iron oxidation.

Table III. Growth in various culture media one week^a after inoculation with acid mine water samples

Growth in media containing the energy sources designated							
Sample	S ⁼	Pyrite	Pyrite	Fe ⁺⁺	SO ₄ ⁼ (anaerobic tubes)	SO ₄ ⁼ (capillary tubes)	S
1	-	+	+	+	-	-	+
2	-			+	+	+	+
3	-			+			+
4	-	+	+	+	+	+	+
5	+			+	-	-	+
6	-	-	-	-			+
7	-	+	+	+			+
8	+	+	+	+	+	+	+
9	-	-	-	-			-
10	-			+			-
11	-			+			+
12	+	+	+	+	+	+	+
13	-	-	-	-	-	-	-
14	-			-	-	-	+
15	-	-	-	-			+

a Medium 9KS^o examined after 10 days of shaking.

The cultures were carried through serial transfer on the appropriate media; determination of growth was made by a combination of microscopic examination and visual inspection.

The activity of resting cells of Ferrobacillus ferrooxidans on pyrites was tested by means of the Warburg technique. This technique is excellent for the determination of: (1) the ability of selected cultures to oxidize pyrite, (2) differences in the susceptibility of the various pyrites to oxidation, and (3) the physiology of pyrite oxidation by bacteria in short-term experiments. Pyrite samples (65 mesh) were weighed and placed in the Warburg vessel with sufficient cell suspension (pH 3.5) and water (pH 3.5) to bring the volume to a predetermined value. Cell suspensions for the experiments were adjusted to 0.4 mg. bacterial-N/ml. Oxygen uptake was measured in the conventional manner. Results of two such experiments with concentration of pyrites and cells as variables are shown in Figures 1 and 2. The rate of pyrite oxidation was increased only two-fold by a twenty-fold increase in pyrite concentration with these 65 mesh samples.

A series of Warburg experiments demonstrated the role of particle size of the substrate on oxidation rates. The results (shown in Table IV) demonstrate that reduction in particle size enhanced bacterial action six-fold in the case of the pyrite concretion and 35- to 70-fold when the pyrite concentrates were used as substrates. Oxidation with the bacteria was 20 to 40 times that of the controls for 3 of the 4 pyrites tested.

Table IV. Oxidation of pyritic material of two particle sizes in the presence of Ferrobacillus ferrooxidans

Sample No.	Microliters oxygen taken up in three hours ^a			
	Approximately 65 mesh		Passing through 325 mesh	
	No cells	Cells	No cells	Cells
29	28 ⁺	40	60	1342
30	12	16	51 ⁺	1137
34	23 ⁺	11 ⁺	91	29 ⁺
35	24 ⁺	336	46	2040

a Oxygen uptake/1.2 mg. bacterial-nitrogen/three hours.

+ Apparent evolution of gas.

In separate shaken-flask experiments the release of hydrochloric acid-soluble iron was determined instead of oxygen uptake, as a means of demonstrating oxidation of the pyrites. Results of iron determinations in one such experiment are shown in the following table (Table V). The 25 ml. conical flask used contained 100 mg. of pyritic material, an aliquot of cell suspension containing 0.84 mg. bacterial nitrogen and sufficient H₂SO₄-acidified water, pH 3.5, to bring the total volume to 4.0 ml. After 24 hours, 4.0 ml. of 2.0N HCl was added and the mixture heated 30 minutes on a steam bath. The HCl-soluble iron content of suitable filtered aliquots was determined as given in the section on Methods.

TABLE V. Production of hydrochloric acid-soluble iron from pyritic material in the presence of Ferrobacillus ferrooxidans

Sample No.	Cells	Micrograms HCl-soluble iron released ^a			
		Initial	24 hours	Net	Pyrite oxidized, %
29	+	1024 ^b	4400	3376	9.42
	-	808	1080	272	0.76
30	+	1250	4000	2750	9.34
	-	1034	1376	342	1.22
35	+	3040	7200	4160	11.99
	-	2824	3140	316	0.91

a Production of iron from 100 mg. pyritic material in the presence of 0.84 mg. bacterial-N.

b 216 μ g. Fe were carried over with the cell suspension.

The ability of Thiobacillus thiooxidans to accelerate the oxidation of the pyrite samples was also tested in Warburg experiments. It was found that this organism was unable to accelerate oxidation rates over those of control vessels. The ability of T. thiooxidans and F. ferrooxidans to accelerate oxidation of museum grade samples (large crystals free of inclusions and contaminating materials) of pyrite and marcasite was tested. It was found that both strains attacked the marcasite, Ferrobacillus being more effective; neither culture accelerated the oxidation of museum grade pyrite. Results of these experiments are seen in Table VI.

Table VI. Effect of Thiobacillus thiooxidans or Ferrobacillus ferrooxidans on the oxidation of museum grade sulfide minerals
Microliters oxygen taken up in 3 hours per mg. bacterial-nitrogen

Sample	Cells	Microliters oxygen taken up in 3 hours per mg. bacterial-nitrogen	
		<u>T. thiooxidans</u>	<u>F. ferrooxidans</u>
Pyrite	-	15	38
	+	70 ^a	19 ^a
Marcasite	-	82	209
	+	128	734

a Apparent gas evolution.

Efficacy of use of a mixture of the two strains was also tested. In these Warburg experiments a resting cell suspension of Ferrobacillus was placed in the vessel and oxygen uptake was measured for one hour. At the end of this time the sulfur-oxidizing Thiobacillus was tipped into the reaction mixture. The effect on oxidation of samples 29, 30, 35, and museum grade marcasite was determined. The effect of addition of Thiobacillus is seen in Figure 3.

The rate of oxidation of ferrous iron and elemental sulfur by the strains of Ferrobacillus ferrooxidans and Thiobacillus thiooxidans in use in the experiments has been calculated from the data obtained in the preceding experiments. These are presented in Table VII.

Table VII. Rates of oxidation of ferrous iron and elemental sulfur by Ferrobacillus ferrooxidans and Thiobacillus thiooxidans

Organism	$Q_{O_2} (N)^a$	
	S (1000 μ moles)	Fe ⁺⁺ (500 μ moles)
T. thiooxidans	557	0
F. ferrooxidans	148	3672

a $Q_{O_2} (N)$ represents μ liters oxygen uptake/mg. cell-nitrogen/hour.

Other manometric experiments with polycyclic aromatic hydrocarbon-grown cells of a strain of Pseudomonas aeruginosa were carried out to study the activity of bacteria regarding sulfur-containing organic compounds. It was found that cells grown with phenanthrene as source of carbon would take up more oxygen than cells grown on naphthalene when benzthiophene was provided them as a substrate. Benzthiophene was chosen as a model sulfur containing aromatic of the type thought to be present in coal. If oxygen uptake of both crops with naphthalene as substrate is calculated to a value of 1.0, then uptakes on benzthiophene were: naphthalene-grown, 0.3; phenanthrene-grown, 1.3.

Benzthiophene was provided at a concentration of 3.3 μ moles/ml. At 6.6 μ moles/milliliter, less oxygen was taken up than at the lower concentration. At 3.3 μ moles/ml, addition of benzthiophene to the flask contents served to lower oxygen uptake of cells metabolizing naphthalene and 2-methylnaphthalene (Figure 4). Thus it seems that a competitive inhibition or perhaps simple toxicity of the compound may be evident except in the case of cells grown on or metabolizing phenanthrene (Figure 5).

DISCUSSION OF RESULTS

Results obtained on examination of the microflora of acid mine drainage showed that top waters and rapidly running waters (green) were almost sterile in all cases. The best sources of microorganisms are the muds, which are apparently rich in all forms tested for. The bottom muds (orange) collected at the pool accumulate only where the water is not turbulent or flowing too rapidly. Where water flow is rapid, bottom mud does not accumulate, the orange color of oxidized iron products is absent, and the number of microorganisms present is quite small. In the laboratory, samples of such moving clear water after two weeks of incubation give evidence of iron oxidation (orange precipitate, heavy). The reason for their clarity is probably that they are simply flowing too rapidly for oxidation of iron to occur. Thus, clarity of water is no criterion of its potential yield of ferruginous mud under non-agitated conditions.

The finding that all types of bacteria tested for appear to be present in the samples illustrates that those chemicals present in an environment are usually accompanied by bacteria capable of utilizing them. The importance of these particular types found, in regard to the problems of sulfur removal from coal and treatment of acid mine waters, is as follows:

(1) The same organisms which play a role in the production of acid mine waters, and in whose presence oxidation of large sulfidic concretions, pyrite, and marcasite has been demonstrated are precisely those forms whose abilities must be exploited in any attempt to desulfurize coal by microbiological means.

(2) In any plan for disposal of sulfuric acid microbiologically, the use of anaerobic sulfate-reducing bacteria to convert sulfuric acid to elemental sulfur and/or hydrogen sulfide must be considered. The isolation of such bacteria from the bottom mud samples collected gives hope that strains of these organisms able to tolerate the acid environment necessitated by the use intended can be found or developed. Acid conditions are known not to be optimum for their growth, but their presence in samples 4 and 5 at pHs of 4.1 and 4.9, respectively, indicate they may be more tolerant of acid than previously assumed.

(3) The presence of sulfur oxidizers, iron oxidizers, and sulfate reducers in a given environment (ferruginous mud) indicates that all three forms may participate in a cyclical process for sulfur. Thus, it appears that previous testing of pyrite oxidation with pure cultures of bacteria may not provide the best means possible for carrying out the process. It may well be better to try the natural flora for most efficient activity, although mixed cells of Ferrobacillus and Thiobacillus did not have the desired effect on pyrite (Figure 3).

The manometric studies (Figures 1 and 2) with 65 mesh sample #35 demonstrated that oxygen uptake is significantly greater than that required solely for the oxidation of ferrous iron initially present in the pyrite sample as determined by our extraction procedure.

Significantly higher oxidation rates were obtained when the sulfidic materials were ground to pass 325 mesh (Table IV). The ability of Ferrobacillus to accelerate the oxidation of the pyrite in samples 29 and 30 is encouraging as regards microbial coal desulfurization. These samples are pyrite concentrates from coal. These contain minute crystals of pyrite embedded in the coal with perhaps only one face exposed for oxidation. Yet in the presence of the bacteria oxidation proceeds at a rapid rate as compared to the rates in the absence of the organisms.

Based on the results found in these studies (Tables III-VII, Figures 1-5) certain generalizations regarding microbial processes for coal desulfurization may be drawn. These are that: 1. The rate of pyrite oxidation depends upon available, that is, exposed pyrite. As a corollary to this, the coal must be in a finely divided state in order to expose a maximum of the embedded pyrite. 2. The rate of oxidation of pyrite depends upon the "type" of pyrite present. The word type is used for want of a better description, since X-ray diffraction patterns are identical for the pyrite of samples 29, 30, 34, 35, and museum-grade pyrite.

Only sample #34 and museum-grade pyrite resisted oxidation in the presence of F. ferrooxidans. Sample #34 contained considerable calcite. Preliminary experiments after the calcite had been removed (neutralizing effect of CaCO_3) gave indication of oxidative activity.

The ubiquitous presence of Thiobacillus thiooxidans in acid-mine waters is as yet unexplained. Our results show that only marcasite, a substance rarely present in acid-producing areas, can be attacked by this organism, raising the question of a possible energy source for the organism. The production of free sulfur during the oxidation of pyrite is one explanation. However, the ability of the iron-oxidizing F. ferrooxidans to oxidize elemental sulfur suggests another explanation.

The three organisms found in acid mine waters are listed below together with their proposed energy sources.

<u>Organisms</u>	<u>Energy source</u>
<u>Thiobacillus thiooxidans</u>	Elemental S
<u>Thiobacillus ferrooxidans</u>	Ferrous iron; thiosulfate
<u>Ferrobacillus ferrooxidans</u>	Ferrous iron

The three are morphologically indistinguishable; the chief criteria for their description being energy source. During isolation procedures, it is entirely possible that F. ferrooxidans will grow in an iron medium and be identified as F. ferrooxidans and also be isolated in an elemental S medium and be identified as T. thiooxidans. Thus, F. ferrooxidans may really be a variant of T. thiooxidans and exists in acid-mine waters by virtue of its iron oxidizing capacity. The inability of Thiobacillus thiooxidans to oxidize iron may be due to the loss of adaptive iron-oxidizing enzymes upon growth in elemental sulfur.

The ability of bacteria to accelerate the oxidation of sulfuritic material has been studied primarily by investigators at the Mellon Institute (1) and West Virginia University (9). Their studies involved testing for the production of free iron, sulfate, or increased acidity from insoluble pyrite materials in the presence or absence of bacteria in experiments of long duration. The development of methods and media for the propagation in high yield of the relevant bacteria (5, 7) has enabled us to utilize the manometric method for examining the role of bacteria in the oxidation of pyrites, thus enabling us to accumulate comparable data in a short time. A comparison of the results obtained with those of the Mellon Institute and West Virginia University is given in Table VIII. In general, our findings agree most closely with those of the Mellon Institute.

Table VIII. Acceleration of the rate of oxidation of different pyritic materials by iron- and sulfur-oxidizing bacteria

	<u>Ferrobacillus ferrooxidans</u>			<u>Thiobacillus ferrooxidans</u>			<u>Thiobacillus thiooxidans</u>		
	M.I.	W.V.U.	B.M.	M.I.	W.V.U.	B.M.	M.I.	W.V.U.	B.M.
Sulfur ball	+	N.T. ^a	+	N.T.	+	N.T.	-	+	-
Waste material	N.T.	N.T.	+	N.T.	N.T.	N.T.	N.T.	N.T.	-
Museum-grade marcasite	+	N.T.	+	N.T.	N.T.	N.T.	+	+	+
Museum-grade pyrite	-	N.T.	-	N.T.	+	N.T.	-	N.T.	-

a N.T. = not tested.

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Literature Cited

- (1) Leathen, W.W., Microbiological Studies of Bituminous Coal Mine Drainage. Mellon Inst. of Ind. Res. Special Summary Report (1952) 64 pp.
- (2) Ashmead, D., Influence of Bacteria in the Formation of Acid Mine Waters. Coll. Guard., 190, 694-698 (1955).
- (3) Bryner, L.C., and Anderson R., Microorganisms in Leaching Sulfide Minerals. Ind. Eng. Chem., 49, 1721-1723 (1957).
- (4) Rogoff, M.H., and Wender, I., Methyl-naphthalene Oxidation of Pseudomonads. Jour. Bact., 77, 783-788 (1959).
- (5) Silverman, M.P., and Lundgren, D. G., Studies of the Chemoautotrophic Iron Bacterium Ferrobacillus ferrooxidans I. Jour. Bact., 77, 642-647 (1959).
- (6) Starkey, R.L., Isolation of Some Bacteria Which Oxidize Thiosulfate. Soil Sci., 39, 197-219 (1935).
- (7) Silverman, M.P., and Lundgren, D.G., Studies on the Chemoautotrophic Iron Bacterium Ferrobacillus ferrooxidans II. Manometric Studies. Jour. Bact., 78, 326-331 (1959).
- (8) Umbreit, W.W., Burris, R.H., and Stauffer, J.F., Manometric Techniques, (1957), Burgess Publishing Co., Minneapolis.
- (9) Temple, K.L., and Koehler, W.A., Drainage from Bituminous Coal Mines. West Virginia Univ. Bull. No. 25, 1954.

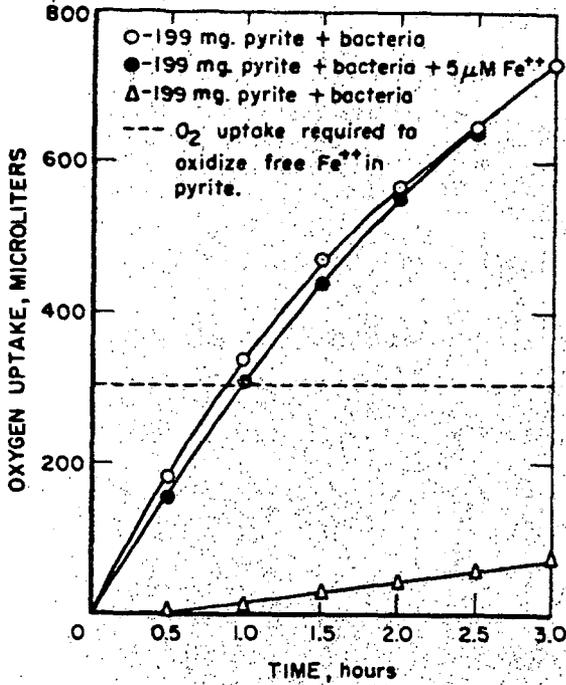


Figure 1.-Oxidation of sulfur ball (199 mg.) by *Ferrobacillus ferrooxidans*.

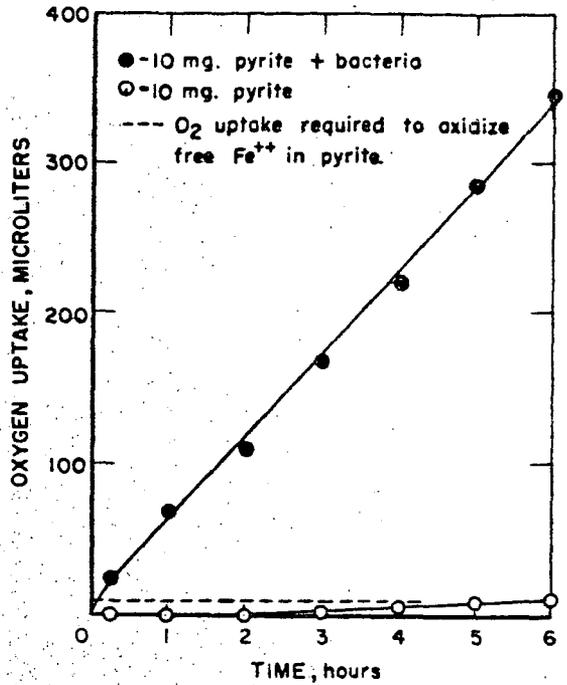


Figure 2.-Oxidation of sulfur ball (10 mg.) by *Ferrobacillus ferrooxidans*.

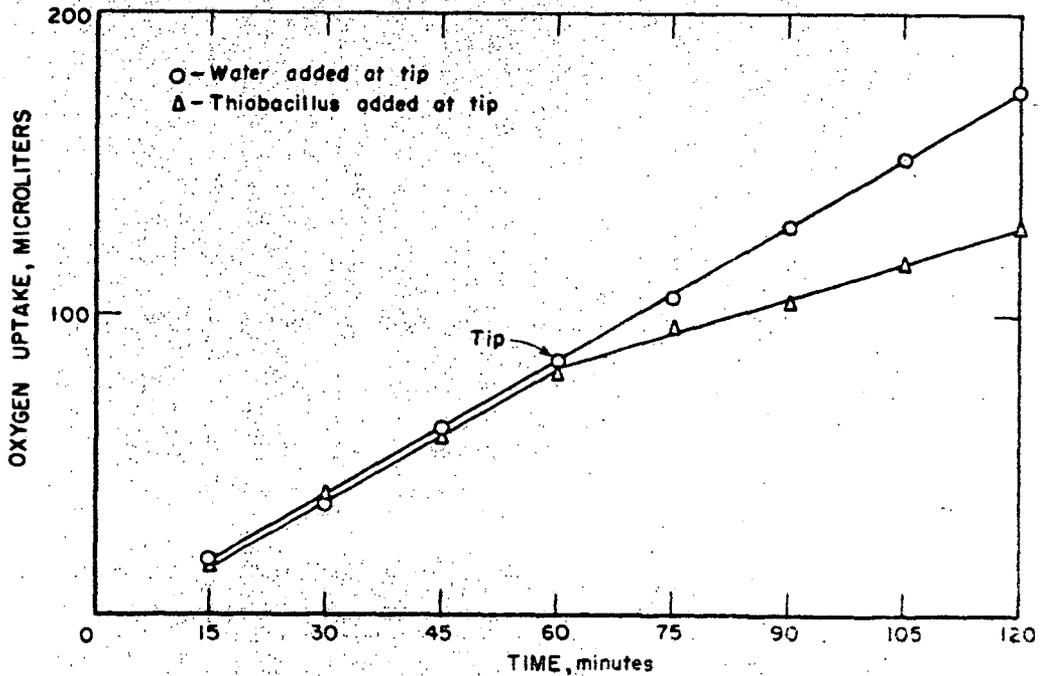


Figure 3.-Oxidation of sulfur ball (20mg.) by *Ferrobacillus ferrooxidans*.

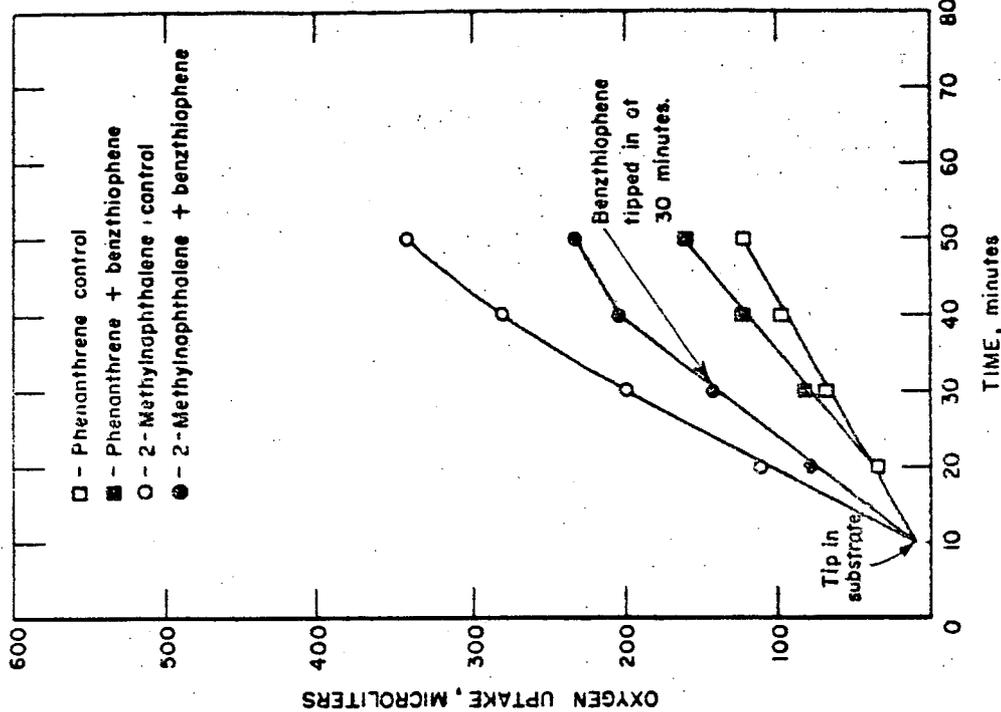


Figure 5.-Oxidation of aromatic hydrocarbons by strain PM-1.

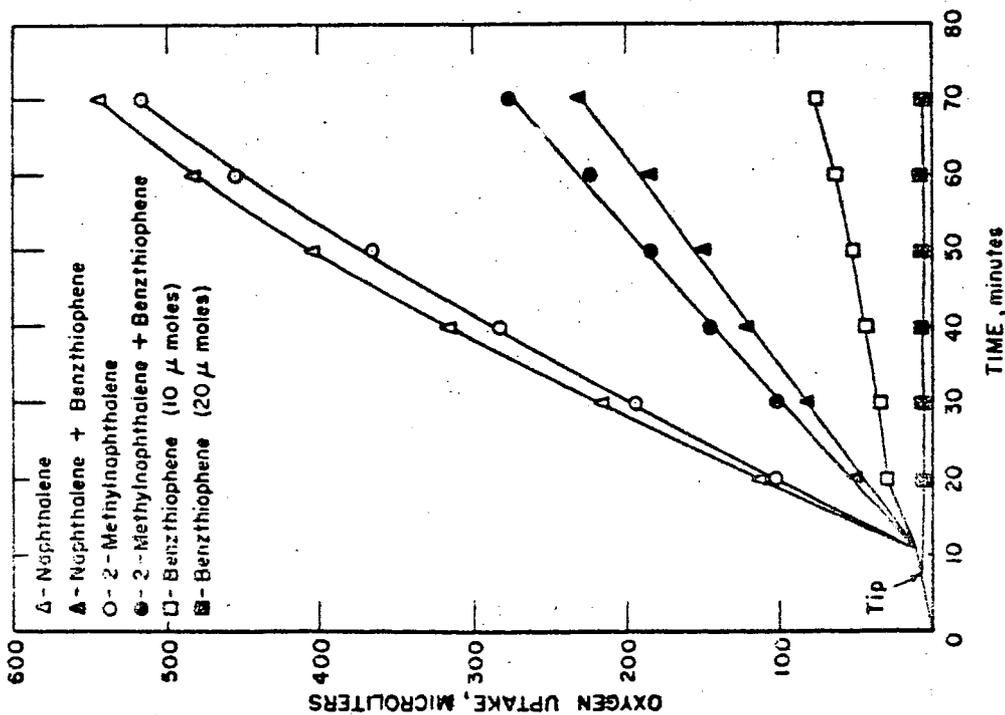


Figure 4.-Oxidation of aromatic hydrocarbons by strain PM-1.

CONSTITUTION OF HYDROCARBON-LIKE MATERIALS DERIVED FROM
KEROGEN OXIDATION PRODUCTS

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Oxidation is one method of converting the insoluble organic material (commonly called kerogen) present in oil shale to soluble degradation products for constitutional studies. The amount of degradation and the molecular weight of the products depend upon the extent of oxidation and severity of the reaction conditions. A variety of oxidants can be used to accomplish this degradation, but some are more suitable than others.

In a previous study (6), organic material from Colorado oil shale was oxidized to high-molecular-weight acids by a boiling solution of alkaline potassium permanganate under controlled conditions, and to carbon dioxide and oxalic acid by exhaustive oxidation for 100 hours. By choosing different ratios of KMnO_4 to kerogen, large or small amounts of intermediate acids were obtained. However, it was not possible to obtain complete conversion to intermediate acids without simultaneously producing carbon dioxide and oxalic acid. In general, small yields of final oxidation products were associated with large yields of high-molecular-weight intermediate acids and vice versa.

In another report (5), the nature of the organic acids that were obtained by oxidizing raw oil shale from the Mahogany-zone beds of the Green River formation near Rifle, Colo., was studied. The oil shale assayed approximately 66 gallons of oil per ton of shale and contained about 34% kerogen. An oxidation product was prepared by treating each part of organic carbon present in the kerogen with eight parts of KMnO_4 . The organic acids obtained were converted to n-butyl esters, fractionated by distillation, and identified, where possible, by mass and infrared spectra of the esters and by X-ray diffraction of selected derivatives. A total of 59% of the organic acids in the oxidation product was identified as C_2 to C_8 difunctional acids of the alkane series. The remaining 41% of the organic acids were not identified by this method because of their complex nature. Identification or classification of this material would contribute to the knowledge of the structure of kerogen and might suggest new commercial uses for oil shale.

In this study by the Federal Bureau of Mines, characterization of the remaining 41% of the organic acids in this oxidation product was accomplished by reducing the carboxyl groups of the acids through a series of reactions. The resulting hydrocarbon-like materials were amenable to fractionation and characterization. Some of the usual methods of decarboxylation were tried, but extensive thermal degradation resulted.

The oxidation product also contained n-paraffinic, isoparaffinic, aromatic, naphthenic, and heterocyclic acids. The naphthenic and heterocyclic acids predominated, which suggested that the structure of Colorado kerogen is mainly alicyclic and heterocyclic, with smaller amounts of straight-chain and aromatic structures.

EXPERIMENTAL PROCEDURE

Preparation of Organic Acids. Kerogen oxidation products were prepared from raw oil shale using a method described in earlier reports (5,6). The raw oil shale was oxidized in two steps by an aqueous solution of alkaline KMnO_4 . The first step was treatment of 1 part of organic carbon of the kerogen with 6 parts of KMnO_4 , 1.6

parts of KOH and 34 parts of water at 70° to 90° C. until the KMnO_4 was reduced. The treatment was repeated in the second step except that only 2 parts of KMnO_4 were used. The alkaline solution was separated from the shale residue, acidified with 1 to 1 sulfuric acid and evaporated to dryness. Nonvolatile organic acids were extracted from this dried product using methyl ethyl ketone. Based upon total carbon, the kerogen was oxidized to 58% nonvolatile acids, 15% carbon dioxide, a trace of volatile acids, and 27% remained unoxidized.

Preparation of n-Butyl Esters. The nonvolatile organic acids were converted to n-butyl esters by reacting 250 grams (0.8 mole) of the acids with 1275 ml. (14 mole) of n-butyl alcohol and 25 ml. (0.5 mole) of concentrated sulfuric acid under reflux conditions for about 100 hours. Water was removed by using an enlarged Dean-Stark tube mounted above the reaction flask. After completion of the reaction, the n-butyl alcohol was removed by distillation. The resulting product was dissolved in ether, was washed free of acid with a solution of sodium carbonate, and finally was dried over anhydrous sodium sulfate and recovered.

Preparation of Alcohols. All the recovered n-butyl esters were reduced to alcohols in the following manner (1): The esters were treated with a total of 61 grams (1.6 mole) of LiAlH_4 in 2500 ml. (23.6 mole) of anhydrous ether in five different batches. An ether solution of the esters was added slowly to an ether solution of LiAlH_4 , then refluxed 4 to 5 hours. Excess hydride was decomposed by cautiously adding water to the reaction mixture. After gas stopped evolving, the complex was treated with 10% sulfuric acid and the reduced product was recovered from the ethereal layer.

Preparation of Iodides. The alcohols were converted to iodides by reacting the alcohols with 115 grams (0.8 mole) of P_2O_5 , 216 ml. (3.2 mole) of 85% H_3PO_4 and 530 grams (3.2 mole) of KI (7). After the reaction mixture was heated at 100° to 120° C. for 3 to 5 hours, the iodides were extracted with ether. The ether solution was washed with sodium thiosulfate and sodium chloride solutions, dried over anhydrous sodium sulfate, and the ether was distilled from the iodides.

Reduction of Iodides. The resulting iodides were reduced with zinc and hydrogen chloride gas (2). Zinc dust was added over a period of 2 hours to a warm glacial acetic acid solution of the iodides, which was constantly stirred. The reaction mixture was stirred and heated at 90° to 95° C. for an additional 24 hours and was saturated with dry HCl gas every 4 hours. A trap, submerged in a dry ice and acetone bath, was connected to the exit gas tube to condense any hydrocarbons with low boiling points formed during the reduction. After completion of the reaction, the mixture was diluted with water, and the product was extracted with ether. After the ether solution was washed free of acid, it was dried over anhydrous sodium sulfate, and the ether was partly distilled from the product.

Fractionation of the Reduced Product. The product and a small quantity of ether were placed in a spinning band distillation column and distilled at atmospheric pressure (580 mm. mercury) up to a head temperature of 70° C. (pot temperature of 175° C.). After the reduced product cooled to room temperature, the distillation was continued at 1 mm. mercury pressure with a head temperature up to 130° C. and a pot temperature of 200° C.

A flow diagram of the fractionation of the distillate and distillation residue is shown in figure 1. The distillate and residue fractions were dissolved in a 40 to 1 volume ratio of pentane, allowed to stand overnight at 0° C., and then filtered. The insoluble material was washed with a small quantity of cold pentane, freed of solvent, and weighed. The pentane-soluble material was fractionated on pretreated columns of alumina (25 to 1 weight ratio of Alcoa XF-21 alumina) using pentane, benzene and a 10% methanol-90% benzene mixture as eluting solvents. The benzene-eluted material, referred to as nonpolar resins, and the benzene-methanol eluted resins, referred to as polar resins, were freed of solvent and weighed.

Wax was separated by dissolving the pentane-eluted fraction (oil plus wax) in a 40 to 1 volume ratio of methyl ethyl ketone (MEK), allowing it to stand at -5°C . for 1 hour. The wax was filtered from the MEK-soluble oil, freed of solvent, and weighed. Urea adducts were prepared by reacting each gram of wax with 21 ml. of a saturated solution of urea in methanol. Excess urea, 1.5 grams per gram of wax, and 6 or 7 drops of benzene, were added. This mixture was stirred at room temperature for 24 hours. The adduct and nonadduct waxes were separated by filtration; the adduct was then decomposed with hot water and extracted with ether. Both fractions were freed of solvent by distillation. Wax was not separated from the distillate fraction.

The distillate oil, the wax fraction, and the distillation residue oil were fractionated by a method similar to that reported by Mair, Marculartis and Rossini (3). Each fraction was placed on a pretreated column of silica gel (25 grams of Davidson analytical grade silica gel to 1 gram of sample) and eluted successively with 2,2,4-trimethyl pentane, benzene, and 2-propanol. The fractions were freed of solvent, weighed and identified as paraffin oil, aromatic oil, and polar oil respectively. The paraffin oil from the distillation residue was adducted with urea by the same technique used for waxes. The aromatic oil from the distillation residue was further fractionated on a pretreated column of alumina using a 25-to-1 ratio of alumina to sample. Eluting materials were a mixture of iso-octenes, benzene, and 2-propanol.

Reduction with Hydriodic Acid. The wax and paraffin oil fractions were completely reduced by concentrated hydriodic acid. Samples of 0.1 to 0.5 gram were reduced by sealing them in glass ampoules with 15 ml. of concentrated hydriodic acid (sp. gr. 1.9) and heating at 175°C . for 24 hours. The treated samples were dissolved in benzene and washed free of iodine with a solution of sodium thiosulfate. The benzene solution was washed with water and finally dried over anhydrous sodium carbonate. Benzene was distilled from the reduced product at reduced pressure.

Physical and Chemical Properties. The elemental composition and functional groups of the fractions were determined by macro methods at the Bureau's laboratory and by micro methods at a commercial laboratory, using conventional methods. Carbon and hydrogen were determined by combustion, nitrogen by the Kjeldahl or Dumas methods, sulfur by ignition in a Parr oxygen bomb, oxygen by difference or by the Unterzaucher direct method, saponification equivalents by hydrolysis and hydroxyl groups by acetylation. Molecular weights were determined from mass spectra and by the rise-in-boiling-point method using benzene as solvent. Infrared and mass spectra, as well as X-ray diffraction, were used to characterize the various fractions.

RESULTS AND DISCUSSION

The total yield of reduced product from 250 grams of kerogen acids amounted to 36 grams after removal of all solvents, or approximately 15 weight percent. The theoretical yield, based on data from a previous study (5), was 198 grams or 79 weight percent. However, approximately 50% of the oxidation product consisted of difunctional acids containing 2 to 4 carbon atoms per molecule. The reduction method used in this study converted these acids to gases that were not recovered in the reduced product. Because of this loss, the overall yield of reduced product was 36% of the theoretical. Typical yields were: esters - 95%, alcohols - 75%, iodides - 95%, and hydrocarbons 50%. Losses were probably due to handling rather than to unreactivity of the components. However, the possibility of fractionation occurring did exist and some unreactive parts of the oxidation product may have been eliminated from the reduced material. Vacuum distillation of the reduced product resulted in a yield of 8.5% distillate and 91.5% distillation residue.

Composition of the Distillate Fraction. In addition to the solvents used, the distillate obtained by atmospheric distillation contained trace amounts of pentanes, hexanes, hexenes, and cyclohexanes. The distillate obtained by vacuum distillation (8.5% of the total reduced product) was fractionated by the method described earlier

and shown in figure 1. Nearly equal amounts of five fractions were obtained, namely paraffin oil, aromatic oil, polar oil, nonpolar resins, and polar resins.

Mass spectra analysis of the paraffin oil fraction showed that it consisted of isoparaffins and cycloparaffins, with the latter predominating. The cyclic part contained 1 to 5 rings per molecule with dinuclear material constituting the largest single type material. The major components of the aromatic fraction were benzenes, indanes/tetralins and naphthalenes.

Infrared analysis of the nonpolar resins, polar resins, and polar oil indicated that these fractions were predominantly cyclic because absorption in the 13.7 and 13.9 micron region was very weak. They also appeared highly saturated as shown by strong absorption in the 3.45 and 6.84 micron regions. The presence of considerable terminal CH₃ groups was suggested by medium to strong absorption in the 7.3 micron region. Absorption in the aromatic region was weak. There was indication of the presence of OH groups and other oxygen functionals; however, the strong absorption in the 5.70, 5.78, and 5.95 micron region may be due to C=O groups of unreduced esters.

Composition of the Distillation Residue. The amount of each of the various fractions from the distillation residue, which represented 91.5% of the reduced product, is shown in table 1. The major fractions consisted of resins and paraffin oil, while wax, aromatic oil, polar oil, and pentane-insoluble material were present in smaller amounts. Molecular weights ranged from about 300 to 1200.

Table 1. Distribution and Molecular Weights of the Distillation Residue Fractions

	Percentage of Total Distillation Residue	Percentage of Total Reduced Product	Molecular Weights
Pentane-insoluble material	3.0	2.7	1220
Resins			
Nonpolar resins	11.9	10.9	530
Polar resins	25.9	23.7	800
Wax			
Urea adduct	3.0	2.7	405
Urea nonadduct	10.4	9.5	400
Oil			
Paraffin oil adduct	1.5	1.4	310
Paraffin oil nonadduct	30.5	27.9	410
Aromatic oil (iso-octene eluted)	9.5	8.7	270
Aromatic oil (benzene eluted)	0.3	0.3	340
Aromatic oil (2-propanol eluted)	0.3	0.3	345
Polar oil	<u>3.7</u>	<u>3.4</u>	-
Total	100.0	91.5 ^a	

^aThe remaining 8.5% consisted of the vacuum distillate fraction.

Ultimate analyses shown in table 2 indicated that the recovered fractions contained appreciable amounts of oxygen. It was necessary to determine the nature of

this oxygen and to eliminate the oxygen from portions of the fractions by HI reduction, so that mass spectra data for ring analysis and carbon chain length would have meaning.

Table 2. Elemental Analyses of Distillation Residue Fractions

	C	H	O	N	S	Atomic H/C
Wax						
Urea adduct	83.6	14.2	1.8 ^a	0.2	0.2	2.04
Urea nonadduct	82.9	11.1	5.4 ^a	0.2	0.4	1.61
Oil						
Adduct paraffin	84.2	14.3	1.2 ^a	0.2	0.1	2.04
Nonadduct paraffin	81.1	11.1	7.6 ^b	0.0	0.2	1.64
Mono/di-aromatic	86.2	11.2	-	2.6 ^c	-	1.56
Resins						
Nonpolar	78.9	10.1	9.4 ^b	0.4	1.2	1.54
Polar	70.2	9.6	19.1 ^b	1.0	0.1	1.64

^aDirect oxygen (Unterzaucher).

^bOxygen was determined by difference.

^cTotal oxygen, nitrogen, and sulfur determined by difference.

An estimate of the type and amount of oxygen functional groups for various fractions was obtained by analyses for hydroxyl, ester, and alkoxy oxygen. Other ether, carbonyl and unaccounted for oxygen was determined by difference. As this difference value was large in all cases, infrared analyses was used to indicate the most likely type oxygen present.

Mass spectra data reported for the oil and wax fractions were obtained from the HI-reduced material. By contrast, infrared spectra was determined on the oil, wax, and resin fractions before reduction with hydriodic acid; also the aromatic oil was not reduced with HI.

Adduct Wax. Based on mass spectra data, this fraction, which represented 2.7% of the total reduced product, contained mostly isoparaffins and normal paraffins with smaller amounts of cycloparaffins (table 3). Isoparaffins appeared to predominate over normal paraffins; the normal paraffins ranged from C₁₃ to C₃₆ carbon chains with an average chain length of C₂₆. (Average carbon chain length of this wax, determined by X-ray diffraction, was 28.) These data showed the presence of long carbon chains, which suggested that the original oxidation product contained a small amount of fatty acids.

Ultimate analyses (table 2) showed that the adduct wax was highly saturated with hydrogen and contained 1.3% oxygen. Infrared analyses of the fraction before reduction with HI, shown in table 4, confirmed the presence of a predominance of chain structures. The average molecular weight of the adduct wax before reduction with HI was 405.

Nonadduct Wax. By contrast, the nonadduct wax fraction, which represented 9.5% of the total reduced product, contained predominantly cyclic structures and only a small amount of normal paraffins and isoparaffins (table 3). The cyclic portion

consisted of aromatic and naphthenic rings with a predominance of the naphthenic rings. The number of rings per molecule ranged from 1 to 6 with an average of 2 to 3 rings per molecule.

Table 3. Constitution of the HI-reduced Wax and Paraffin Oil Fractions Obtained from the Distillation Residue

	Average Composition, mole % ^a			
	Wax		Paraffin Oil	
	Adduct	Nonadduct	Adduct	Nonadduct
n-Paraffins	27	4 ^b	84	6 ^b
Isoparaffins	66	-	7	-
Naphthenes				
Mono and noncondensed naphthenes	3	11	-	18
Condensed naphthenes				
2 rings	1	19	1	22
3 rings	1	14	2	13
4 rings	1	5	2	3
5 rings	1	19	2	7
6 rings	-	6	2	6
Aromatics	-	22	3	25
Total	100	100	100	100

^aDetermined from mass spectra.

^bTotal normal and isoparaffins.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. The fraction contained 5.4% oxygen (table 2), which appeared to be mostly in the form of ether or carbonyl oxygen with smaller amounts of ester, but no hydroxyl oxygen. Infrared spectra before reduction with HI, shown in table 4, indicated medium to weak absorption for ester, ketone, alcohol, and anhydride oxygen suggesting a predominance of ether oxygen. The presence of only small amounts of long carbon chains was also confirmed by infrared analyses; however, strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH₃ groups. This fraction had an average molecular weight of 400 before reduction with HI and 360 after reduction.

Adduct Paraffin Oil. The adduct paraffin oil, one of the smaller fractions representing only 1.4% of the reduced product, was composed largely of normal paraffins with smaller amounts of cycloparaffins and isoparaffins (table 3). The normal paraffins ranged from C₁₅ to C₃₀ carbon chains with an average chain length of C₂₃. (The average chain length determined by X-ray diffraction was C₂₂.) The naphthenic material contained 2 to 6 rings per molecule.

Ultimate analyses (table 2) showed that this fraction was highly saturated with hydrogen and contained 1.2% oxygen. Because of limited size of the fraction, oxygen functional groups were not determined by chemical methods. Infrared spectra of this fraction, shown in table 4, indicated the presence of very little oxygen functional groups. This suggested that most of the oxygen was ether oxygen. Strong absorption in the 13.7 and 13.9 micron region confirmed the presence of considerable

Table 4. Infrared Spectra of Wax and Oil Fractions Obtained From the Distillation Residue

Band Locations, Microns	Intensity ^a				Possible Interpretations
	Adduct Wax	Nonadduct Wax	Adduct Paraffin Oil	Nonadduct Paraffin Oil	
2.9	W	W	W	W	OH (bonded)
3.45	S	S	S	S	CH ₂ , CH ₃
5.70	M-W	M-W	W	W	C=O (ester)
5.78	M-W	M	W	M-W	C=O (ester)
5.95	None	M-W	W	W	C=O, aromatic
6.25, 6.35	W	M-W	W	M-W	C=C (aromatic), carboxylate ion
6.84	S	S	S	S	CH ₂ , CH ₃
7.30	M-W	S	M	S	CH ₃
7.55	W	M	W	W	-
8.10	W	M	None	None	Ester,
8.45	W	M	None	None	ketone, alcohol,
8.55	W	M	W	None	anhydride
11.25	W	M-W	M-W	W	-
11.5	W	M	W	M-W	Aromatic
12.7	M	M	M	M-W	-
13.45	None	None	None	None	Aromatic
13.7, 13.9	S	W	S	W	Alkyl chains

^aW - weak, M- medium and S - strong.

Table 5. Oxygen Functional Groups of Various Fractions

	Percent of Total Oxygen			
	Hydroxyl	Ester	Alkoxy	Ether, Carbonyl and Others ^a
Nonadduct wax	0	36	-	64
Nonadduct paraffin oil	2	27	3	68
Nonpolar resins	0	45	15	40
Polar resins	6	27	3	64

^aDetermined by difference.

normal paraffins. There was also some evidence for the presence of terminal CH₃ groups. The molecular weight of this fraction was 310 before reduction with HI.

Nonadduct Paraffin Oil. This fraction, which was the largest single fraction and amounted to 27.9% of the original reduced product, was predominantly naphthenic with smaller amounts of aromatic and paraffinic constituents (table 3). The naphthenic material had 1 to 6 rings per molecule with an average of 2 to 3 rings per molecule. The normal paraffinic and isoparaffinic constituents represented only a small portion of the total fraction; however, about 25% of the material was of aromatic composition.

Oxygen functional groups were determined by the methods described earlier and the results are shown in table 5. Of the 7.6% oxygen present in this fraction (table 2), the majority appeared to be present in the form of ether or carbonyl oxygen with smaller amounts of ester, hydroxyl and alkoxy functional groups. A predominance of ether oxygen was indicated by infrared analyses (table 4) since the absorption for carbonyl and other oxygen was weak. Also, weak absorption in the 13.7 and 13.9 micron region indicated the absence of long alkyl chains; however, strong absorption in the 7.3 region indicated the presence of considerable terminal CH_3 groups. This fraction contained very little nitrogen and sulfur and had an average molecular weight of 410 before reduction with HI and 350 after reduction.

Aromatic Oil. The aromatic fraction, which represented 9.3% of the total reduced product, was separated into 3 additional fractions; namely, iso-octenes, benzene, and 2-propanol eluted material (figure 1). These fractions are referred to as mono/di, tri, and tetra nuclear aromatics, respectively. Piperonal chloride color tests indicated that the iso-octene eluted material, which was the major aromatic fraction (table 1), was predominantly mono/di nuclear aromatics. This was confirmed by mass spectra data shown in table 6, which indicated that the material was mostly indanes and tetralins with smaller amounts of the other series of aromatic compounds. The benzene series had large peaks at m/e 268 and m/e 259. The m/e 288 peak was a parent peak that lost an ethyl radical to form m/e 259 and may represent the molecular weight of 1 compound or several isomeric compounds. A molecular weight of 288 indicated that 15 carbon atoms in alkyl groups larger than n-propyl were attached to the benzene ring. Considering all possible substitutions and eliminating some by infrared analyses, 3-ethylpropyl substitution appeared most likely. In addition to tri-substituted benzenes (Mol. wt. 288) there was evidence of di-substituted benzenes (Mol. wt. 216), di-substituted indanes (Mol. wt. 258)/di-substituted tetralins (Mol. wt. 272), and di- and tri-substituted indenenes (Mol. wt. 256, 326). These substitutions are shown diagrammatically in figure 2. The location of the substituted groups is not known; however, there is some evidence for the presence of symmetrical tri-substituted benzenes. Also, it is not meant to imply that other series of aromatics with the same "X-number" are not present, but the ones indicated appeared to be the best possibilities. It was assumed that the aromatic compounds isolated were degraded from kerogen and were not formed during the oxidation or reduction procedures. Therefore, each substituted group may represent a ruptured ring or ring system and suggests the presence of carbon skeleton structures in kerogen similar to that present in these compounds. Ring systems that would be readily ruptured by KMnO_4 to produce similar substitution on aromatic nuclei after reduction are cyclopentanone, cyclopentanol, cyclopentene or others.

Table 6. Constitution of Aromatic Oil Fractions From the Distillation Residue

	Volume, % ^a	
	Iso-octene eluted ^b	Benzene eluted ^c
Benzenes	12	16
Indanes and tetralins	41	29
Indenes and dihydronaphthalenes	14	16
Naphthalenes	10	10
Acenaphthenes	8	10
Acenaphthylenes	5	3
Anthracenes and phenanthrenes	10	11
Total	100	100

^aDetermined from mass spectra.

^bThe ratio of calculated to observed total ionization was 0.65.

^cThe ratio of calculated to observed total ionization was 1.09.

Resins. The resinous material obtained from the original product consisted of nonpolar (Mol. wt. 530) and polar resins (Mol. wt. 800) and represented 12 and 26% of the total material, respectively. Elemental analyses (table 2) of each fraction showed that they contained large amounts of oxygen and smaller amounts of nitrogen and sulfur. Oxygen functional groups were determined by the previous methods (table 5) and appeared to be present as ester and ether or carbonyl oxygen with smaller amounts of alkoxy oxygen. The polar resins contained some hydroxyl and little alkoxy oxygen. Infrared analyses of the two resin fractions are shown in table 7. Both fractions showed weak or no absorption in the 13.7 and 13.9 micron region, indicating few carbon chains with more than four methylene groups. Strong absorption in the 7.3 micron region indicated the presence of considerable terminal CH₃ groups. Absorption in the aromatic region was weak; consequently, these materials appeared to be composed predominantly of saturated cyclic structures. Infrared spectra showed evidence for hydroxyl, carbonyl and other oxygen functional groups, some of which was due to unreduced ester groups.

Table 7. Infrared Spectra of Resin Fractions Obtained From the Distillation Residue

Band Location, Microns	Intensity ^a		Possible Interpretation
	Nonpolar Resins	Polar Resins	
2.9	M-W	M-W	OH (bonded)
3.45	S	S	CH ₂ , CH ₃
5.75	S	S	C=O (ester)
5.95	W	None	C=O, aromatic
6.25, 6.35	M-W	W	C=C (aromatic), carboxylate ion
6.84	S	S	CH ₂ , CH ₃
7.30	S	S-M	CH ₃
8.10	W	S-M	Esters, ketones,
8.9	S	None	alcohols, anhydrides
11.4	W	None	Aromatic
11.5	None	W	Aromatic
13.45	S	None	Aromatic
13.7, 13.9	W	None	Alkyl chains

^aW - weak, M - medium and S - strong.

Polar Oil and Pentane-insoluble Material. No analytical data were obtained for these fractions.

Composition of the Original Acids. Approximately 59% of the original acid fraction was identified by a previous study (4). In the present study, the remaining 41% was characterized as shown in table 8. These complex acids, whose molecular weights have a maximum of more than 1200, consisted of small amounts of straight-chain and aromatic acids, but were predominantly saturated cyclic and heterocyclic acids.

There was evidence that the oxidation product contained appreciable amounts of ether oxygen. Fractions of the material obtained by the reduction of the oxidation product contained 7 to 19% oxygen, of which 40 to 70% may be ether oxygen. A quantitative estimate was obtained from the remainder of the reduced product and a comparison of the oxygen present in the original kerogen from which these products were obtained. The total oxygen accounted for in the reduced product equaled 22% of the oxygen present in the original kerogen, which indicated that at least 10 to 15% of the oxygen present in kerogen may be ether oxygen.

Table 8. Composition of Acid Fraction Obtained from Kerogen by Alkaline Permanganate Oxidation

	Percentage of Reduced Product ^a	Percentage of Total Acids ^b
Normal paraffin acids (C ₂ to C ₈)	-	59
Normal paraffin acids (C ₁₆ to C ₃₈)	2	1
Isoparaffin acids	2	1
Cycloparaffin acids (1 to 6 rings)	34	14
Aromatic acids (1 to 2 rings)	15	6
Heterocyclic acids	<u>47</u>	<u>19</u>
Total	100	100

^aDetermined from mass spectra.

^bBased on analyses obtained from data presented in this report and a previous report (4).

By choosing other oxidation conditions different yields of complex acids could have been obtained. For example an 8-step-oxidation procedure produced 4% oxalic acid, 17% CO₂, 2% volatile acids and 77% complex organic acids. About 50% of the organic acids had molecular weights from 1200 to 1400 and did not undergo the reactions used in this study. Consequently, the oxidation used in the present study appeared to be a compromise between the two extremes and no attempt was made to obtain maximum yield of any one type of constituent.

SUMMARY AND CONCLUSIONS

The oxidation product obtained from Colorado oil-shale kerogen consisted of n-paraffinic, isoparaffinic, aromatic, naphthenic and heterocyclic structures; the naphthenic and heterocyclic types predominated.

The n-paraffins ranged from C₂ to C₃₈ compounds. The cycloparaffins contained 1 to 6 rings per molecule with di- and tri-nuclear material being most prevalent. Also, mono/di-nuclear aromatics appeared to predominate over compounds having more rings. The aromatic fraction contained nuclei with 3-ethylpropyl substitution at two and three points. The presence of this type of compound in the degradation products suggested that the permanganate oxidation cleaved 5-membered ring systems such as cyclopentene, cyclopentanone, or cyclopentanol that were substituted on benzene, tetralin, indane or indene nuclei. This structure has not been identified previously in kerogen degradation products.

Evidence was found for the presence of ether oxygen in the original kerogen. The four major fractions obtained by the reduction of the oxidation product still contained appreciable amounts of oxygen, most of which was unreduced ester and ether

oxygen. This indicated that Colorado kerogen contains some cyclic or bridge ether oxygen. It seems unlikely that stable ether groups would have been formed during any of the treatment procedures.

In general, these data show that Colorado oil-shale kerogen is predominantly a cyclic material, highly saturated with hydrogen and contains oxygen, nitrogen and sulfur atoms associated with ring structures. There is evidence for the presence of some aromatic and long-chain structures, each representing small portions of the kerogen. The nature of the oxidation products suggests that the kerogen is composed mostly of ring systems connected through short carbon chains, bridges or hetero atoms and is not composed of highly condensed ring structures (2 to 3 rings predominate). These conclusions are in agreement with those obtained from previous studies (4,5,6).

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Adams, Roger, "Organic Reactions," vol. VI, pp. 469-509, John Wiley and Sons, Inc., New York, N. Y., 1951.
- (2) Blatt, A. H., "Organic Synthesis," Collective vol. II, pp. 320-1, John Wiley and Sons, Inc., New York, N. Y., 1943.
- (3) Mair, B. J., Marculartis, W. J., Rossini, F. D., Anal. Chem. 29, 92 (1957).
- (4) Robinson, W. E., Cummins, J. J., J. Chem. Eng. Data 5, 74-80 (1960).
- (5) Robinson, W. E., Cummins, J. J., and Stanfield, K. E., Ind. Eng. Chem. 48, 1134-38 (1956).
- (6) Robinson, W. E., Heady, H. H., and Hubbard, A. B., Ind. Eng. Chem. 45, 788-91 (1953).
- (7) Schreiber, R. S., "Organic Synthesis," vol. 31, pp. 31-2, John Wiley and Sons, Inc., New York, N. Y., 1951.

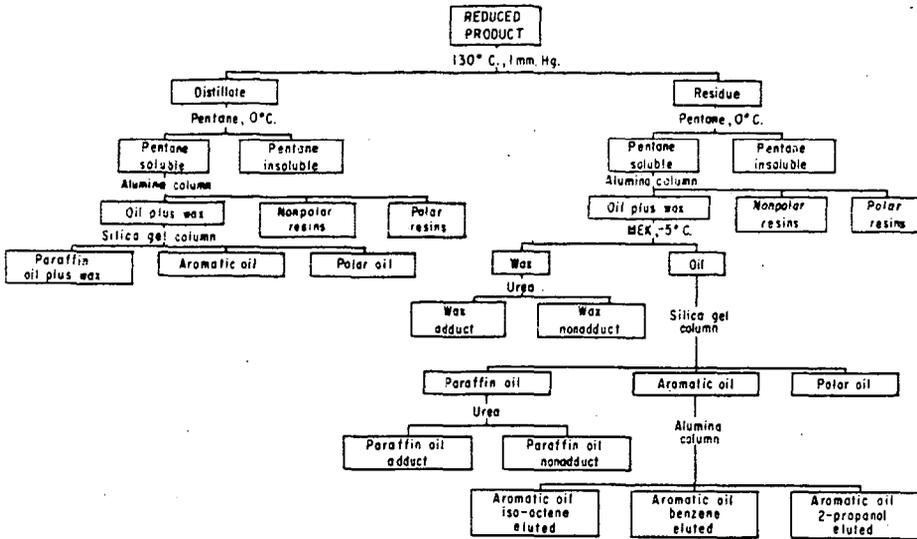


FIGURE 1.- FRACTIONATION OF REDUCED PRODUCT

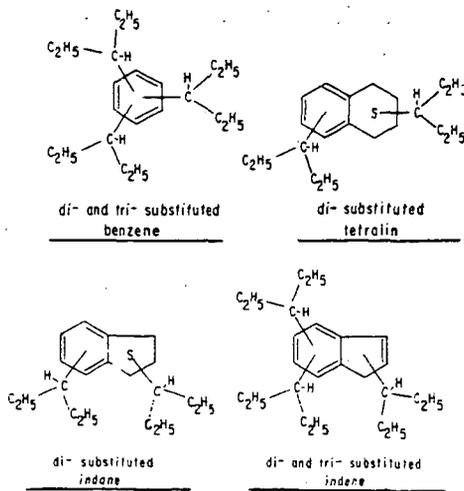


FIGURE 2.- POSSIBLE STRUCTURES PRESENT IN THE MONO/DI-NUCLEAR AROMATIC OIL.

COMPRESSIBILITY FACTOR OF NATURAL GASES
AT 60°F AND ONE ATMOSPHERE

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INTRODUCTION

Modern analytical techniques have markedly improved the accuracy with which the composition of a gas can be measured. For many years fuel gases were analyzed by volumetric techniques, such as the Orsat or Podbielniak. Heating values and specific gravities were also determined at atmospheric conditions for pure components and fuel gas mixtures, thus resulting in real gas values. However, because of low accuracy in the analytical methods, particularly with respect to determination of the heavier hydrocarbons, differences between calculated and observed heating values were generally ascribed to experimental techniques, and not interpreted on the basis of gas law deviations.

With the advent of the mass spectrometer, more accurate and complete analyses of gas mixtures may be obtained. These analyses are on a true mole fraction, or ideal gas, basis. Also, accurate ideal gas heat of combustion values can now be derived from the work of Rossini et al., API Project 44⁹. However, full utilization of this improved accuracy can not presently be obtained in the calculation of real gas heating values and specific gravities. The lack of sufficient data to permit accurate prediction of the compressibility factor for real gas mixtures may result in significant differences between measured values and those calculated from the gas analysis. Largest deviations occur in fuel gases containing appreciable quantities of heavier constituents.

An experimental program was therefore planned to obtain compressibility factor data at 60°F and one atmosphere on fuel gas components and mixtures. It was anticipated that these data would provide the basis for development of generalized procedures for prediction of compressibility factors of gas mixtures. This project was undertaken as part of the continuing basic research program of the Institute of Gas Technology, and was sponsored by The Peoples Natural Gas Company. The results obtained for natural gas components and mixtures are reported here.

Methods used for determination of gas compressibility factor fall into two groups: 1) gas density, and 2) pressure-relative volume measurement. In the first group of methods, gas density is measured by gas balance or by direct weighing in a bulb. The compressibility factor is calculated from the expression:

$$z = \frac{pV}{RT} \quad (1)$$

where V is the volume of one mole calculated from the density and molecular weight of the gas. The accuracy of this method depends on absolute values of pressure, volume and temperature.

In the second group of methods, measurements of pressure and relative volume are made over a range of pressure, and pV or a related parameter is extrapolated to zero pressure, as in the Burnett method.² A method of this kind for use at pressures near atmospheric was described by Jessen and Lightfoot.⁶ Data are obtained at two or three different pressures by confining the sample of gas in progressively larger volumes over mercury. The compressibility factor is calculated by fitting the pV measurements (V is the measured volume here) with an equation such as:

$$pV = (pV)_0 \quad z = (pV)_0 (1 + \beta p) \quad (2)$$

Here the accuracy depends primarily on relative volume and pressure measurements, and constancy of temperature, rather than on absolute values of these quantities. Absolute values of pressure and temperature affect the result in a much less critical way; that is, by the dependence of z on pressure and temperature, and not by the dependence of pV and RT . Similarly the accuracy of z for mixtures is not affected by the dependence of gas density on composition. However, the method is dependent on the linearity of z with pressure.

According to the statistical mechanical expressions for virial coefficients in the equation

$$pV = RT (1 + Bp + Cp^2 + \dots) \quad (3)$$

the second virial coefficient, B , represents the deviation from ideal behavior involving collisions between two molecules.⁵ From this theory it also follows that the second virial coefficient for mixtures involves only binary interaction terms, and is of the form:

$$B_m = x_1^2 B_1 + x_2^2 B_2 + x_3^2 B_3 + \dots \\ + 2x_1 x_2 B_{12} + 2x_1 x_3 B_{13} + 2x_2 x_3 B_{23} + \dots \quad (4)$$

where B_1, B_2, B_3, \dots are second virial coefficients of the pure components, and $B_{12}, B_{13}, B_{23}, \dots$ are interaction coefficients. The latter can be evaluated by experimental determination of B_m 's on binary mixtures, together with knowledge of the B 's for pure components. The effect of the third virial coefficient at one atmosphere is very small and is considered later.

Five components usually occur in natural gases in concentrations of 5% or more: methane, ethane, propane, carbon dioxide and nitrogen. Minor amounts of isobutane, *n*-butane, isopentane and *n*-pentane also occur, together with traces of heavier hydrocarbons. A review of the literature indicated that sufficiently reliable values of atmospheric pressure compressibility factors are available for the major components,^{1,4} but not for the minor components. Also, although only very limited data were available on mixtures of these components, the data indicated that composition had a very sizeable effect on compressibility factor.

Therefore, compressibility factor measurements were made on the pure butanes and pentanes, and on a series of selected mixtures. The interaction coefficients among the five major components, and of methane with the four minor components, were determined. In addition, the interaction coefficients of n-butane with all major components was measured to provide a basis for prediction of those not determined experimentally.

APPARATUS

The apparatus is shown in Fig. 1. The mixture preparation system, gas expansion system, mercury reservoir and the lower part of the mercury manometer are mounted in a water bath with a plate-glass front. The temperature of the bath was maintained within 0.05° of 15.55°C (60°F), and did not vary more than 0.01°C during any one run.

A and B are Hoke stainless steel cam-closing valves. Connection to glass parts is made through stainless steel Swagelok fittings and 1/8-in. stainless steel tubing sealed to the glass with Dekhotinsky cement. Other valves are Hoke toggle or needle valves. The upper part of the long manometer arm extends out of the bath and is equipped with a jacket for water circulation. Manometer arms and jacket are constructed of precision bore tubing; arms 1 and 2, 12 mm ID; arm 3, 13.8 mm ID. Vacuum is maintained at 0.02 mm or less with a mechanical vacuum pump and dry ice cold trap, and is read with a tilting McLeod gage sensitive to 0.01 mm Hg. Mercury levels are read to 0.05 mm with a Gaertner 100 cm cathetometer.

The mixture preparation bulbs, gas expansion bulbs, and manometer arm 1 were calibrated by weight of mercury delivered. The volume of valve B and the capillary manifold in the expansion system, and the volume between valves A and B and the top of the upper bulb in the mixture preparation system, were determined with a 10 cc gas burette. The volume between the top and bottom menisci of the manometer arm 1, and corrections for capillary depression, were taken from Kistemaker^{7,8}.

MATERIALS

The hydrocarbons used were Phillips research grade. According to the supplier, purity of the methane was 99.68 mole %, with impurities of ethane and nitrogen. Purity of the other hydrocarbons was 99.9% or better. The carbon dioxide was Matheson, bone dry grade; the nitrogen was Matheson prepurified. Components other than nitrogen and methane were condensed in the freezeout trap to remove air. The part of the apparatus being filled was flushed with the component before filling.

PROCEDURE

In making binary mixtures the first component was measured in the gas expansion system. The second component was measured in the mixture preparation system by means of manometer arms 2 and 3. Then valve A was closed and the gases were mixed by being forced from one buret to the other several times. A similar procedure was followed in making multicomponent mixtures, except that the intermediate components were measured one at a time in the mixture preparation buret and transferred to the gas expansion buret. Gas

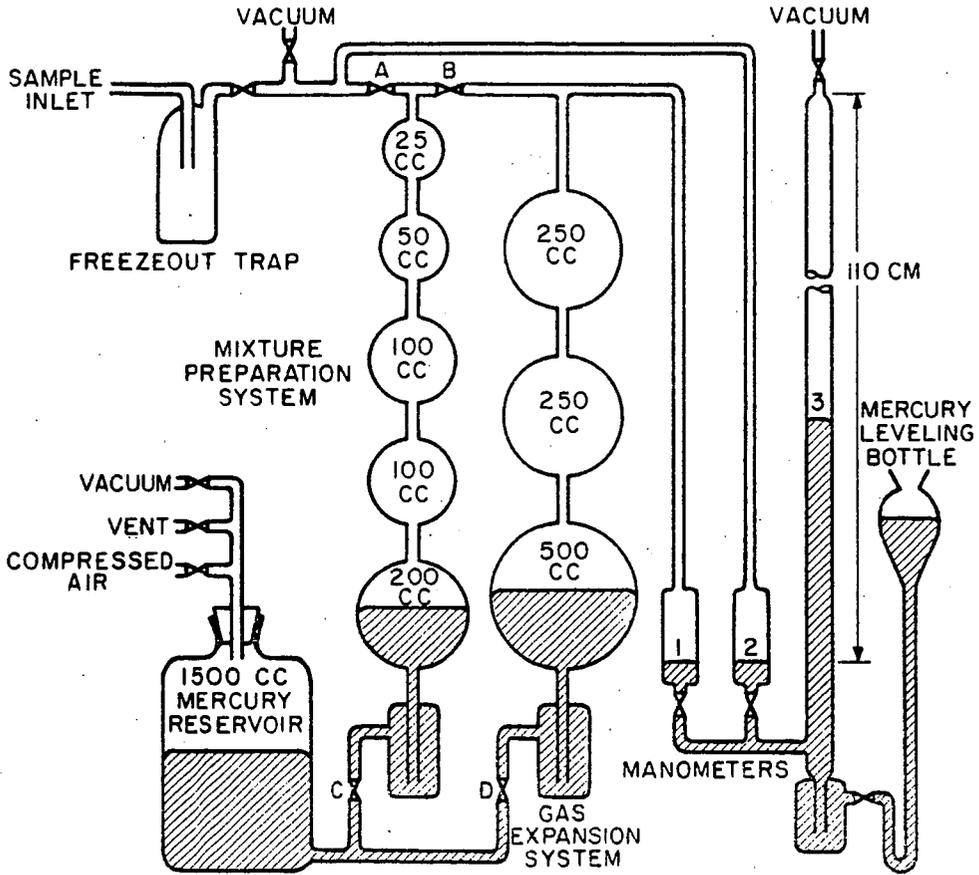


Fig.1.-SCHEMATIC DIAGRAM OF LOW PRESSURE P-V APPARATUS WITH INTEGRAL VOLUMETRIC MIXTURE PREPARATION SYSTEM

remaining in the section between valves A and B after the transfer was discarded.

In most cases, the two upper bulbs of the gas expansion buret were filled to a pressure of about 950 mm Hg. Three to five readings of the top and bottom of the mercury menisci in the two arms of the manometer, and of a reference point on manometer arm 1 were taken. The position of the mercury was changed a millimeter or so for each reading, to minimize the effect of local imperfections of the manometer tubing and plate glass window. Similar readings were taken after the gas was expanded to fill all three bulbs. Measurements on C₅ hydrocarbons had to be taken at lower pressures; a maximum of about 80% of saturation pressure was used.

The apparatus was constructed with three bulbs to allow measurements at three different pressures on the same charge of gas in order to detect variation of the slope β in equation (2) with pressure. However, from variances of the pV measurements at different pressures, it was concluded that better accuracy might be obtained if only the larger volumes were used since volume measurement as well as pressure measurement contributed to the error. Accordingly, data at lower pressures was obtained by removal of part of the sample and repeating measurements on the same two combinations of bulbs.

Data were fitted to equation (2) by least squares computation on an Alvac III digital computer.

COMPRESSIBILITY FACTORS OF PURE COMPONENTS

Results for the coefficient β equation (2) obtained on C₄ and C₅ paraffin hydrocarbons are presented in Table 1. Determinations at lower pressures were made as a part of Runs 2 and 6 on n-butane, and of Runs 3 and 4 on isobutane, to detect the change of coefficient with pressure. A trend in the direction of smaller numerical values of the coefficient at lower pressures is evident. Such tests were confined to the C₄ hydrocarbons, since the effect is barely detectable with them and is likely to be less with lighter hydrocarbons and with mixtures. Determination on the C₅ hydrocarbons at necessarily lower pressures would not yield significant results on this question.

In order to obtain the best value of 1-z (1 atm, 60°F), the third virial coefficient was introduced to account for the observed trend of β with pressure:

$$\frac{pV}{(pV)_0} = z = 1 + Bp + Cp^2 \quad (5)$$

An approximation formula was derived from which values of B and C/B could be evaluated from two measured values of β and the average initial and final pressures, p₁ and p₂ of each run

$$B = \beta \left[1 - \frac{C}{\beta} (p_1 + p_2) \right] \quad (6)$$

The ratio C/B was evaluated by application of formula (6) to the data from pairs of runs on the same sample, one made at normal pressures

Table 1. GAS LAW DEVIATIONS OF C₄ AND C₅ PARAFFIN HYDROCARBONS
AT 60° F.

Run No.	β (atm ⁻¹)	$p_1 + p_2$ (atm)	Atmospheric Gas Law Deviation $b = 1 - 2$
<u>n-Butane</u>			
1	-0.03413	1.901	0.03361
2a	-0.03466	1.826	0.03417
2b	-0.03433	1.437	0.03410
2c	-0.03422	1.044	0.03419
3	-0.03423	1.849	0.03374
4	-0.03453	1.830	0.03404
5	-0.03411	1.846	0.03362
6a	-0.03437	1.862	0.03387
6b	-0.03397	1.458	0.03370
6c	-0.03416	1.027	0.03414
			Weighted Avg. \pm 0.03394
			-0.00008 (a)
<u>Isobutane</u>			
1	-0.03022	1.894	0.02982
2	-0.02993	1.891	0.02953
3a	-0.03013	1.889	0.02973
3b	-0.02973	0.937	0.02970
4a	-0.03022	1.881	0.02982
4b	-0.02942	0.895	0.02947
			Weighted Avg. \pm 0.02971
			-0.00010 (a)
<u>n-Pentane</u>			
1	-0.05504	0.578	0.05570
2	-0.05632	0.525	0.05703
			Weighted Avg. \pm 0.0565
			-0.0007 (b)
<u>Isopentane</u>			
1	-0.05199	0.723	0.05236
2	-0.05076	0.766	0.05107
			Weighted Avg. \pm 0.0518
			-0.0005 (b)

(a) From pooled variance of b values for both butanes.

(b) From variance of the pV measurements.

and the other at about half the normal pressures. Runs 2a with 2c, and 6a with 6c, on n-butane, and Runs 3a with 3b, and 4a with 4b, on isobutane, give C/B ratios of 0.016, 0.007, 0.014 and 0.026, respectively. The average of the four, weighted according to the variance of the pV measurements, was 0.016; its standard deviation, also calculated from the variance of the pV measurements, was 0.006.

It was desirable to apply similar corrections to our results for C₅ hydrocarbon and mixtures. However, the C/B ratio for lighter gases at 60°F is smaller than those observed for the butanes, e.g., ethane, 0.006^{1,3}, while higher ratios are theoretically expected for heavier hydrocarbons³. The observed ratio of C/B for the butanes was approximately equal to B/2. In order to correct our results on a consistent basis over the complete range of deviations, we adopted a C/B ratio of B/2 for all the hydrocarbons and mixtures.

Gas law deviations of the C₄ and C₅ hydrocarbons, in the form of 1-z for easy comparison with the uncorrected β values, are shown in Table 1. Maximum error of the compressibility factors of the butanes is estimated to be 0.03%, and for the pentanes, 0.1%.

Values of gas law deviations for pure components used in the calculation of data on mixtures are collected in Table 3.

BINARY INTERACTION COEFFICIENTS

Interaction coefficients determined by measurement of the compressibility factors of binary mixtures of natural gas components are presented in Table 2. These have been calculated by means of the mixture rule of equation (4) but using the gas law deviation (1-z) rather than actual second virial coefficients. Since the third and higher virial coefficients make only a small contribution (maximum about 1%) to the deviation, error from this approximation should not be significant.

Estimated standard deviations of the methane - n-butane and methane - n-pentane averages are 0.00034 and 0.00045, respectively. The estimated standard deviation of other average interaction coefficients is 0.00022.

Agreement of experimental gas law deviations with the mixture rule was tested by determinations of interaction coefficients on 1:3 and 3:1 mixtures of methane with n-butane, and of carbon dioxide with n-butane. On the carbon dioxide - n-butane system, agreement is within experimental error and no trend is apparent. On the methane - n-butane system, a trend of increasing interaction coefficient with increasing methane content is noticeable; however, the difference between 3:1 and 1:3 coefficients is not significant at the 90% confidence level. Compressibility factors of the methane - n-butane mixtures calculated from the average interaction coefficient reported in Table 2 agree with the determined values within 0.06% maximum deviation, and agree to 0.03% on the average.

Table 2.-COMPRESSIBILITY AND INTERACTION COEFFICIENT OF BINARY MIXTURES OF NATURAL GAS COMPONENTS

Mixture	Composition Mole % First Component	Gas Law Deviation b_m^*	Interaction Coefficient $b_{1,2}^*$	Mixture	Composition Mole % First Component	Gas Law Deviation b_m^*	Interaction Coefficient $b_{1,2}^*$
Methane-Ethane	50.6 50.7	.00472 .00441	.00436 .00376 AVG .00406	Nitrogen-Methane	50.0 50.6	.00091 .00093	.00072 .00078 AVG .00075
Methane-Propane	49.7 50.3	.00798 .00771	.00590 .00558 AVG .00574	Nitrogen-Ethane	50.1 50.3	.00344 .00334	.00254 .00236 AVG .00245
Methane-Isobutane	48.6 49.9	.01155 .01137	.00651 .00688 AVG .00669	Nitrogen-Propane	48.4 48.4 48.4	.00682 .00650 .00682 AVG .00671	- - - - - - - - - AVG .00334
Methane-n-Butane	72.1 74.8 75.1 48.5 48.7 23.6 23.7 24.6	.00702 .00626 .00583 .01326 .01323 .02251 .02190 .02174	.00843 .00806 .00711 .00765 .00773 .00724 .00567 .00634	Nitrogen-n-Butane	49.7 49.8 49.3	.00622 .01039 .01070	.00334 AVG .00348 AVG .00352 AVG .00382 AVG .00367
Methane-Isopentane	59.8 59.7	.01345 .01358	.00917 .00933 AVG .00925	Carbon dioxide-Methane	49.6 49.5	.00318 .00323	.00260 .00270 AVG .00265
Methane-n-Pentane	59.2 60.5 59.9	.01542 .01479 .01544 Weighted AVG .01132	.01107 .01103 .01180 AVG .01132	Carbon dioxide-Ethane	49.5 49.1	.00630 .00602	.00532 .00494 AVG .00523
Ethane-Propane	50.5 50.2	.01266 .01259	.01222 .01162 AVG .01192	Carbon dioxide-Propane	49.0 50.1	.00977 .00992	.00744 .00800 AVG .00777
Ethane-n-Butane	49.9 49.8	.01830 .01859	.01542 .01592 AVG .01567	Carbon dioxide-n-Butane	74.5 49.5 50.2 24.6	.00924 .01498 .01456 .02322	.00975 .00990 .00942 .01021 AVG .00978
Propane-n-Butane	50.4 49.6	.02504 .02499	.02426 .02388 AVG .02407	Carbon dioxide-Nitrogen	49.6 50.0	.00220 .00259	.00144 .00218 AVG .00181

* $b_m = x_1^2 b_{11} + 2 x_1 x_2 b_{12} + x_2^2 b_{22}$ where b_1, b_2 are gas law deviations (1-2) at one atmosphere for the mixture, pure component 1, and pure component 2, respectively, at mole fractions x_1 and x_2 of the components in the mixture.

COMPLEX MIXTURES

In the Benedict-Webb-Rubin equation the linear square root combination is used to predict constants for mixtures from constants for the pure components for the second virial terms. Applied to our parameter this yields:

$$b_m = \left[\sum_i x_i b_i^{1/2} \right]^2 = \sum_i x_i^2 b_i + 2 \sum_{i \neq j} x_i x_j b_i^{1/2} b_j^{1/2} \quad (7)$$

Comparison with equation 4 indicates that interaction coefficients for a given component i should lie on a straight line of slope $b_i^{1/2}$ if plotted against $b_j^{1/2}$. This plot is shown in Fig. 2. Experimental points fall reasonably close to the predicted value, except for carbon dioxide mixtures. In order to retain the advantages of the linear square root combination for calculating the compressibility factor of complex mixtures, a pseudo b value for carbon dioxide has been calculated (Table 3).

Two four-component mixtures were prepared and their gas law deviations measured to test methods of predicting the compressibility factors of complex mixtures. The measured values are presented in Table 4, together with values calculated by:

- 1) Linear combination of gas law deviations of components,
- 2) Mixture rule with binary interaction coefficients, equation (4), and
- 3) Linear square root combination of gas law deviations of pure components equation, (7), with the pseudo deviation for carbon dioxide.

These results indicate that the compressibility factor of complex mixtures can be calculated by either 2) or 3) with an accuracy of 0.03% or better. This represents a distinct improvement over the linear combination.

Heating values of gas mixtures are sometimes calculated by a summing of terms of the form $x_i H_{g,i}$, where $H_{g,i}$ is the real gas heating value of the pure component. This formula yields values for the two mixtures in Table 4 which are about 3 Btu per SCF, or almost 0.3%, too high. As a result of this study it is recommended that the heating value be calculated on the basis of the ideal gas heating values, and be corrected for nonideality by the mixture compressibility factor, calculated by either of the recommended combining rules, methods 2) or 3). By this procedure the error of calculation for the mixtures in Table 4 is reduced to only 0.3 Btu/SCF, or 0.03%.

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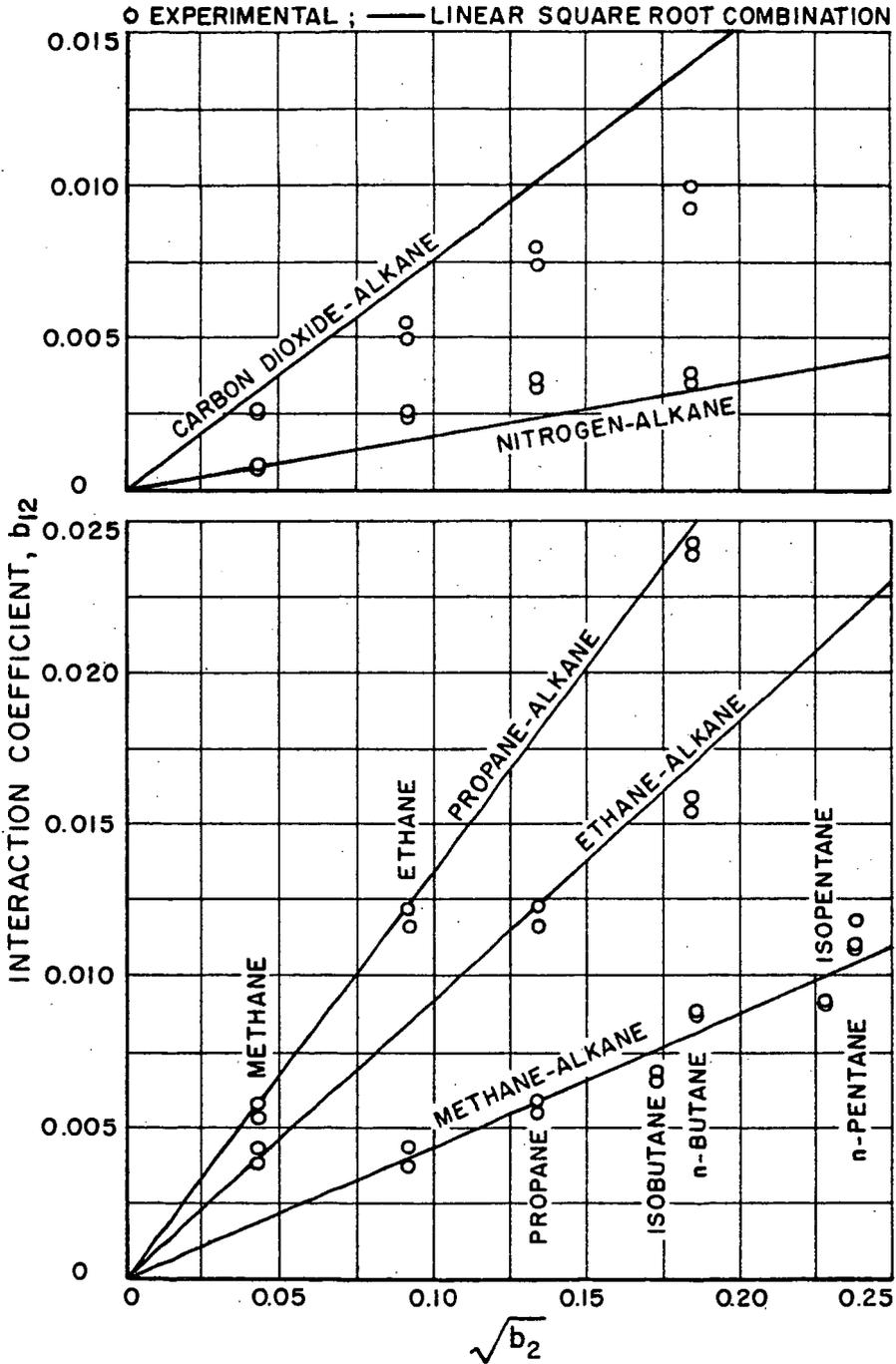


Fig. 2.- COMPARISON OF EXPERIMENTAL AND CALCULATED INTERACTION COEFFICIENTS OF NATURAL GAS COMPONENTS

Table 3. GAS LAW DEVIATIONS OF NATURAL GAS COMPONENTS AT 60°F AND ONE ATMOSPHERE

<u>Hydrocarbon</u>	<u>Gas Law Deviation b = 1 - z</u>	<u>Source</u>
Methane	0.0019	API ¹
Ethane	0.0084	API ¹
Propane	0.0180	API ¹
Isobutane	0.0297	IGT
n-Butane	0.0339	IGT
Isopentane	0.0518	IGT
n-Pentane	0.0565	IGT
Nitrogen	0.0003	NBS ⁴
Carbon Dioxide	0.0057*	NBS ⁴

* For calculation by linear square root combination, use the pseudo value, b = 0.0041.

Table 4. GAS LAW DEVIATIONS OF FOUR-COMPONENT MIXTURES AT 60°F AND ONE ATMOSPHERE

	<u>Mixture 1</u>	<u>Mixture 2</u>
Methane, mole %	67.44	64.14
Ethane, mole %	16.37	20.68
Propane, mole %	5.30	5.02
Nitrogen, mole %	10.89	0.00
Carbon Dioxide, mole %	0.00	10.16
b _m measured	0.00274	0.00331
b _m calculated*	(1) 0.00364	0.00444
	(2) 0.00292	0.00357
	(3) 0.00285	0.00362

* b_m calculated from (1) $b_m = \sum x_i b_i$
 (2) $b_m = \sum x_i^2 b_i + \sum 2x_i x_j b_{ij}$
 (3) $b_m = (\sum x_i b_i^{1/2})^2$

LITERATURE CITED

- (1) American Petroleum Institute, "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44. Pittsburgh: Carnegie Institute of Technology, October 31, 1958.
- (2) Burnett, E. S., J. Applied Mechanics 3, A-136-40 (1936).
- (3) David, H. G. and Hamann, S. D., in Institution of Mechanical Engineers, "Thermodynamics and Transport Properties of Fluids," 74-78. London: The Institution, 1958.
- (4) Hilsenrath, J. et al., "Tables of Thermal Properties of Gases." NBS Circular 564. Washington, D. C.: Govt. Print. Office, 1955.
- (5) Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., "Molecular Theory of Gases and Liquids," 132. New York: John Wiley and Sons, Inc., 1954.
- (6) Jessen, F. W. and Lightfoot, J. H., Ind. Eng. Chem. 28, 870-71 (1936) July.
- (7) Kistemaker, J., Physica 11, 270-76 (1945) December.
- (8) Kistemaker, J., Physica 11, 277-86 (1945) December.
- (9) Rossini, F. D. et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44. Pittsburgh: Carnegie Press, 1953.