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THE "COAL–METHANE" NATURAL EQUILIBRIUM SYSTEM AND METHODS FOR STUDYING IT

I. L. Ettinger

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1. METHANE–COAL DEPOSITS

Deposits of ordinary coal and lignite constitute a gas-producing region of the Earth's crust which is unique and of great practical importance.

The principal components of the gases of coal seams are carbon dioxide, nitrogen, and methane. The appearance of carbon dioxide in coal seams is linked with the oxidation of the coal by oxygen, the metamorphism of the rocks, the migration of the products of the activity of living creatures in the soil layer, and the migration of atmospheric carbon dioxide. The nitrogen has only an atmospheric origin, and the methane is a product of the metamorphism of coal.

The gas phase is not in a quiescent state in the depths of the coalfields: the gases from the metamorphism of coal and rocks move upwards the terrestrial surface, and the gases of atmospheric origin and from biochemical processes move in the opposite direction. The existence of

two steady flows leads to the establishment of dynamic equilibrium between them. Individual gaseous zones will separate out[1] in stable equilibrium in the coal seams and some or others of the components will predominate: a nitrogen–carbon dioxide zone; a zone of nitrogenous gases; a nitrogen–methane zone; and a zone of methane gases.

The present gas-bearing capacity of the coal seams depends on the local geological conditions as well as on the gas-dynamical processes; these conditions include the different coals in the bed and the degree of subsidence of the seams, the presence in them of geological disturbances and outcrops, differences in the gas permeability of the coals and rocks, the action of the infiltrating waters, etc.; all this can assist or impede the migration of coal gases to the day surface.

During the formation of ordinary coal of an average degree of metamorphism, approximately one-quarter of the total organic mass is converted into methane. In the further conversion of the coal into anthracite, another 10% of its total mass is transferred to the gas phase[2].

However, in contemporary coal seams this quantity of methane is not observed. Mining workers find that the methane which is now encountered in coal seams is only about 1 wt.% of the coal mass[2].

The solubility of methane is low; consequently the infiltration water carries very little methane with it. There has been hardly any chemical reaction of the methane with the rocks in the lithosphere, since at the temperatures at which coal formation takes place methane is inert and does not react with either acid or with basic rocks.

For methane, there is only one path for leaving the coal seam — diffusion into the atmosphere; however, if the quantity of methane evolved throughout the whole time of existence of the coal deposits is calculated and the stocks of methane remaining bound with the coal are subtracted, then it appears that 0.02–0.03% of the atmosphere should consist of methane, even without taking into account possible sources of methane other than coal formation (volcanoes, natural gases, petroleum wells, surface decay of plants, etc.). Nevertheless, methane is not detected in the atmosphere in any appreciable amounts.

The most probable hypothesis concerns the oxidation of the methane in those layers of the gaseous envelope of the Earth's crust where there is an appreciable amount of ozone and also in lightning discharges, in which the methane is oxidised to carbon dioxide, by-passing the stages of formaldehyde and carbon monoxide.

However, the quantity of methane which saturates the coal seams in their present condition is so great that the coal deposits can be considered as methane–coal deposits. The methane of the coal seams is often considered only as a hazard in coal mining, but then natural gases should also be considered only as secondary fossil fuel, the exploitation of which is a sideline in petroleum engineering.

The volume of gas liberated from coal in coal mines increases each year; the maximal methane liberation is already approaching 100 m^3 (in some instances 300 m^3) per tonne of coal mined; the total calorific value of this gas equals 15% or more of that of the coal[3,4]. Therefore in calculating reserves and appraising coal deposits it is necessary to consider them as complex deposits of solid and gaseous fuel and accordingly plan the complex working of both fossil fuels. A coal mine now becomes a producer of not only coal but also the more valuable (in calorific value and convenience of use) fuel — firedamp, the energy of which has until now been lost in flushing it out by a ventilation stream.

TABLE 1. Quantity of methane released from all the mines of a country, 10^6 m^3 d^{-1}.

USA	11.0	Japan	2.8
Federal Republic of Germany	8.5	Belgium	2.6
		Czechoslovakia	1.2
England	8.0	Poland	1.0
USSR	7.0	Netherlands	0.4
France	3.0		

The reserves of methane in coal seams of industrial importance (on conversion into conventional fuel) occupy the second place (after coal) among fuel sources and are seven times greater than the investigated reserves of natural gas[4].

The firedamp released each year in English coal mines is equivalent to 23×10^8 kcal, or 13×10^6 tonnes of good-quality coal[2].

Lidin and Airuni's table (Table 1), which relates to the beginning of 1962, gives an idea of the quantity of methane liberated in the main coal-mining countries in the working of coal deposits.

With the liberation (as subsidiary to coal mining) of such large quantities of methane (2.5×10^9 m^3 a^{-1} for the USSR) it is impossible to evade the question of the use of this gas in the national economy.

Of course, not all the methane of coal deposits can be used, in view of its low concentration in the ventilation stream, but in the artificial harnessing of the methane, which in ever-increasing degree is being developed here and abroad, firedamp is used as illuminating gas, an industrial and motor fuel, and a chemical raw material.

In the USSR it is planned[3] to increase the recovery of firedamp from 250×10^6 m^3 in 1961 to 1×10^9 m^3 a^{-1} for 1965.

The problem of the recovery of metamorphic methane from coal has, apart from the increase in energy reserves, also another, no less important, side. Because of the explosiveness of oxygen–methane mixtures, firedamp has always threatened the lives of miners, who have considered it their chief enemy and obstacle in work.

In the contemporary development of seams of the most valuable coking coals the depth of mining operations is rapidly increasing and in addition the quantity of gas which is liberated with each tonne of coal mined is also increasing.

In the USSR, up to 1 January 1960 84% of all the coal mined was worked by underground operations and in that over 66% of all pits were gas-bearing, and 30% belonged to the supercategory, that is, to those in which more than 15 m^3 gas per tonne of coal mined were liberated in separate regions[5].

Creating safe conditions of work for miners and increasing the profitability of coal deposits are the two sides of the same question, which boils down to how to make coal a competitive source of energy in comparison with natural gas, petroleum, water power, and nuclear energy.

For a scientific and practical solution of these problems, a detailed and thorough study of the natural equilibrium of the "coal–methane" system which exists in most of coal seams being worked is necessary.

2. METHODS OF STUDYING THE "COAL–GAS" NATURAL SYSTEM

Study of the structure of coal was started in the 1830's and undertaken by the methods of "classical" chemistry, which achieved much in the study of the chemical nature and composition of the fossil coals and also in establishing the chemistry of the processes in various stages of coal formation. These methods seemed useless when the investigation came to hypotheses about the fine structure and the constitution of the surface of coal, a study of which is necessary for the modern technology of its mining and utilisation.

Over the last 15–20 years a coal science has been formulated[6,7] which united chemico-analytical methods of studying coal with the modern approaches of exact sciences. Both in the USSR and abroad, extensive geological, petrographic, physical, chemical, mechanical, and physicochemical investigations of coal as a source of energy, a metallurgical and chemical raw material, and a medium in which people have to work underground, have been carried out.

An attempt can be made now to present a general picture of the methods for studying fossil coals and to show the utility of each method of investigation. Like every classification of natural phenomena and the sciences of studying them, this scheme has a great element of complexity.

In the geology of coal deposits, by *coal* is meant a solid, combustible, sedimentary rock of plant origin, containing mineral impurities[8].

In the petrology of coal the unit being studied is the coal seam, determinable as a compact stratification, consisting of coal blocks, different in the degree of the chemical modification of the vegetable residues, and also of mineral inclusions and intercalations[9].

In coal petrography, the principal method of investigation of which is optical microscopy, coal is seen as a heterogeneous substance consisting of various petrographic components, which differ from one another in colour, physicomechanical and optical properties, and degree of retention of the plant structure[10].

Physicochemical methods of investigation increase the resolution by three orders of magnitude in comparison with optical microscopy, that is, to 10^{-7} cm; they permit the state and area of the surface of fossil coals, their porous structure, and the size distribution of the pores to be studied.

From the viewpoint of the physical chemistry of fossil coals, coal is a highly porous natural sorbent.

Colloidal investigations of coal do not increase the resolution in the study of structure but give a new approach to ideas about coals. In the initial stages of coal formation the coal substance is a heterogeneous, highly disperse system, which consists of the products of conversion of the plant residues, dispersed in water, and possessing aggregate stability.

Such a system can arise by two paths: (1) by dispersion of a coarsely dispersed multi-phase system, or (2) from a single-phase system, by enlargement of the molecules and their aggregates. Both these methods of formation of colloidal systems took place at the time of the peat and lignite stages of coal formation[11].

Ordinary coals are also colloids of the second type, that is, high-molecular-weight systems in which both the disperse phase and the dispersion medium are in the solid state[12].

In the metamorphism of such solid systems there occur the stages of swelling, dispersion, formation of colloidal systems, their aging, and breakdown.

The heterogeneous nature of coal-chemical reactions in which natural coals participate, the non-uniform participation in these reactions of different reactive groups of coals[13] leads to ideas about their macromolecular structure; coal appears to be a three-dimensional polymer in which plane polycyclic networks of atoms of aromatic carbon are linked to one another by side-chains (phenol, hydroxyl, quinone ether, etc. side-chains)[14,15].

Physical methods penetrate deepest of all into the structure of coal. Studies by X-ray diffraction gives information about the dimensions of the polycyclic elements of the macromolecules. Infrared spectroscopy determines the different forms of C–H bonds and the quantitative relation between aromatic and aliphatic compounds.

Thanks to the use of physical methods it has been shown that during metamorphism the coal substance is converted into carboid, in which the plane polycyclic networks of carbon atoms are turned round, tending to be arranged in small piles; some of the electrons of the carbon atoms thereby enter into the space between the atomic layers and bring about an increase in the electrical and thermal conductivities[11].

The eight listed main approaches to coal are different in terminology and methods of investigation, degree of penetration in the structure of coal and possible practical use of their concepts for studying the nature of the "coal–gas" natural system.

The conditions of agglomeration in which the coal deposits were created determine the quantity of gas retained in the seams; the presence of various petrographic micro-components of coals gives the different sorption capacities of coals with the same degree of metamorphism; the mechanical and geological properties of the coal colloids are linked with the different degree of gas-saturation of the coal; the quantitative relation between cyclic condensed nuclei and aliphatic side groups is determined by the degree of natural activity of coals as sorbents; the degree of ordering of the graphite lattice leads to the disappearance of the sorption properties in fossil coals, etc.

The study of the "coal–gas" system is based mainly on physicochemical investigations, but it is unthinkable without geology, petrology, and petrography, colloid science, and coal chemistry and physics.

3. COAL AS A COMPONENT OF THE "COAL–GAS" SYSTEM

The properties of coal as a highly porous sorbent are determined by the range of structural sizes, which differ by at least five orders of magnitude (from 10^{-3} to 10^{-8} cm).

To discriminate between such a large number of structural elements it is necessary to classify coal structures according to their nature and dimensions.

In coal it is possible to distinguish: (1) a molecular structure, determining the chemical nature and reactivity

of the coal, and (2) a disperse (colloidal) structure determining the behaviour of coal in non-chemical processes.

It is possible to discriminate between the rather complex molecular structure of coal only if the classification is continued further and the molecular structure is divided into two, which can be studied by different methods: (a) low-molecular, and (b) polymeric or macromolecular structure.

These three principal structures of coal (molecular, macromolecular, and colloidal) mainly determine its behaviour on reaction with gases.

On the one hand these border on coarser dispersoids (petrographic components and plant residues), and on the other, atomic structures.

(a) Molecular Structure of Coal.

The molecular structure of fossil coals is characterised by the carbon atoms being situated at the vertices of regular hexagons [16]. The carbon skeleton is based on hexagonal systems of cyclic construction, the different orientation of which determines the character of the molecular structure of the coals.

In the metamorphism of mineral coals there is a carbonisation of the substance, that is, an increase in the carbon content relative to the oxygen and hydrogen and also to the "secondary" elements (nitrogen, sulphur, etc.).

However, X-ray investigations of coals destroyed the conception of them as a molecularly homogeneous system in which on moving along the metamorphic series there is only an increase in the number of identical bricks. The coal substance appeared heteromolecular.

The X-ray investigations revealed two types of molecular structures in fossil coals: disordered, which cause general scattering of the X-rays, and more ordered, which cause their diffraction in a definite direction [17].

The more ordered parts of the structure are layers of hexagons; the number of condensed rings in such two--dimensional lattice is from four to ten [6]; with metamorphism, the diameter of these plates of hexagonal-cyclic structure increases from 7 to 16 Å; most of them are orientated at random with respect to one another and do not form a regular graphitic three-dimensional lattice; the maximal number of regularly orientated layers varies from three to ten for coals having an equal stage of metamorphism [18]. The diffraction of X-rays by coals varies for the coals in a metamorphic series (Fig. 1) and differs significantly from the diffraction which is characteristic for graphite [7,19].

Hence there are no graphitic crystals in coals, but only those elements from which the crystals can be formed under appropriate conditions of temperature and pressure. These rudiments of future crystalline structures (crystallites) are the nuclei of the molecular structure of the coal substance.

The framework of graphite-like crystallites is connected together by side groups — unique bridges. These side groups are the most disordered part of the molecular structure, which bring about the general scattering of X-rays. The side radicals of aliphatic structure can contain (in addition to carbon) hydrogen and oxygen, and even sulphur, nitrogen, and other elements. The destructive breakdown of coal when heated in the absence of air leads first to the detachment of unstable side groups; the rest are consolidated into coarse aggregates with an increase in the carbon content and a decrease in the yield of volatile products.

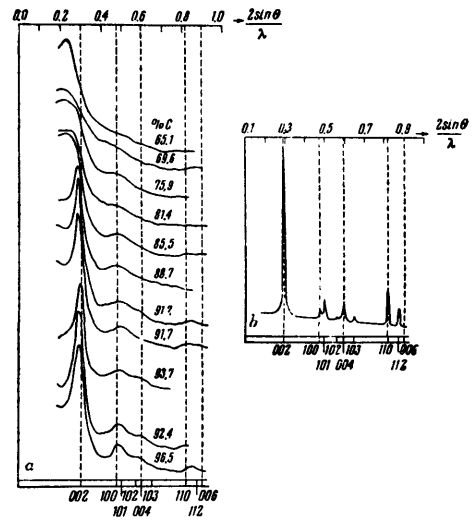


Fig. 1. Photometric trace of X-ray diagrams of: *a*) coal; *b*) graphite.

The nuclei of the polycyclic layers and the side aliphatic groups which connect the nuclei, together form the primary molecular structure of the coal. Hirsch [18] proposed a similar structural model of coal.

The mechanism of the formation of gases from the coal substance, which take place in the bowels of the Earth's crust, is connected with the detachment of the side groups. Gas formation is brought about by homolytic reactions, which proceed in the weakest parts of the molecular structure, that is, at the points of attachment of the side groups to the hexagonal graphite-like layers.

Whereas 82.6 kcal mole^{-1} is required for the rupture of the bond between the carbon atoms in the C_2H_6 molecule, only 10–12 kcal mole^{-1} is needed to break a bond between carbon atoms where each is connected with three aromatic rings.

(b) Macromolecular Structure of Coals

In many respects coal is reminiscent of artificial polycondensed resins. The physical and chemical properties of coals are not constant, but change within definite limits; coals are involatile and do not have definite melting or freezing points; the solubility of coals varies with the amount of solvent and the duration of heating, in that coals swell in solvents; vitrification is observed instead of crystallisation in coals; coals are subject to slow plastic deformation and this is highly sensitive to temperature; in the plastic state coals exhibit high viscosity.

In the process of metamorphism fossil coals are subject to polymerisation, which leads to the creation for them of a special amorphous state with a dual nature to the molecular structure, which consists of crystallites and amorphous parts.

Intramolecular reactions (dehydration, decarboxylation, etc.) are characteristic only for the lignite stages of coal

formation; the main processes in the metamorphism of ordinary coals are intermolecular condensations, that is, a growth of the molecule of the coal substance, with an increase in the carbon content from 75 to 95%. For such reactions to take place a definite activation temperature and intermolecular contact are necessary, the latter being achieved in the coal seams owing to the pressure of the overlying rocks.

In the metamorphism of ordinary coals, the polymerisation of their molecular structure proceeds mainly by detachment of side chains; condensed polycyclic layers approach within ~ 3.5 Å in this process; the coal substance acquires the property of a carboid with a characteristic black colour, and electrical and thermal conductivity; starting from the coking coals stage aromatic properties gradually disappear, since the coals are neither nitrated nor sulphonated, that is, they do not give the reactions typical of aromatic compounds [11].

In the detachment of side groups, chemical valencies are left at the place of their removal unsaturated; this facilitates the condensation of the molecular structure.

The primary molecular structure, consisting of nuclei and side groups, forms particles, which serve as elements of a second-order structure [20]. During this, gigantic macromolecules, polymeric in nature, are formed in the coal substance. In the macromolecules of coals, close-range order is observed only within the limits of each crystallite in the form of a two-dimensional lattice. Beyond the limits of the crystallites this order does not exist. The crystallites — small orientated fragments — fasten the coal polymers, like hoops, and make the whole system stable (Fig. 2). Each crystallite is turned somewhat relative to the next, the direction of the rotations being purely random [21].

Natural coals belong to a group of solid polymers whose importance in biology and technology is very great (rubber, cellulose, albumins, plastics, etc.). In solid polymers up to 60% of the material is in an amorphous state, whereas in low-molecular-weight substances the amorphous phase disappears completely during crystallisation [22].

In low-molecular-weight substances crystallisation sharply changes their structure and thermodynamic properties; this is because the whole amorphous mass is reconstructed into crystals with sharp surfaces of separation. In polymers, however, like natural coals, the ordered and disordered parts of the structure are indivisible; the crystallites contain only a small number of atoms, sufficient to diffract X-rays but insufficient to change the thermodynamic properties of the substance.

At the end of the last century, coal chemists made many attempts to devise structural-chemical hypotheses about the macromolecules of ordinary coals and lignites and represent them by formulae [23], but not one of these attempts led to the creation of a generally acceptable model. This is explained by the difficulties of reaching agreement between the concepts of organic chemistry and the results of the physical investigation. Kasatochkin's model [19] gave the most successful representation of the dual nature of the coal macromolecules (Fig. 3).

Van Krevelen's model [7] was devised on the basis of investigations of the optical and mechanical properties and the elemental composition of coals. In this model, which is based on the concepts of organic chemistry, cells of the cyclic parts of the structure are isolated. Such parts are not precisely the same as one another — as is observed in linear polymers with regular repetition of the monomer unit [24]. The value of the model lies in the concept of the existence of "nuclei" and side chains in the macromolecules of the coal substance.

The molecular weight of the macromolecules of the polymers varies within very wide limits — from 10^3 to 10^6. Other authors usually give lower values for the macromolecules of the coal substance. On the basis of his statistical structural analysis of coals, van Krevelen considers [24] that as the carbon content rises from 81.5 to 96.0%, the number of rings in the ordered layers increases from four to ten, and the molecular weight rises from 0.5×10^3 to 1.25×10^3.

Whitaker [25] in determining the molecular weight by an osmometric method obtained values of 9×10^3–12×10^3 for the products of the thermal dissolution of coals in ethylenediamine.

Probably the most correct ideas [26] are that coal exists as a monolithic aggregate system and has an infinite molecular weight, like a crystal of indefinite size.

(c) Colloidal Structure of Coal

The colloidal (disperse) structure of the coal substance is coarser than the atomic, molecular, and macromole-

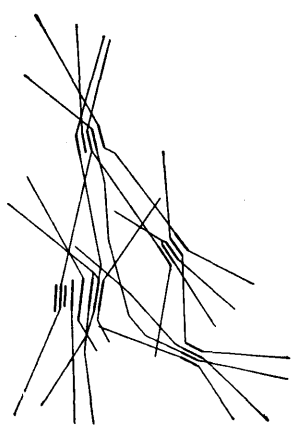


Fig. 2. Macromolecules of a polymeric character (after P. P. Kobeko).

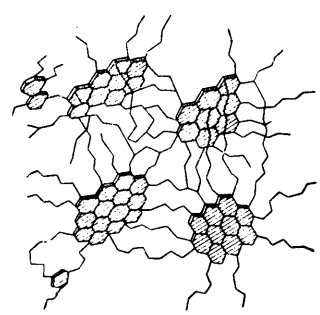


Fig. 3. Macromolecules of coal (after V. I. Kasatochkin).

cular structures. Even at the peat bog stage the aggregates of particles of humus and sapropelite materials acquire such large dimensions that they begin to show colloidal properties.

A complex colloidal structure is superimposed on the molecular structure of the coal substance, distorts its properties, and gives the coal a special quality which determines its behaviour as a component of the "coal–gas" system. The colloidal properties for different coals can differ markedly from one another, even when there is a very great similarity in their molecular composition [20]. The colloidal structure of the coal substance relates to particles with dimensions of 10^{-5} to 10^{-7} cm, pores and capillaries, with their associated capillary forces, inhomogeneous parts of the surface (where surface forces play the principal part), etc.

Coal colloids occupy a special position, since they can be assigned to both the main types of colloid: disperse heterogeneous systems and high-molecular-weight systems, which are formed by an increase in the size of the macromolecule or the formation of polymers. This explains why during the course of the long process of coal formation the structure and properties of the coal colloids changed sharply.

In the first stage, which can be considered to be mainly biochemical, the plant residues become peat at the bottom of the bog; during this, colloidal hydrosols (that is, disperse heterogeneous systems of the first type) were formed.

Then the hydrosols lost their aggregate stability and conglomeration of the colloidal particles began. The hydrosols were converted into hydrogels — a reticular three-dimensional structure of rigid colloidal particles and capillaries filled with water (peats and earthy lignites). Such gels occupy a position intermediate between liquid colloids and solid polymers.

In the second stage of coal formation (geochemical) the elastic gels were converted into solid polymers owing to the increase in size of the macromolecules of the coal substance (second type of colloidal systems).

In the early stages of coal formation water is the disperse medium; in subsequent stages it was mechanically absorbed by the cells of the hydrogel; in the metamorphic stages of ordinary coals water in the free state almost disappears. The remaining water is held either by close-acting adsorption forces or exists in ordinary coals as a thin film of liquid water, held by adhesion forces. In such a state the water has already lost the properties of a solvent or a dispersion medium.

In further metamorphism, which is accompanied by further loss of water and compaction of the molecular structure, particles of the second order (macromolecules) form still coarser aggregates — elements of a disperse structure of the third order. The coal is converted into a three-dimensional solid polymer. The colloidal properties of such a polymer are already determined not so much by the particle sizes as by the presence of a large boundary with a considerable free surface energy.

The compaction of the molecular structure of coals is accompanied by the detachment of side groups; during this, vacancies are formed in the molecular structure of the coal substance. The forces of molecular attraction tend to compress these vacancies and bring about shrinkage of the coal [20]. However, coals, being three-dimensional polymers with partly ordered packets of a two-dimensional crystalline lattice, are characterised by low elastic limits and rather large moduli of elasticity (up to 15×10^{10} dyn cm^{-2}). [2] Therefore the coal substance resists compression and the vacancies in it are retained to a considerable degree. This is assisted by the vacancies containing gases formed in the detachment of side groups, conditions being such that migration from the seam is prevented. Ultraporosity appears in the coals, which determines the high sorption activity of the fossil coals and creates a real basis for the prolonged existence in the coal seams of a "coal–gas" system.

Pores in coals are often considered as vacancies, the walls of which serve as the usual phase boundaries, but the surface of the ultrapores, thanks to their small size, is at the limit of disappearance of the phase and does not possess the features of a microscopic surface [20,22]. Calculation of the internal surface of the pores from the sorption by coals of gases which are condensed on phase surfaces is uncertain because of the above reasons.

Usually, in speaking of the colloidal structure of coals the term "micelle" is employed to denote the colloidal particles. The term "micelle of coal substance" has a double meaning.

In a state of colloidal hydrosol a coal micelle, as in the case of all other sols, consists of a central nucleus of a solid substance and, surrounding the nucleus, an electrical double layer of solvated ions; the first layer of stabilising ions is adsorbed on the surface of the central nucleus. The system as a whole is electrically neutral.

A second concept of the micelle of coal is more frequently encountered: this relates to its state in the form of a solid three-dimensional polymer. In this concept the micelle of coal substance should represent a complex of macromolecules, that is, a structural unit of the third order in relation to the molecules and macromolecules. This is colloidal particle (10^{-5}–10^{-7} cm) with a phase boundary and a partly ordered structure (crystallites or nuclei of macromolecules). The chain of separate macromolecules forms a more or less spherical micelle, either by the bending of macromolecules and their accumulation in the form of bundles, bound by cross-linking or by radial packing of the macromolecules with later formation of cross-links between them [12].

From determinations of the heats of wetting of coals in methanol, Bangham and coworkers [27] found the internal surface of coals to be 20–200 $m^2 g^{-1}$ and calculated from this the following micelle diameters: 230 Å for gas coals and 2500 Å for coking coals.

The colloidal properties of the solid polymer appear particularly distinctly in what is petrographically the most homogeneous component of coal — vitrain. The parent substance of vitrain is a hydrogel of peat seams, which owing to syneresis has lost part of its water, hardened, and become non-elastic.

4. GAS AS A COMPONENT OF THE "COAL–GAS" SYSTEM

The role of the gaseous component of the "coal–gas" system existing in coal seams is determined by its origin, by the qualitative and quantitative composition of the gas mixture saturating the seam and the forces which bind the gas to the coal.

The gases which are formed at the various stages of carbonisation almost completely leave the coal seams,

migrating by various paths to the surface. Coverings packed by subsequent rock beds hinder the migration of gases and create conditions for their accumulation; the comparatively short (from a geological viewpoint) interval of time was insufficient for the coal seams to give off the gases which were formed in the later stages of regional metamorphism and originated in tectonic processes [24,25].

Different geological conditions in the coal seams and geochemical processes accompanying the metamorphism of coals lead to different gas contents in the seams, gas compositions, and zonalities in their vertical distributions. The processes of intraseam migration of gases do not obliterate the non-uniformity in their distribution in the seam, which is associated with the genesis of the gases [28,29]. Coal deposits have a gas zonality (Fig. 4) in which the zone boundaries vary for different deposits and even for different parts of the same deposit.

Ideas about the zonal distribution of the gases in coal allow the main components of the coal seam gases and their proportion in the various zones to be distinguished and show how these ratios vary in different seams and at different depths.

For small deposits, attempts have been made to speak of the mean composition of the gas which saturates the coal seams within the scale of the deposit concerned; with all their tentativeness, such data give some illustration of which gases are held in the seams in their present state and within what concentration limits.

For example, Coppens [30], from analyses of 50 specimens of gas, from 63 Belgian pits, sampled in the zone of methane gases found the compositions of the gases of the Belgian deposits given in Table 2.

Below the zone of gas ventilation the main component of the coal seam gases is methane.

The problem of the origin of carbon dioxide cannot be considered solved. According to Graham [31], gas formation in the carbonisation of plant residues proceeds through the following stages: initially, when the carbon concentration is rising from 65 to 79%, predominantly CO_2 is liberated; during the subsequent rise in the carbon concentration from 79 to 85.8%, CO_2, H_2O, and CH_4 are liberated, the volume of the CO_2 being twice that of the methane; during the increase in carbon concentration to 88%, the amount of CH_4 formed increases; and at 92.3% carbon, methane is already the principal product; above 92.3%, only methane is liberated.

The experiments of Bergius [32] on the artificial carbonisation of peat are indirect confirmation of the predominant

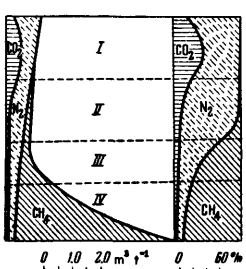


Fig. 4. Gas zonality of coal deposits (after G. D. Lidin).

TABLE 2. Composition of the gases of the Belgian coal seams.

	CH_4	C_2H_6 (+ higher hydrocarbons)	H_2	CO_2	N_2(+Ar)	He(+Ne)
Minimal content	92.9	0.02	0.000	0.03	0.0	0.001
Maximal content	99.6	2.79	0.235	3.38	6.1	0.330
Mean content	97.3	0.47	0.044	0.74	1.5	0.044

formation of CO_2 in the various stages of carbonisation. During the heating of dry peat, Bergius obtained so-called "lignite" containing 75.4% C. In heating 10 g peat, 1110 ml gas containing CO_2 88.1, CH_4 8.4, H_2 2.2%, etc. was evolved. In further experiments on the carbonisation of this "lignite" at pressures up to 6000 atm, Bergius obtained a product with 89% C; the gas liberated contained CH_4 70–80, CO_2 8–11%.

The carbon dioxide formed in the various stages of carbonisation left the coal seams by escaping into the atmosphere, disolving in the seam waters, and reacting with the containing rocks, forming carbonates.

The carbon dioxide which is contained in the coal seams of today has various but different origins: (1) juvenile carbon dioxide (frequently of volcanic origin) penetrates into the coal seams from sources situated below them [24,32]; (2) carbon dioxide which is the final product of deep oxidation of coals, to which lignites are particularly susceptible, which explains, for example, the high concentration of CO_2 in the sub-Moscow basin [33].

Hence for contemporary coal seams CH_4 is an endogenic gaseous component and CO_2 an exogenic.

Ideas about the local penetration of higher hydrocarbons — homologues of methane — into coal seams from petroleum deposits or petroleum-formed substances are still unproved. Other suggestions about the formation of higher hydrocarbons together with methane in the metamorphism of coal and their loss during subsequent natural degassing of the seam are more probable.

The amounts of methane formed throughout the carbonisation process significantly increase the quantities of gas which are now observed in the coal seams. According to Lidin [1], the amount of methane formed during the change from lignite to long-flame coal reaches 30–40 $m^3\ t^{-1}$, that to fat coals 70–80, to lean coals 120–150, and to semi-anthracite up to 200 $m^3\ t^{-1}$. Patteisky [34] considers that these quantities are higher (300–350 $m^3\ t^{-1}$ on conversion into fatty coals) and Vidal [35] gives figures of up to 1300 $m^3\ t^{-1}$ (for anthracites).

In the peat stage of coal formation, when the coal macromolecules originated and the hydrosols were formed, conditions did not yet exist for the creation of an equilibrium system with gaseous components; the gases being liberated in the coal formation reactions escaped.

In subsequent stages, when the hydrosols were converted into hydrogels, which were then subjected to syneresis and lost water, cavities of various dimensions were formed in them. A porous structure was created in the coals; this structure was qualitatively and quantitatively modified both during the conversion of peat into lignite and during the conversion of lignite into ordinary coal.

In the porous structure of fossil coals there appeared forces bonding the coal with the gas which made possible the creation and retention up to the present of the natural equilibrium of the "gas–coal" system. The valence bonds between the carbon atoms in the hexagonal-cyclic parts of the coal macromolecule are characterised by close action and large bonding forces ($\sim 10^2$ kcal mole^{-1}); the forces bonding the cyclic part of the molecules with the side chains have an energy an order of magnitude less (10^1 kcal mole^{-1}); the van der Waals forces which bond the coal substance with the gases have a bond energy again a whole order of magnitude less (10^0 kcal mole^{-1}), but are characterised by a comparatively large sphere of influence, non-specificivity, and additivity.

The van der Waals forces, which determine the sorption capacity of fossil coals with respect to gases, begin to appear noticeably when water is lost from the coals during metamorphism and side-groups are removed, which screened the sorption surface of the coal.

Hence, as a result of the physical and physicochemical processes taking place throughout the genesis, diagenesis, and metamorphism of coals, there was created in them the specific structure which conferred on the coals the properties of active natural sorbents and was the prerequisite for setting up the "gas–coal" natural system.

A thorough study of such a system has great significance for theoretical and practical problems in not only the mining, but also the utilisation of coals, since in many instances one should now speak not of coal, but of methane–coal deposits.

Study of the "gas–coal" system includes a series of problems, the most important of which are: study of the form of the bond of the coal with the absorbed gases, the sorption and collector properties of coal, the physical and physicochemical conditions of equilibrium of the system at various depths and in different geological circumstances, the conditions of the shift in the equilibrium in the system during changes in pressure, temperature, mechanical influences, etc.

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SYNTHESES INVOLVING REACTIONS OF PEROXIDE COMPOUNDS WITH SALTS OF TRANSITION METALS IN SOLUTION

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