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Thermochemistry of the formation of fossil fuels

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Abstract—Photosynthesis liberates O_2 from a mixture of CO_2 and H_2O in forming biological substances. Formation of fossil fuels is also associated with progressive depletion of oxygen from biological substances. The two processes are thus sequential in terms of deoxygenation. To evaluate thermochemical relations of the deoxygenation processes in a simple manner, the concept of deoxygenation free energy G_{deox} and deoxygenation enthalpy H_{deox} (defined as Gibbs energy and enthalpy, respectively, of reaction to release unit mole of O_2 in forming a compound $C_xH_yN_zO_w$ from CO_2, H_2O, and N_2) are computed for over 150 compounds. If compound A changes to compound B by dehydration and/or decarboxylation, and A has a higher G_{deox} value than B, energy is released and the transformation can occur spontaneously; likewise heat is released if A has a higher H_{deox}. The computed results indicate that energy input is required only for the initial stage of photosynthesis, and progressive deoxygenation and aromatic condensation during diagenesis should decrease free energy and release heat. Catagenesis and metagenesis are also most probably spontaneous and exothermic because both low C-number paraffinic hydrocarbons and polycondensed aromatic kerogens have the lowest G_{deox} and H_{deox} values among various homologous groups even at room temperature. The ultimate products of the spontaneous evolution of fossil fuels are methane and graphite. The role of increased temperature associated with deeper burial is not to change the position of equilibrium, but simply to increase the reaction rate exponentially so that the extremely slow reactions would proceed in geologic time.

INTRODUCTION

SOLAR ENERGY IS chemically stored, *via* photosynthesis, as an unstable coexistence of free oxygen and organic matter near the Earth's surface. When organisms die, most of the biological matter is aerobically degraded to gases and water-soluble compounds and is recycled to the atmosphere and hydrosphere. Only about 0.1% escapes chemical and microbial oxidation within the first few centimeters of burial and undergoes anaerobic transformation to fossil fuels in sediments. Because of accumulation over geologic periods of time, however, the total amount of fossilized organic matter is estimated to be orders of magnitude (about 2000 times according to WELTE, 1970) greater than the live biomass, warranting a thorough understanding of the nature of the transformation process.

Much biogeochemical work was devoted to the molecular identification and quantification of the organic substances in relation to geologic factors (basin structure, burial depth, age, temperature, etc.) to deduce the rate and chemical mechanisms of the degradation of biological matter and transformation to fossil fuels (BREGER, 1963; TISSOT and WELTE, 1978; HUNT, 1979). Consequently, recent investigators have arrived at the deduction that the maturation process occurs spontaneously in stages when the temperature increases due to burial along a normal geothermal gradient. The present work is an attempt to provide an explicit thermochemical basis for this deduction.

BACKGROUND

Photosynthesis may be viewed as a natural process in which photosynthetic organisms liberate oxygen from a mixture of mainly H_2O and CO_2, and some N and S compounds, to form biological substances. Transformation of biological remains to fossil fuels may also be viewed as a process in which oxygen is removed from biological substances. Graphic presentations by OWEN (1948), VAN KREVELEN (1961), and others show at a glance that O as well as N and S are depleted progressively from biological substances (*e.g.*, carbohydrates, proteins, lipids, and lignin) during their transformation to fossil fuels (*e.g.*, kerogen, petroleum hydrocarbons, natural gas, and coal). In this sense, photosynthesis and fossil fuel formation are natural sequential processes in which the compounds of the C-H-O-(N-S) system are deoxygenated.

As caloric values of organic compounds generally increase with increasing degree of deoxygenation, some earlier investigators searched for the sources of the energy thought to be necessary for the transformation, analogous to the solar energy input in photosynthesis. Bacteriological processes, radioactivity, heat, and pressure have been studied as the possible sources of the transformation energy (BREGER, 1963). Except perhaps for the effect of heat in thermal metamorphism of coal to anthracite, however, the search for these energy sources had remained uncertain.

More recent studies in the field and laboratory (summarized by TISSOT and WELTE, 1978; HUNT, 1979), have indicated that most biological compounds undergo rapid and extensive anaerobic chemical changes within several hundred meters of burial, where the temperature remains within the biologically active range (<50°C). Diagenetic processes, both chemical and microbial, transform reactive biological substances to more inert, insoluble polymers such as humic acids and kerogen. Further burial with accompanying temperature rise (to about 150–200°C) causes thermal degradation of kerogen to petroleum-range hydrocarbons, a process called catagenesis. Burial deeper than several kilometers (>200°C) results in metagenesis and metamorphism, in which methane and other gaseous hydrocarbons and carbonized residues are formed.

In the above scheme of fossil fuel evolution, temperature seems to play a controlling role. Because of the inevitable association of the depth of burial with increased time, temperature, and pressure, it is difficult to clearly determine if energy input as heat is indeed necessary, or if the late stages of transformation are merely hindered by high activation energies (mechanism) and require higher temperatures to proceed even given geologic periods of time. The ambiguities are especially strong in the discussions of thermal degradation, and "cracking" of geopolymers.

THERMOCHEMICAL CONSIDERATIONS

Evaluation of free energy changes for reactions involving natural organic substances is handicapped by the fact that too many complex and sometimes ill-defined compounds are involved, and also many reaction paths are still insufficiently understood. The approach described below, however, bypasses the complexities arising from uncertainties in reaction paths and outlines energy relations among many organic compounds. The approach is based on the assumption that the deoxygenation during maturation of fossil fuels proceeds *via* loss of H_2O and CO_2, a model well documented for coalification (VAN KREVELEN, 1963) and kerogen evolution (TISSOT and WELTE, 1978, p. 149).

The principle of the approach is that when one organic compound can theoretically be obtained from another by releasing H_2O and/or CO_2 (and N_2 if nitrogen is involved; sulfur is not considered here as it is a minor component), the free energy balance in the overall reaction, however complex the actual mechanism may be, is directly related to the difference between the Gibbs free energies required to make the two compounds from a mixture of H_2O, CO_2, and N_2 upon releasing 1 mole of free oxygen (O_2).

For example, the formation of ethanol (C_2H_6O) from glucose ($C_6H_{12}O_6$) at 25°C and 1 atm:

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2, \qquad \Delta G_r = -226.44 \text{ kJ} \quad (1)$$

(where ΔG_r is the Gibbs free energy of reaction, and kJ is kilojoule) may be regarded as being composed of two reactions, each of which releases 1 mole of O_2, in opposite directions:

$$CO_2 + H_2O = (1/6)\,C_6H_{12}O_6 + O_2, \qquad \Delta G_r = 479.82 \text{ kJ} \quad (2)$$

$$(2/3)\,CO_2 + H_2O = (1/3)\,C_2H_6O + O_2, \qquad \Delta G_r = 442.08 \text{ kJ}. \quad (3)$$

It is easy to see that $(1/6)\,\Delta G_r\,(1) = \Delta G_r\,(3) - \Delta G_r\,(2)$. Heat is known to be generated during the fermentation of carbohydrates. Reaction (1) can occur spontaneously as indicated by the negative free energy of reaction, although the presence of enzymes in malt increases the reaction rates multifold. The spontaneity of the conversion of glucose to ethanol is also indicated by the fact that $\Delta G_r\,(3) < \Delta G_r\,(2)$.

As seen above, whether one organic compound should spontaneously be converted to another, upon losing H_2O, CO_2, and/or N_2, could easily be surveyed by calculating the Gibbs free energy necessary to remove 1 mole of O_2 in forming each compound from CO_2, H_2O, and N_2 (if needed), and by comparing the computed free-energy values. Such a free energy of reaction may be defined as *deoxygenation free energy*, G_{deox}, and can be obtained from the Gibbs free energy of reaction for the general reaction:

$$x\,CO_2 + \frac{y}{2}\,H_2O + \frac{z}{2}\,N_2 = C_xH_yN_zO_w + \left(\frac{4x + y - 2w}{4}\right) O_2 \quad (4)$$

as

$$G_{\text{deox}} = \frac{4\Delta G_r(4)}{(4x + y - 2w)} \quad (5)$$

and

$$\Delta G_r(4) = \Delta G_f^0(C_xH_yN_zO_w) - x\Delta G_f^0(CO_2) - \frac{y}{2}\,\Delta G_f^0(H_2O) \quad (6)$$

where ΔG_f^0 is the Gibbs energy of formation for each chemical species involved at 1 atm pressure and at a specified temperature (25°C in this paper unless otherwise noted). If compound A changes to compound B via dehydration, and/or decarboxylation, the transformation can proceed spontaneously with a release of energy when A has a higher G_{deox}.

Similarly, *deoxygenation enthalpy,* H_{deox}, may be defined on the basis of equation (4) as

$$H_{\mathrm{deox}} = \frac{4\Delta H_{\mathrm{r}}(4)}{(4x + y - 2w)} \tag{7}$$

where the enthalpy of the reaction can be obtained from the enthalpy of formation, $\Delta H_{\mathrm{f}}^{0}$, of the chemical species involved as:

$$\Delta H_{\mathrm{r}}(4) = \Delta H_{\mathrm{f}}^{0}(C_xH_yN_zO_w) - x\,\Delta H_{\mathrm{f}}^{0}(CO_2) - \frac{y}{2}\,\Delta H_{\mathrm{f}}^{0}(H_2O). \tag{8}$$

The availability of Gibbs energy of formation data for complex solid and liquid organic compounds is rather limited, and an estimation is often difficult, particularly for uncharacterized geopolymers. In contrast, enthalpy of formation data or heat of combustion (H_{c}) data are available for a large number of organic substances in fair to good accuracy. In fact, combustion calorimetry constitutes the basis for obtaining thermochemical data for the majority of organic substances. It may be noted here that reaction (4) is exactly reverse of the combustion reaction, and that $H_{\mathrm{c}} = \Delta H_{\mathrm{r}}$ (4). Hence,

$$H_{\mathrm{deox}} = \frac{4H_{\mathrm{c}}}{(4x + y - 2w)}\,. \tag{9}$$

If compound A changes to compound B via dehydration and/or decarboxylation, the transformation reaction is exothermic when A has a higher H_{deox}. In view of complexity of estimating G_{deox} values for complex compounds as discussed later, the H_{deox} relation may be substituted for the G_{deox} relation in certain cases.

In summary, if compound A changes to compound B by dehydration and/or decarboxylation, and A has a higher G_{deox} value than B, energy is released and the transformation can occur spontaneously; heat is released if A has a higher H_{deox} than B.

In order to relate the G_{deox} or H_{deox} values of various compounds to the degree of deoxygenation, which is an index of maturation of fossil fuels, another quantity called *deoxygenation quotient,* Q_{deox}, is introduced. The deoxygenation quotient indicates the fraction of oxygen atoms removed from the total oxygen atoms present in the starting mixture of CO_2 and H_2O (and N_2) in forming a compound in the C-H-O-(N) system:

$$Q_{\mathrm{deox}} = \frac{4x + y - 2w}{4x + y} \tag{10}$$

where x, y, and w are defined in equation (4). Note that nitrogen as N_2 is not involved in determining Q_{deox} (it may if incorporated in the deoxygenation equation as NH_3 and/or NO_2, but for simplicity we disregard this possibility for now). The Q_{deox} for glucose, for example, is 0.667, and that for ethanol is 0.857, according to the above definition.

The G_{deox} and Q_{deox} values have been computed for some 150 common organic compounds, for which the Gibbs free energy data are available at 25°C (STULL *et al.,* 1969) and listed in Table 1. Some of these values have been plotted on a G_{deox} *vs.* Q_{deox} diagram (deoxygenation free energy diagram) in Fig. 1. Also, the G_{deox} values of some hydrocarbons (all $Q_{\mathrm{deox}} = 1$) are plotted against the atomic H/C ratio in Fig. 2.

Figures 1 and 2 show many interesting facts regarding the thermochemical relations among the common organic compounds. Notable points are listed below.

(a) Among the oxygenous homologous series, fatty acids have the lowest G_{deox} for a given Q_{deox}, followed by amino acids, proteins, alcohols, carbohydrates, aldehydes, and finally by ethers, in ascending order.

(b) Within each oxygenous homologous series, the G_{deox} decreases regularly with increasing C number, and the slope of the decrease against Q_{deox} also decreases regularly, approaching zero at $Q_{\mathrm{deox}} = 1$. The differences in G_{deox} among various oxygenous homologous series also decrease as Q_{deox} approaches 1.

(c) Among hydrocarbons, the G_{deox} of the olefinic series decreases regularly (allowing some reversals within the limits of uncertainties in the thermochemical data) with increasing C number, whereas that of the paraffinic series has the reverse trend. The cycloparaffinic series roughly follows the trend of the olefinic series, but the pattern is highly irregular.

(d) When the C number increases, the G_{deox} values of most common nonaromatic homologous series converge to a single value, which is about 424.7 kJ at 25°C (this value will be referred to as "the convergence value" of the G_{deox}). The G_{deox} values of aromatic rings uniquely diverge from the convergence value as the C number increases, decreasing toward the graphite value (394.4 kJ) as the degree of condensation increases.

Table 1. A list of H_{deox} (deoxygenation enthalpy) and G_{deox} (deoxygenation free energy), and Q_{deox} (deoxygenation quotient) values of common compounds of the C-H-N-O system. For hydrocarbons, atomic H/C ratio is given instead of Q_{deox} (all 1.00)

SECTION A

Name	Formula	State	Q_{deox}	Q_{deox} (kJ)	G_{deox} (kJ)
Fatty acids					
Formic acid	CH_2O_2	(l)	.333	509.17	540.24
Acetic acid	$C_2H_4O_2$	(l)	.667	437.30	436.89
Butyric acid	$C_4H_8O_2$	(l)	.833	436.70	429.72
Valeric acid	$C_5H_{10}O_2$	(l)	.867	436.57	428.57
Palmitic acid	$C_{16}H_{32}O_2$	(s)	.958	433.78	425.61
Polybasic and hydroxy acids					
Oxalic acid	$C_2H_2O_4$	(s)	.200	485.82	649.61
Lactic acid	$C_2H_6O_3$	(s)	.667	447.98	457.27
Succinic acid	$C_4H_6O_4$	(s)	.636	425.90	440.48
Pyruvic acid	$C_3H_4O_3$	(l)	.625	467.07	477.66
Fumaric acid, trans.	$C_4H_4O_4$	(s)	.600	444.88	466.08
Maleic acid	$C_4H_4O_4$	(s)	.600	451.70	473.57
Citric acid · H_2O	$C_6H_{10}O_8$	(s)	.529	471.63	499.84
Fatty alcohols					
Methanol	CH_4O	(l)	.750	484.41	468.36
Ethanol	C_2H_6O	(l)	.857	455.85	442.07
Propanol	C_3H_8O	(l)	.900	448.74	435.83
Butanol	$C_4H_{10}O$	(l)	.923	446.23	433.73
Pentanol	$C_5H_{12}O$	(l)	.938	443.28	431.18
Hexanol	$C_6H_{14}O$	(l)	.947	442.50	430.56
Heptanol	$C_7H_{16}O$	(l)	.955	442.14	430.11
Hexadecanol	$C_{16}H_{34}O$	(s)	.980	436.29	426.79
Polyhydric and other alcohols					
Ethylene glycol	$C_2H_6O_2$	(l)	.714	475.84	470.78
Glycerol	$C_3H_8O_3$	(l)	.700	472.93	472.82
Erythritol	$C_4H_{10}O_4$	(s)	.692	465.06	472.67
Pentaerythritol	$C_5H_{16}O_4$	(s)	.778	476.43	465.08
Fufuryl alcohol	$C_5H_6O_2$	(l)	.846	463.40	459.87
Pentamethylene glycerol	$C_5H_{12}O_2$	(l)	.875	463.26	451.82
Cyclopentanol	$C_5H_{10}O$	(l)	.933	442.37	432.86
Cyclohexanol	$C_6H_{12}O$	(l)	.944	438.57	430.13
Aldehydes					
Formaldehyde	CH_2O	(g)	.667	563.45	521.66
Acetaldehyde	C_2H_4O	(g)	.833	476.93	451.94
Propionaldehyde	C_3H_6O	(g)	.889	461.50	441.07
Butylaldehyde	C_4H_8O	(l)	.917	450.67	437.65
Heptanal	$C_7H_{14}O$	(l)	.952	444.37	432.04
Furfural	$C_5H_4O_2$	(l)	.833	468.85	466.77
Ketones, esters					
Aceton	C_3H_6O	(l)	.889	447.48	434.83
2-Butanone	C_4H_8O	(l)	.917	444.38	431.80
2-Pentanone	$C_5H_{10}O$	(l)	.933	442.39	430.06
2-Octanone	$C_8H_{16}O$	(l)	.958	439.15	427.15
Ketene	C_2H_2O	(g)	.800	505.88	482.83
Furan	C_4H_4O	(l)	.900	462.97	456.03
Ethyl acetate	$C_4H_8O_2$	(l)	.833	447.67	438.72
Ethers					
Methyl ether	C_2H_6O	(g)	.857	486.82	462.47
Ethyl methyl ether	C_3H_8O	(g)	.900	468.32	447.61
Ethyl ether	$C_4H_{10}O$	(l)	.923	453.95	440.09
Isopropyl ether	$C_6H_{14}O$	(l)	.947	445.63	433.43
Carbohydrates					
Glucose, D	$C_6H_{12}O_6$	(s)	.667	466.94	479.82
Alpha-Galactose, D	$C_6H_{12}O_6$	(s)	.667	465.12	478.20
Sorbose, L	$C_6H_{12}O_6$	(s)	.667	467.58	480.03
Beta-Lactose	$C_{12}H_{22}O_{11}$	(s)	.686	469.13	481.23
Sucrose	$C_{12}H_{22}O_{11}$	(s)	.686	470.35	483.09
Alpha-Lactose · H_2O	$C_{12}H_{24}O_{12}$	(s)	.667	474.40	487.45
Beta-Maltose · H_2O	$C_{12}H_{24}O_{11}$	(s)	.667	474.40	487.45
Galactitol	$C_6H_{14}O_6$	(s)	.684	463.86	473.24
Manitol, D	$C_6H_{14}O_6$	(s)	.684	465.33	474.52
Xylose, D	$C_5H_{10}O_5$	(s)	.667	469.47	484.35
Peptides—amino acids, proteins, etc.					
Glycine	$C_2H_5NO_2$	(s)	.692	428.61	446.25
Alanine, D, L	$C_3H_7NO_2$	(s)	.789	431.30	437.67
Valine, L	$C_5H_{11}NO_2$	(s)	.871	432.84	432.22
Leucine, L	$C_6H_{13}NO_2$	(s)	.892	432.99	430.42
Isoleucine, L	$C_6H_{13}NO_2$	(s)	.892	434.05	431.62
Phenylalanine, L	$C_9H_{11}NO_2$	(s)	.915	432.25	431.86
Serine, L	$C_3H_7NO_3$	(s)	.684	447.57	462.81
Tyrosine, L	$C_9H_{11}NO_3$	(s)	.872	433.38	435.93
Tryptophan, L	$C_{11}H_{12}N_2O_2$	(s)	.929	432.96	434.00
Arginine, D	$C_6H_{14}N_4O_2$	(s)	.895	439.80	445.45
Creatinine	$C_4H_7N_3O$	(s)	.913	444.94	453.06
Aspertic acid, L	$C_4H_7NO_4$	(s)	.652	426.96	447.33
Glutamic acid, L	$C_5H_9NO_4$	(s)	.724	427.45	439.62
Hippuric acid	$C_9H_9NO_3$	(s)	.867	432.71	435.61
Alantoin	$C_4H_6N_4O_3$	(s)	.727	428.49	460.72
Aspargine, L	$C_4H_8N_2O_3$	(s)	.750	428.41	443.57
Glycylglycine	$C_4H_8N_2O_3$	(s)	.750	430.25	452.38
Alanylglycine, L	$C_5H_{10}N_2O_3$	(s)	.800	428.38	437.54
Leucylglycine, D, L	$C_8H_{16}N_2O_3$	(s)	.875	435.76	436.51
Hippurylglycine	$C_{11}H_{12}N_2O_4$	(s)	.857	434.22	438.85
Others					
Graphite	C	(s)	1.00	393.51	394.38
Carbon monoxide	CO	(g)	.500	565.93	514.21
Carbon dioxide	CO_2	(g)	0.00	0	0
Hydrogen	H_2	(g)	1.00	571.68	474.38
Water	H_2O	(l)	0.00	0	0
Hydrocyanic acid	HCN	(g)	1.00	533.57	506.48
Ammonia	NH_3	(g)	1.00	510.76	452.85
Hydrazine	N_2H_4	(g)	1.00	666.86	632.91
Urea	CH_4N_2O	(s)	.750	421.34	447.74

Table 1. (Continued)

SECTION B

Name	Formula	State	H/C	H_{deox} (kJ)	G_{deox} (kJ)
Paraffins					
Methane	CH_4	(g)	4.00	445.17	408.97
Ethane	C_2H_6	(g)	3.00	445.67	419.26
Propane	C_3H_8	(g)	2.67	444.00	421.69
Butane	C_4H_{10}	(g)	2.50	439.32	422.84
Pentane	C_5H_{12}	(l)	2.40	438.67	423.20
Hexane	C_6H_{14}	(l)	2.33	438.22	423.40
Heptane	C_7H_{16}	(l)	2.29	437.90	423.57
Octane	C_8H_{18}	(l)	2.25	437.65	423.70
Nonane	C_9H_{20}	(l)	2.22	437.46	423.79
Decane	$C_{10}H_{22}$	(l)	2.20	437.31	423.88
Dodecane	$C_{12}H_{26}$	(l)	2.17	437.10	424.04
Hexadecane	$C_{16}H_{34}$	(l)	2.13	436.69	424.10
Tetracosane	$C_{24}H_{50}$	(s)	2.08	434.98	424.70
Dotriacontane	$C_{32}H_{66}$	(s)	2.06	434.12	423.98
Olefins					
Ethylene	C_2H_4	(g)	2.00	470.33	443.76
Propene	C_3H_6	(g)	2.00	457.43	434.99
1-Butene	C_4H_8	(g)	2.00	452.87	432.93
1-Pentene	C_5H_{10}	(l)	2.00	446.67	431.48
1-Hexene	C_6H_{12}	(l)	2.00	444.85	430.32
1-Heptene	C_7H_{14}	(l)	2.00	443.57	429.51
1-Octene	C_8H_{16}	(l)	2.00	442.60	428.89
1-Decene	$C_{10}H_{20}$	(l)	2.00	441.26	428.05
1-Hexadecene	$C_{16}H_{32}$	(l)	2.00	439.41	426.97
Cycloparaffins and other saturated alicyclic hydrocarbons					
Cyclopropane	C_3H_6	(g)	2.00	464.74	444.25
Cyclobutane	C_4H_8	(g)	2.00	453.41	439.62
Cyclopentane	C_5H_{10}	(l)	2.00	438.78	425.90
Cyclohexane	C_6H_{12}	(l)	2.00	435.54	424.01
Cycloheptane	C_7H_{14}	(l)	2.00	437.84	426.20
Cyclooctane	C_8H_{16}	(l)	2.00	438.80	427.54
Methycyclopentane	C_6H_{12}	(l)	2.00	437.52	424.55
Ethylcyclopentane	C_7H_{14}	(l)	2.00	437.32	424.60
Propylcyclopentane	C_8H_{16}	(l)	2.00	437.13	424.65
Bytylcyclopentane	C_9H_{18}	(l)	2.00	435.35	423.73
Methylcyclohexane	C_7H_{14}	(l)	2.00	434.78	422.99
Ethylcyclohexane	C_8H_{16}	(l)	2.00	435.21	423.47
Propylcyclohexane	C_9H_{18}	(l)	2.00	435.24	423.59
Butylcyclohexane	$C_{10}H_{20}$	(l)	2.00	435.35	423.73
Cyclohexylheptane	$C_{13}H_{26}$	(l)	2.00	434.76	423.17
Cyclopentyldecane	$C_{15}H_{30}$	(l)	2.00	436.62	424.73
Cyclohexyldecane	$C_{16}H_{32}$	(l)	2.00	435.46	423.99
Diolefins and acetylides					
Allene	C_3H_4	(g)	1.33	486.08	464.98
1,3-Butadiene	C_4H_6	(l)	1.50	457.62	443.40
Isoprene	C_5H_8	(l)	1.60	451.46	437.99
1,4-Pentadiene	C_5H_8	(l)	1.60	455.21	441.13
Acetylene	C_2H_2	(g)	1.00	519.83	494.06
Propyne	C_3H_4	(g)	1.33	484.41	462.99
1-Bytyne	C_4H_6	(l)	1.50	467.81	453.26
2-Butyne	C_4H_6	(l)	1.50	463.89	449.89
Aromatic hydrocarbons					
Benzene	C_6H_6	(l)	1.00	435.68	426.96
Naphthalene	$C_{10}H_8$	(s)	0.80	429.71	424.47
Anthracene	$C_{14}H_{10}$	(s)	0.71	428.33	423.82
Phenanthrene	$C_{14}H_{10}$	(s)	0.71	427.54	422.95
Fluoranthene	$C_{16}H_{10}$	(s)	0.63	427.84	423.73
Pyrene	$C_{16}H_{10}$	(s)	0.63	423.78	419.76
Naphthacene	$C_{18}H_{12}$	(s)	0.67	426.53	422.90
Perylene	$C_{20}H_{12}$	(s)	0.60	424.69	420.96
Toluene	C_7H_8	(l)	1.14	434.43	424.80
Ethylbenzene	C_8H_{10}	(l)	1.25	434.74	424.83
Propylbenzene	C_9H_{12}	(l)	1.33	434.85	424.74
m-Xylene	C_8H_{10}	(l)	1.25	433.51	423.68
Mesitylenebenzene	C_9H_{12}	(l)	1.33	432.76	423.03
Tetramethylbenzene	$C_{10}H_{14}$	(s)	1.40	430.18	421.63
Pentamethylbenzene	$C_{11}H_{16}$	(s)	1.45	432.00	422.87
Hexamethylbenzene	$C_{12}H_{18}$	(s)	1.50	432.16	423.32
Biphenyl	$C_{12}H_{10}$	(s)	0.83	431.16	425.71
Diphenylethane	$C_{14}H_{14}$	(l)	1.00	431.94	424.39
Bibenzyl	$C_{14}H_{14}$	(l)	1.00	432.08	425.65
Styrene	C_8H_8	(l)	1.00	439.53	430.62
Stilbene, trans.	$C_{14}H_{12}$	(s)	0.86	432.89	427.18

(e) Among unpolymerized species, carbohydrates have exceptionally high G_{deox} for the number of carbon atoms. They are exceeded only by a handful of compounds such as oxalic, formic, citric acids and formaldehyde.

Calculations now in progress for G_{deox} values at 127°C (400 K) and 227°C (500 K) also indicate that the above relations observed for 25°C remain unchanged. Except for condensed aromatic compounds, the G_{deox} values converge to 424.3 kJ with increasing carbon number at 127°C.

ESTIMATION OF DEOXYGENATION PARAMETERS FOR NATURAL POLYMERS

Certain organic substances have the ability to form macromolecules upon polymerization. Compared to the respective monomers, these polymers are much less water-soluble and inherently slow to react, and thus have a better chance of being preserved in sediments upon resisting microbial and chemical oxidation. In fact they are the dominant precursors of fossil fuels. Biopolymers such as cellulose, lignin, resins, and proteins are used as the structural material to support free-standing weights by land plants. Upon burial these polymers undergo extensive aromatic condensation to kerogen, which makes up more than 90% of the total organic matter in the Earth's crust (Hunt, 1979). For thermochemical consideration of fossil fuel formation, therefore, it is important to estimate the deoxygenation parameters for these polymers, although only rough approximations are possible because (1) the entropy change associated with polymerization is generally difficult to accurately assess, and (2) most of these polymers are compositionally variable within a range.

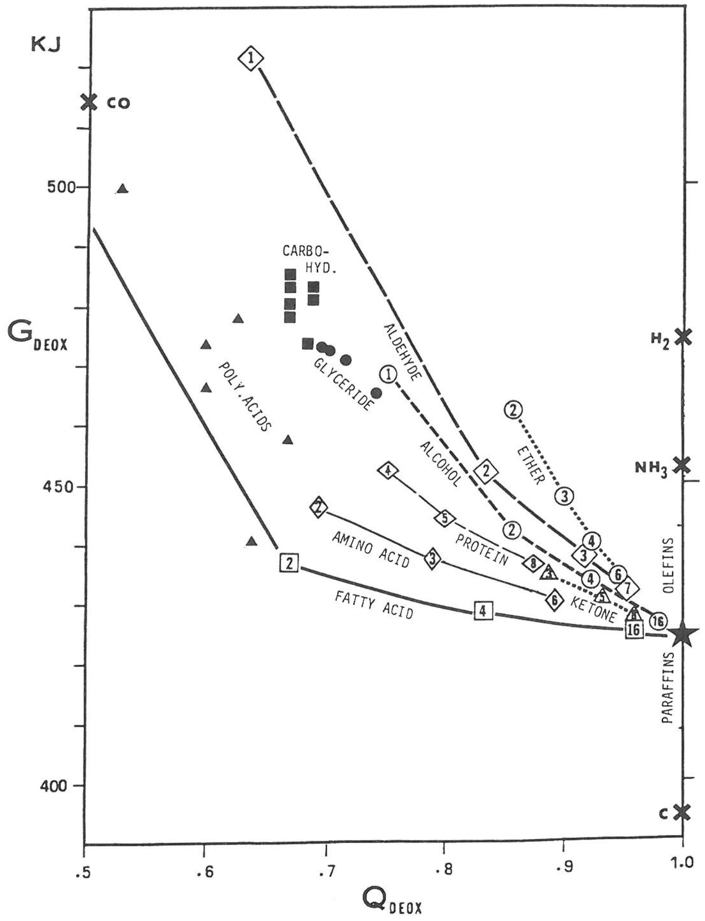

FIG. 1. Plots of G_{deox} (deoxygenation free energy) versus Q_{deox} (deoxygenation quotient) for some compounds of the C-H-N-O system. Homologous series are identified by labelled connecting lines. Arabic numerals indicate the number of carbon atoms in these homologues. Some other groups are also identified with labels, where possible. Inorganic compounds are individually labelled. Except for labelling, hydrocarbons are excluded in this diagram. The star indicates the convergence value of the homologous series.

Many methods have been proposed for estimating thermochemical properties of organic compounds (reviewed by JANZ, 1967) including the method of VAN KREVELEN and CHERMIN (1951) for Gibbs energy of formation based on group contributions. However, most of these methods are derived for the ideal gas state, and, hence, are applicable only to gaseous compounds and condensed compounds with known heat of vaporization and measurable vapor pressures. Biopolymers and geopolymers have negligible vapor pressures at room temperature and decompose if heated. So in some cases it is preferrable to use the heat of combustion data and rely on the similarity of H_{deox} relation to the G_{deox} relation as the first approximation.

If heat of combustion is available only for the monomer or major components of a complex polymer, and particularly if the monomer is gas or liquid, there may be a significant change in entropy associated with polymerization. The entropy of polymerization may be ignored if the transformation is from an amorphous solid to a crystalline state. For example, the transformation of amorphous Se to linear macromolecule trigonal Se (a simple model case of polymerization) decreases entropy by 6.77 J/mol · K at 25°C according to GAUER *et al.* (1981), which corresponds to a polymerization energy of about 2 kJ per mole of the monomer compound.

Cellulose

Cellulose is the basic structural material for higher plants. It is a highly polymerized polysaccharide consisting of several thousands glucose (cellbiose) units in chains. Upon hydration it produces glucose. The chemical formula, $(C_6H_{10}O_5)_n$, gives Q_{deox} of 0.706. The heat of combustion of cellulose at 25°C is given as 2812.4 kJ/mole (COLBERT *et al.*, 1981), which gives H_{deox} as 468.7 kJ according to Equation (9). The H_c value gives ΔH_f^0 of cellulose as −977.88 kJ/mole. The S^0 for cellulose is estimated at 205 J/mole · K by subtracting the entropy of macrochain polymerization (6.77 J/mole · K for Se) from the entropy of glucose (212.13 J/mole · K, STULL *et al.*, 1969, p. 680). The entropy change in the substitution of 2(-OH) by (-O-) linkage in a solid polyhydroxy compound may be neglected (JANZ, 1967, Table 4.1). This gives ΔG_f^0 for cellulose as −681.5 kJ/mole and G_{deox} as 478.5 kJ. The G_{deox} value is 0.7 kJ lower than that of glucose. The reversal in the order of H_{deox} and that of G_{deox} between the two compounds is due to the entropy of liquid H_2O liberated in the dehydration-polymerization.

Lignin

Lignin is a collective term for amorphous aromatic macromolecular substances, which cement cellulose in land plants, and is an important precursor to coal. It is basically constructed from phenyl-propane derivatives, such as coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol, that are biosynthesized from carbohydrates (SARKANEN and LUDWIG, 1971; KIRK *et al.*, 1980). The polymerization of these monomer units are associated with replacement of two end hydroxyls by an ether linkage. The atomic composition ranges typically from $(C_{11}H_{12}O_3)_n$ to $(C_9H_8O)_n$, depending on the average number of the methoxyl ($-OCH_3$) groups attached to the phenol ring, giving a Q_{deox} range of 0.893 to 0.955. A compound that is closest to these monomers in structure, and for which the heat of combustion or enthalpy of formation is known, is isoeugenol $CH_3CH{:}CH \cdot C_6H_3(OCH_3)OH$. To make a chain polymer of coniferyl lignin from isoeugenol, it is required that one each of the (C-H) and (C-OH) bonds are replaced by one (C-O-C) bond. Using the bond contributions for heats of combustion of liquids (applicable to amorphous solids) given by LAIDLER (1956), and 5345.5 kJ for the H_c of isoeugenol, the H_c and H_{deox} for the coniferyl lignin is computed as 5170 kJ/mole and 450 kJ, respectively.

The variations in H_{deox} by addition or subtraction of a methoxyl group is estimated at about 5 kJ per mole of the lignin unit. This is made on the basis of the difference in ΔH_f^0 between 4-hydroxy-*m*-anisolaldehyde (vanillin) $C_6H_3(OH)(OCH_3)CHO$ and *p*-hydroxybenzaldehyde $C_6H_4(OH)CHO$ (STULL *et al.*, 1969), which is 168.6 kJ/mole (510.7 kJ in terms of H_c between the two), and applying equation (7) to the chemical formula of the lignin monomers. Ignoring the small differences in the entropy term, the approximate H_{deox} value for the lignin group ranges from 455 kJ (for dimethoxy sinapyl unit, Q_{deox} 0.893) to 445 kJ (for *p*-coumaryl unit, Q_{deox} 0.955). Other more complex and random configurations would probably average out to this range.

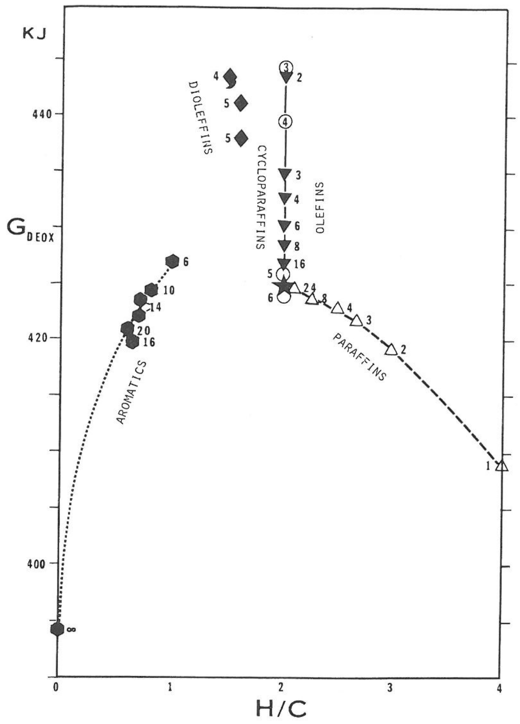

FIG. 2. Plots of G_{deox} versus H/C atomic ratio for common hydrocarbons. Arabic numerals indicate the number of carbon atoms. For paraffinic and olefinic series, only those of straight chains are plotted. Graphite is considered to be the product of infinite aromatic condensation, and included in the aromatic series. The star indicates the convergence value of the oxygenous homologous series shown in Fig. 1.

There is no simple reliable way of estimating the G_{deox} of lignins because of their complex structures.

Humic matter

This is an operational term applied to polymerized, water-insoluble brown to black substances formed, under restricted oxidative conditions in soil and also in young sediments in swamps and other subaqueous environments, from the residue of biological matter unused by microorganisms. Humic substances are soluble in dilute alkali solutions, but only partially so in dilute acid solutions. The acid soluble fraction is called "fulvic acids" and have a range of composition of C: 30–40%, H: 6–8%, O: 45–55%, N: 4.5–5.5% in weight. The acid-insoluble fraction is called "humic acids" and have the compositional range of C: 50–55%, H: 5.5–6.5%, O: 30–35%, N: 1–4% (GALIMOV, 1980), and atomic ratio range of H/C: 0.5–1.5, and O/C: 0.2–0.5 (TISSOT and WELTE, 1978). Fulvic acids tend to disappear early during the diagenesis. On their way to becoming protokerogen and eventually to kerogen, humic acids are increasingly depleted of oxygen, and become more aromatic.

Molecular characterization of humic acids is very incomplete. A general consensus is that the biological precursors are dominantly lignins and tannins which are widespread in plants. Probably proteins and perhaps carbohydrates are also involved. Laboratory studies indicate that both aromatic and aliphatic/alicyclic substances are incorporated. Functional groups detected are carboxyls, carbonyls, phenolic and enolic hydroxyls, and amides in the order of abundance. Methoxyls are present only in low concentrations. For example, a typical humic acid from peat described by CHRISTMAN and OGLESBY (1971) contains C: 58.35%, H: 4.97%, O: 32.2%, N: 2.62% in weight, and the following functional groups in millimoles/gram: 0.2 methoxyl, 2.9 phenolic hydroxyl, 2.2 enolic hydroxyl, 5.5 carbonyl, and 8.6 carboxyl. The functional groups in total take up 63.4% of the dried, ash-free humic acid, the balance presumably being hydrocarbon chains and rings. None of the proposed structural models (reviewed by SWAIN, 1963; CHRISTMAN and OGLESBY, 1971; HUC, 1980; GALIMOV, 1980) appears to accommodate the abundant carboxyls and carbonyls, and, at the same time, conform with an approximate C:H:O ratio of 2:2:1 indicated by the above weight composition. The alicyclic quinones could account for the carbonyls but have too high O/C ratios. Ketonic bridges between H-rich structures may resolve this problem. Such a unit may be constructed, for example, from one molecule of quinic acid $(OH)_4 \cdot C_6H_7 \cdot COOH$ and one molecule of protocatechuic acid $C_6H_3(OH)_2COOH$, bridged by a ketonic or ether bond (Fig. 3a or 3b). A ketonic bond of this type is found in benzoin $C_6H_5 \cdot CHOH \cdot CO \cdot C_6H_5$. Quinic acid is an alicyclic polyhydroxy acid derived from carbohydrate and, upon dehydration, changes to aromatic protocatechuic acid (CONNANT, 1936, p. 458). Protocatechuic acid is also formed by oxidation of the *p*-coumaryl alcohol unit of lignin. Such units may be linked together by ether, ketonic, or ester (SCHNITZER and NEYROND, 1975) bonds upon releasing H_2O.

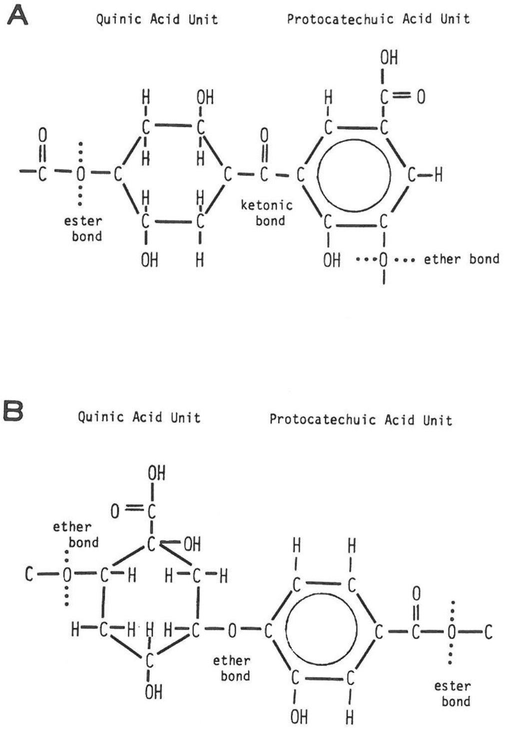

FIG. 3. Suggested models of humic acids that could be derived from lignin and cellulose, and versatile in the aliphatic *vs.* aromatic ratio; (A) a model in which the aliphatic and aromatic groups are bridged by a ketonic bond, and (B) that bridged by an ether bond.

In view of the uncertainties of the chemical structure of humic acids, direct estimation of G_{deox} values of humic acids is not attempted. Instead, a list of chemicals that have been identified upon degradation of humic matter, or proposed to be likely components on theoretical grounds, are listed, together with their H_{deox} (and G_{deox} in rare cases where Gibbs energy of formation is given in the literature) in Table 2. Nitrogenous compounds are excluded for simplicity. Compounds with methoxyls are eliminated in view of the low abundance of this group. Needless to say, compounds without heat of combustion or enthalpy of formation data are excluded. Sample calculations show that G_{deox} or H_{deox} values are very similar among isomers when they have more than several C atoms. Only the most stable isomer is listed when H_{deox} values vary by less than 1 kJ among the isomers. The compound name is given by a structural name in such a case. Alicyclic quinoids are grouped together with aromatic polyhydroxy compounds because of the close relationship existing between the two groups.

The Q_{deox} values for humic acids inferred from the Van Krevelen (H/C vs. O/C) diagrams (Fig. II. 2.9 in TISSOT and WELTE, 1978; Fig. 7-6 in HUNT, 1979) are in the range of 0.778 to 0.927, and a typical value is 0.88. The range is richer in oxygen than the above model lignins.

Kerogen

This term was originally applied to the organic matter in oil shales that produced waxy oils (keros = wax in Greek) upon heating, but the term has been broadened in recent years to include all the disseminated organic matter of sedimentary rocks insoluble in nonoxidizing acids, bases, and organic solvents regardless of capacity for oil distillation.

On the basis of microscopic characterization, kerogens are classified into sapropelic and humic. Sapropelic kerogens originate in decomposition and polymerization products of lipid-rich biological remains such as spores and algae and deposited in subaquatic muds, usually under oxygen-poor conditions, and have relatively high H/C ratios (1.3–1.7, HUNT, 1979). Oil shales and boghead coals mature from organic-rich sapropelic deposits and correspond to Type I of the three kerogen evolution types recognized by TISSOT *et al.* (1974). The molecular sizes are dominantly in the range of C_{15} to C_{40} and have average chemical composition ranging from $C_{40}H_{68}O_5$ (Q_{deox} 0.956) to $C_{40}H_{54}O_1$ (Q_{deox} 0.991) on a C_{40} basis. Q_{deox} increases as the depth of burial increases. This kind of H-rich composition requires predominance of saturated hydrocarbons of aliphatic/alicyclic groups and lesser amount (in terms of carbon numbers) of aromatic hydrocarbons. The oxygenous functional groups are scarce, and consist of ester and ether linkages, hydroxyls, carboxyls, and carbonyls in varying proportions (VITOROVIC, 1980). The G_{deox} values are probably somewhere between those of palmitic acid (Q_{deox} 0.958, G_{deox} 425.6 kJ, Table 1) and the convergence value (Q_{deox} 1.00, G_{deox} 424.7 kJ) discussed earlier.

Humic kerogens correspond to Type III of TISSOT *et al.* (1974), and include humic coals. Atomic ratios on C_{40} basis vary approximately from $C_{40}H_{32}O_{12}$ (Q_{deox} 0.875) to $C_{40}H_{28}O_4$ (Q_{deox} 0.957) as they evolve during diagenesis. This type has the lowest H content among the three types. The compositional boundary between humic kerogen and humic acids is not well defined and the two overlap substantially in the Q_{deox} range. In contrast to the aliphatic-rich Type I, this type is characterized by a high proportion of aromatic carbons. Chemical and physicochemical evidence suggest that aromatic carbon atoms increase from about 70% in hard brown coals to over 90% in anthracites (TISSOT and WELTE, 1978, p. 210). Also the formation of polycyclic aromatic rings is suggested (several to tens of rings). The main functional groups are ketonic and carboxyl groups, but ester group is missing (ROBIN *et al.,* 1977). Similar to humic acids, Gibbs energy data are available only for a small number of solid or liquid compounds which tend to be low in C-number. H_{deox} can be estimated from polycyclic aromatic compounds with carboxyl and carbonyl groups in Table 2.

DISCUSSIONS

The significance of the G_{deox} versus Q_{deox} relations shown in Fig. 1 regarding the transformation of plant matter to fossil fuels becomes apparent when one notes that typical photosynthetic products have higher G_{deox} and lower Q_{deox} values compared with fossil fuel substances. A higher G_{deox} means, by definition, that more energy is chemically stored in liberating a unit quantity of free oxygen from a mixture of H_2O, CO_2, and N_2, and also that a substance could be deoxygenated spontaneously by loss of CO_2 and/or H_2O to produce another substance of a lower G_{deox}. This fact clearly has an important bearing on the flow of energy in the biosphere as discussed below.

Photosynthesis

The higher G_{deox} values for primary photosynthetic products indicate that photosynthetic organisms chemically capture as much solar energy as possible at the initial stage of photosynthesis by utilizing the thermochemical nature of the C-H-(N)-O system with regard to deoxygenation. When starting out from CO_2, H_2O, and N_2 of ultimate volcanic origin, the most effective chemical storage of solar energy by deoxygenation can be achieved by forming compounds with highest G_{deox} values, which turn out to be compounds of low Q_{deox} values. In terms of G_{deox}, oxalic acid (Q_{deox} 0.200, G_{deox} 649.6 kJ), formic acid (0.333, 554.7 kJ), formaldehyde (0.667, 521.7 kJ), and citric acid (0.529, 499.8 kJ) lead other compounds. The formation of formaldehyde, followed by its polymerization to monosaccharides, has been suggested as the initial stage of photosynthesis by many investigators (CONANT, 1936, p. 561). This path is energetically workable. Carbohydrates (G_{deox} 464 to 487 kJ) can form from formaldehyde spontaneously with release of energy as indicated by the higher G_{deox} of the latter. The organic acids mentioned are also found in plants. These acids will change to saccharides spontaneously if catalyzed by suitable enzymes, as exemplified by the ripening of citric fruits.

Table 2. Deoxygenation parameters of compounds relevant to humic matter

Name	Formula	State	Q_{deox}	H_{deox}	G_{deox}
Biopolymers					
Cellulose	$(C_6H_{10}O_5)_n$	(s)	.706	468.7	478.5
Lignin (conyferyl)	$(C_{10}H_{10}O_2)_n$	(s)	.920	450.0	—
Aromatic acids, hydroxyacids, anhydrides					
Benzoic acid	$C_7H_6O_2$	(s)	.882	430.26	430.27
p-Hydroxylbenzoic acid	$C_7H_6O_3$	(s)	.824	432.51	436.52
Salicylic acid	$C_7H_6O_3$	(s)	.824	432.39	436.31
Phthalic acid	$C_8H_6O_4$	(s)	.789	429.78	436.68
Phthalic anhydride	$C_8H_4O_3$	(s)	.833	434.54	439.79
Protocatechuic acid	$C_7H_6O_4$	(s)	.765	435.78	—
Gallic acid	$C_7H_6O_5$	(s)	.706	441.97	—
2,4-Cresotic acid	$C_8H_8O_3$	(s)	.850	432.41	—
Phenylacetic acid	$C_8H_8O_2$	(s)	.900	432.80	—
Phenoxyacetic acid	$C_8H_8O_3$	(s)	.850	444.72	—
p-Toluic acid	$C_8H_8O_2$	(s)	.900	429.13	—
p-Anisic acid	$C_8H_8O_3$	(s)	.850	440.68	—
Piperonylic acid	$C_8H_6O_4$	(s)	.789	448.55	—
Atropic acid	$C_9H_8O_2$	(s)	.909	437.32	—
Cinnamic acid, trans	$C_9H_8O_2$	(s)	.909	434.77	—
Hydrocinnamic acid	$C_9H_{10}O_2$	(s)	.913	432.68	—
p-Cumaric acid	$C_9H_8O_3$	(s)	.864	437.39	—
Uvitic acid	$C_9H_8O_4$	(s)	.818	431.84	—
Trimesic acid	$C_9H_6O_6$	(s)	.714	428.16	—
Phenylpropiol acid	$C_9H_6O_2$	(s)	.905	449.76	—
p-Isopropylbenzoic acid	$C_{10}H_{12}O_2$	(s)	.923	432.03	—
Aromatic hydroxyl derivatives, aldehydes					
Phenol	C_6H_6O	(s)	.933	436.22	432.49
Benzyl alcohol	C_7H_8O	(l)	.944	439.63	433.17
o-Cresol	C_7H_8O	(s)	.944	434.53	—
o-Hydroxybenzyl alcohol	$C_7H_8O_2$	(s)	.889	442.15	—
p-Ethylphenol	$C_8H_{10}O$	(s)	.952	435.25	—
Thymol	$C_{10}H_{14}O$	(s)	.963	434.79	—
Isoeugenol	$C_{10}H_{12}O_2$	(l)	.923	445.84	—
Pyrocatecohol	$C_6H_6O_2$	(s)	.867	441.16	—
Hydroquinone	$C_6H_6O_2$	(s)	.867	438.83	—
p-Benzoquinone	$C_6H_4O_2$	(s)	.857	457.65	459.17
Phloroglucinol	$C_6H_6O_3$	(s)	.800	430.78	—
2-Naphthol	$C_{10}H_8O$	(s)	.958	430.76	—
1,4-Naphthaquinone	$C_{10}H_6O_2$	(s)	.913	438.94	—
Benzaldehyde	C_7H_6O	(l)	.941	440.37	—
o-Anisaldehyde	C_8H_8O	(l)	.900	447.72	—
Cinnamaldehyde	C_9H_8O	(l)	.955	443.63	—
Phenylpropiol aldehyde	C_9H_6O	(l)	.952	452.37	—
Aromatic ethers, ketones					
Anisole	C_7H_8O	(l)	.944	444.50	—
Phenetol	$C_8H_{10}O$	(l)	.952	441.57	—
p-Dimethoxybenzene	$C_8H_{10}O_2$	(s)	.905	447.24	—
m-Methylanisole	$C_8H_{10}O$	(l)	.952	441.99	—
p-Allylanisole	$C_{10}H_{12}O$	(l)	.962	447.12	—
Methylisoeugenol	$C_{11}H_{14}O_2$	(l)	.931	448.95	—
Diphenyl ether	$C_{12}H_{10}O$	(s)	.966	437.11	433.05
Acetophenone	C_8H_8O	(l)	.950	436.73	430.19
Banzophenone	$C_{13}H_{10}O$	(l)	.968	435.12	—
Benzoion	$C_{14}H_{12}O_2$	(s)	.941	435.99	—

Table 2. (Continued)

Name	Formula	State	Q_{deox}	H_{deox}	G_{deox}
		Others			
Cumen	C_9H_{12}	(l)	1.00	434.61	424.74
p-Cymen	$C_{10}H_{14}$	(l)	1.00	433.90	424.00
Decahydronaphthalene, trans	$C_{10}H_{18}$	(l)	1.00	432.89	423.19
2-Methylnaphthalene, trans	$C_{11}H_{10}$	(s)	1.00	429.82	423.46
Inositol	$C_6H_{12}O_6$	(s)	.667	461.98	—
p-Cymen-2,5-diol	$C_{10}H_{14}O_2$	(s)	.926	437.85	—
Borneol	$C_{10}H_{18}O$	(s)	.966	438.26	—
Terpinol	$C_{10}H_{18}O$	(s)	.966	439.25	—
Campholic acid	$C_{10}H_{16}O_2$	(s)	.929	439.59	—
Cyclohexane carboxylic acid	$C_7H_{12}O_2$	(s)	.900	434.23	—
Diphenyl carbonate	$C_{13}H_{10}O_3$	(s)	.903	438.81	438.36
Eicosanoic acid	$C_{20}H_{40}O_2$	(s)	.967	433.59	—
Phenylurea	$C_7H_8N_2O$	(s)	.944	433.27	—
Quinolin	C_9H_7N	(l)	1.00	436.40	432.03

The monosaccharides and glycerol (0.700, 472.8 kJ), once synthesized, become the primary ingredients for a variety of biological substances of higher Q_{deox} values. As long as the biosynthesis proceeds *via* loss of H_2O and/or CO_2, the process is most probably spontaneous, because both CO_2 and H_2O are far more stable than the parental substance. Structural material (*e.g.*, cellulose, lignin, waxes, resins) and energy storage material (*e.g.*, starch, fats, oils) are probably produced from the primary ingredients without net addition of energy. In the presence of NH_3 (G_{deox} 452.8 kJ), which is found in volcanic condensates as NH_4Cl (WHITE and WARING, 1963), proteins may also be synthesized from these ingredients.

Transformation to fossil fuels

Fossil fuel substances, such as natural gas (methane), petroleum (paraffins, cycloparaffins, aromatic hydrocarbons), coal (polycyclic aromatic compounds), and oil shale (Type I kerogen), all have higher Q_{deox} and lower G_{deox} values than do primary photosynthetic products. Methane has the lowest G_{deox} (409.0 kJ) among organic substances. Most hydrocarbons found in petroleum in nature have G_{deox} lower than 427.2 kJ. The only known exception appears to be cyclobutane (439.2 kJ), which was reportedly found in a trace quantity (0.001%) in a Venezuelan oil (WHITEHEAD and BREGER, 1963, p. 252). Kerogens in oil shale and boghead coal (Type I) probably have G_{deox} values between 424.7 kJ and 425.6 kJ as discussed earlier.

There may be slight reversals in Q_{deox} and G_{deox} when humic acids form from lignin because of addition of oxygen during oxidative degradation. In the absence of definitive chemical characterization of humic acids and entropy data for lignins, this point is very uncertain. The portion of humic acid derived from cellulose and other carbohydrates have definitely lower G_{deox} values than the precursor substances. The formation of quinic acid from carbohydrates and its subsequent transformation to protocatechuic acid by dehydration and oxidation mentioned earlier may be cited as an example.

Type III humic kerogens and coals, ranging in Q_{deox} from 0.875 to 0.957, probably cluster around 430 kJ in G_{deox} as discussed earlier. With the decrease of functional groups as burial depth increases, it is probable that G_{deox} falls below 430 kJ in bituminous coal, and below 420 kJ in anthracitic coal judging from that of perylene $C_{20}H_{12}$ (421 kJ). The aromatic polycondensation ultimately results in the formation of graphite (394.4 kJ).

In the overall deoxygenation energy relation of fossil fuels, a significant point is that the G_{deox} values of fossil fuel substances are very close to or lower than the convergence G_{deox} value (424.7 kJ) for nonaromatic compounds mentioned earlier. This fact appears to indicate that no net input of energy has taken place during the fossilization of biological remains and the evolutionary history of fossil fuels. If energy had been added, in net, during the processes, some fossil-fuel substances would show substantially higher G_{deox} values than the convergence G_{deox} value. It is well known that thermal cracking of petroleum produces olefins (443.5 to 426.8 kJ). Hydrogen (H_2, 474.4 kJ) is scarce in natural gas. It may be argued that H_2 escapes readily because of its high buoyancy and mobility, but the accumulation of helium, which is equally mobile, in natural gas reservoirs does not support this argument. In the presence of unsaturated organic compounds, H_2, if ever produced, is expected to be consumed readily for hydrogenation of the unsaturated compounds. It is more probable, however, that so-called hydrogenation reactions are caused by intra- or inter-molecular proton transfer and that H_2 partial pressure never reaches a significant level during the transformation and maturation.

Chemical changes of organic sedimentary deposits are rapid at the beginning of burial and soon reach a plateau stage when the carbon content reaches about 85 weight percent (Q_{deox} about 0.96) (BREGER, 1963). This is where the mode of energy release changes from deoxygenation to hydrogen disproportionation, and a sharp bend in the kerogen evolution lines occurs in the Van Krevelen diagram. The H/C ratio begins to decrease rapidly at this point. With most of the oxygen depleted (the atomic $O/C < 0.1$), the dominant form of the energy release shifts to simultaneous polycondensation of aromatic rings and production of methane and, in case of aliphatic Type I kerogens, other light paraffinic hydrocarbons. As polycondensation continues, H atoms are liberated from condensing alicyclic, ketonic, and benzene rings and spontaneously partition to form saturated light (C_8 or smaller) hydrocarbons. These compounds all have G_{deox} values lower than the convergence G_{deox}. This stage is catagenesis.

The ultimate state of energy release without oxidation is the graphite (393.4 kJ) and methane (409.0 kJ) combination. This is the extreme result of the spontaneous hydrogen partioning, a process that operates in metagenesis. Methane escapes easily so that graphite becomes the ultimate *in situ* product of spontaneous evolution of organic matter in an anaerobic environment.

The large positive G_{deox} values for all organic substances of the C-H-N-O system indicate that isolation from free oxygen is essential for fossil-fuel formation. The Gibbs free energies of reaction evolved in the direct oxidation by free oxygen are at least an order of magnitude greater than those in the deoxygenation and hydrogen disproportionation reactions. An access to free oxygen would change the course of reactions, ultimately oxidizing the whole organic matter back to the pre-photosynthetic material, *i.e.*, H_2O, CO_2, and N_2.

Higher temperatures (up to a few hundred °C) do not appear to change the energy relations, but they surely would increase the reaction rates, which increase exponentially following the Arrhenius equation, $k = Ae^{-Ea/RT}$, where Ea is the activation energy and k the rate constant. Because the spontaneity of evolution of fossil fuels is indicated even at room temperature, the role of increasing temperature associated with increasing depth of burial is to increase, by orders of magnitude, the rates of reactions which would otherwise not proceed detectibly even in geologic time scale. The activation energy for the polycyclic aromatic condensation to cause hydrogen disproportionation must be large, requiring catagenic temperatures (100 to 150°C) for the process to proceed in geologic time. This, however, does not necessarily imply that a heat input is essential for advanced stages of fossil fuel evolution. A large mass of organic sediment could create its own thermal environment, if heat is trapped by impervious overlying sediments, as the transformation reactions are generally exothermic. Also, adiabatic compression of fluids may elevate the temperature in a large sedimentary basin such as the Gulf of Mexico (JONES, 1970).

A totally confined environment, on the other hand, may not favor evolution of fossil fuels. The mass action law indicates that, at equilibrium, the removal of the reaction products facilitates for a reaction to proceed. The removal is particularly important when the free energy of reaction is small, as in the late stages of fossil fuel evolution. Geological settings in which fluids (H_2O, CO_2, CH_4, and other light hydrocarbons) can escape through porous media or fractures, or be absorbed by reactions with lithic material (such as unhydrated volcanic ash), would accelerate the evolutionary process.

In conclusion, I would like to emphasize that this work is a preliminary attempt to obtain a broad picture of the significance of the thermochemical relationship of organic substances to the process of fossil-fuel formation. Thermochemical data for important natural substances such as lignin, humic acids, and kerogens are incomplete and only a very broad framework can be constructed. Also, computations at elevated temperatures and pressures are yet to be completed. Hopefully a better framework will be built in future.

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