THE TIME FACTOR IN MAKING OIL GAS; DESSERTATION

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DISSERTATION

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THE TIME FACTOR IN MAKING OIL GAS

The production of oil gas is dependent upon certain chemical laws which relate to gas reactions in general and which embody the principles of both thermodynamics and chemical kinetics.

In an investigation on the effect of the variables, temperature, pressure, and concentration on the thermal decomposition of petroleum and petroleum distillates, Whitaker and Rittman[1] have carefully considered the theoretical principles of thermodynamics as applied to gas reactions. Their experimental results verified their theoretical conclusions and showed that the principles of thermodynamics apply to the decomposition of petroleum hydrocarbons as well as to more simple reactions.

In the above work, however, conclusions were drawn on the assumption that chemical equilibrium was attained under the experimental conditions adopted. It then became a question whether or not equilibrium was reached. Undoubtedly this question could be answered by the application of the principles of chemical kinetics, which introduced the time factor. In the present study of oil gas production, therefore, four variables—time, temperature, pressure and concentration—are recognized.

Difficulties were foreseen, however, in the accurate adjustment of the above variables in commercial plants and a basis for control was sought which would fall within the range of engineering requirements. Under constant temperature and pressure conditions, the time factor, which can be controlled by variation of the rate of oil feed, offers the most available means for the study of the thermal decomposition of petroleum and petroleum distillates on the basis of the principles of chemical kinetics.

Design of apparatus is fixed for any one construction and hence remains a constant factor while the variables are controllable within certain operating limits.

[1] *J. I. E. C.,* **6** (1914), 383, 472.

The concentration factor above is considered in the sense of changes involved in the admixing of other substances with the initial material, such as the decomposition of oil in an atmosphere of hydrogen, carbon monoxide, etc.

THEORETICAL

According to chemical kinetics, a reaction tending toward a state of equilibrium will require time to reach such a state.

A reversible reaction may be represented thus:

$$n_1A_1 + n_2A_2 \rightleftarrows n_1'A_1' + n_2'A_2'\ldots$$

Such an equation represents two reverse reactions, each with a separate reaction velocity:

$$v = k(A_1)^{m_1}(A_2)^{m_2}\ldots \qquad v' = k'(A_1')^{m_1'}(A_2')^{m_2'}\ldots$$

The difference between these two velocities at any moment of time under constant conditions will give a certain change per unit of time in one direction or the other toward equilibrium. This change per increment of time, $\dfrac{dx}{dt}$, is commonly shown as follows:

$$\frac{dx}{dt} = v - v' = k(A_1)^{m_1}(A_2)^{m_2}\ldots - k'(A_1')^{m_1'}(A_2')^{m_2'}\ldots$$

in which k and k' are the velocity constants of the two reverse reactions, (A_1), (A_2), etc., are the concentrations of the reacting substances, and n_1, n_2, etc., their respective molecular exponents as obtained from a properly balanced equation.

The above velocity constants vary with temperature[1] and as a result temperature has a very marked effect upon the reaction velocities of the two reverse reactions. The effect of temperature on a number of gas reactions has been very carefully studied by Bodenstein[2] and the fundamental equations applied mathematically to the experimental results.

At equilibrium, the velocities of the opposing reactions are equal and hence the change per increment of time, $\dfrac{dx}{dt}$, must become zero.

$$\frac{dx}{dt} = v - v' = k(A_1)^{m_1}(A_2)^{m_2}\ldots - k'(A_1')^{m_1'}(A_2')^{m_2'}\ldots = 0$$

Hence,

$$\frac{k}{k'} = \frac{(A_1')^{m_1'}(A_2')^{m_2'}\ldots}{(A_1)^{m_1}(A_2)^{m_2}\ldots} = K,$$

[1] Trautz, Z. Elektrochem., 18 (1912), 513; Z. physik. Chem., 68 (1909), 295; 74 (1910). 747; Zellinek, Z. anorg. Chem., 49 (1906), 229.
[2] Bodenstein, Z. physik. Chem., 29 (1899), 147, 295, 315, 429, 665; Bodenstein and Wolgast, Ibid., 61 (1908), 422.

where K is the equilibrium constant. Thus chemical equilibrium deals only with the end state of a reaction and time is not a factor.

Where time is not considered the relations between the state of equilibrium and the thermal values of a reaction can be worked out by the application of thermodynamics. Such relations have been developed by Nernst,[1] Mayer and Altmayer,[2] and others[3] and expressed in terms of mathematical formulas from which equilibrium compositions can be calculated: e. g., the Nernst approximate formula:

$$\log K_p = \log \frac{p_1'^{m'} p_2'^{m'} \dots}{p_1^{m} p_2^{m} \dots}$$

$$= \frac{Q_p}{4.751 T} + 1.75 (\Sigma n' - \Sigma n) \log T + (\Sigma n'C' - \Sigma nC)$$

By the use of such formulas the ultimate composition representative of equilibrium conditions is obtained. This final composition, according to the principles of chemical kinetics, represents the end point of a reaction which can be attained only through a sufficient lapse of time. As applied to the production of oil gas, a progressive decomposition, in which time is an important factor, should proceed to an ultimate state of equilibrium.

The reactions taking place in the decomposition of petroleum hydrocarbons by heat are numerous and not definitely known. In the industries based on these decomposition reactions, as in the making of oil gas, carbureting water gas, and cracking petroleum for light distillates, the chemical nature of only the initial materials and the final products are determined, and this does not give any definite knowledge concerning the intermediate reactions. The breaking down of hydrocarbons of high molecular weights to simpler hydrocarbons apparently consists in numerous consecutive and concurrent reactions,[4] but their actual course from the initial material to the final products has not been established. Even in the absence of

[1] W. Nernst, "Theoretische Chemie."
[2] Mayer and Altmayer, Ber., 40 (1907), 2134.
[3] H. von Wartenberg, Z. physik. Chem., 61 (1907), 366.
[4] Berthelot, Ann. chim. phys. (1866 to 1877); Thorpe and Young, Liebig's Ann., 165 (1872), 1; Proc. Roy. Soc., 21 (1873), 184; Norton and Andrews, Am. Chem. J., 8 (1886), 1; Armstrong and Miller, J. Chem. Soc., 49 (1886), 74; Lewes, J. Soc. Chem. Ind., 11 (1892), 584; Haber, Ber., 29 (1896), 2691; J. Gasbel., 34, 377, 435, 452; Worstall and Burwell, Am. Chem. J., 19 (1897), 815; Bone and Coward, J. Chem. Soc., 93 (1908), 1197; Hempel, J. Gasbel., 1910, p. 53; Kramer and Spilker, Ber., 83 (1910), 2265; Lewes, Trans. Chem. Soc., 69 (1892), 322; Proc. Roy. Soc., 65 (1894), 90; 87 (1905), 394, 450; Bone, J. Gasbel., 51 (1908), 803; Engler, Ber., 80 (1897), 2908.

such knowledge, the theoretical principles of chemical kinetics which apply to single reactions should also hold in the case of the numerous reactions involved in the thermal decompositions of petroleum hydrocarbons.

The importance of the variable time in a few related decompositions has been shown by a number of investigators. Lewes[1] finds that the decomposition of ethylene is dependent not only upon temperature and pressure but also on rate of flow. Clement[2] has shown the importance of the time factor in the manufacture of producer gas. Hempel's[3] experiments with gas oils at temperatures between 700 and 900° C. have demonstrated further the influence of the rate of oil feed upon the composition of the products. J. F. Tocher[4] has also shown some results of a change in the rate of oil feed. A technical application of the time factor can be found in the experiments of Jones.[5]

In varying the rate of oil fed into a retort or furnace for the production of oil gas, one varies the time during which any portion is heated and hence the time allowed for the reaction. With a very slow rate of oil feed, the reaction would attain an equilibrium composition representative of the heating zone conditions. With increasing rates of oil feed the time allowed for reaction is shortened and the products obtained correspond to an earlier stage of the decomposition. The composition of oil gas is therefore dependent upon the time allowed for chemical change. Hence the study of the time factor in the making of oil gas should yield interesting and practical results.

EXPERIMENTAL CONSIDERATIONS

A study of the reactions of gases moving through heated vessels, the method which was used in this investigation and is representative of practice in oil gas production, involves certain features of design which are dependent upon the theoretical considerations of reaction velocity. During the passage of any heating-zone-composition through the cooling zone, there will be a certain change in composition due to a reversal of reactions.[6] The extent of this reversal will depend on the time required in the cooling zone

[1] Lewes, *Proc. Roy. Soc.*, **55** (1894), 90; **67**, 594.
[2] Clement, *Bull.* **30** (1909), D. of Ill. Eng. Exp. Sta.
[3] Hempel, *J. Gasbel.*, **1910**, pp. 53, 77, 101, 137 and 155.
[4] J. F. Tocher, *J. Soc. Chem. Ind.*, **13** (1894), 231.
[5] Jones, *Am. Gaslight J.*, **99** (1913), 273.
[6] Nernst, *Z. anorg. Chem.*, **49** (1906), 213.