Note on Mayers' Theory of Cluster Integrals

Kodi Husimi

One interesting result obtained is that no decenes were found in the products. It has often been claimed that alkyl radicals have a great tendency to disproportionate when produced in solution. Bamford and Norrish,[6] who photolyzed a variety of aldehydes and ketones in paraffinic solvents, claimed that the large (octyl) radicals which were produced by the reaction of the solvent with the smaller alkly radicals formed by the photolysis, disproportionated, and produced

[6] C. H. Bamford and R. G. W. Norrish, J. Chem. Soc. 1544 (1938).

unsaturated compounds which could be detected. The results obtained in the present study are in disagreement with the conclusions of Bamford and Norrish on this point. Our results show clearly that decyl radicals are produced in the mercury photo-sensitized reactions of decane, that the decyl radicals do recombine to form eicosanes and that they do not disproportionate. Bamford and Norrish found significant amounts of lower olefins in their products and it is quite possible that the unsaturation that they ascribed to octene may have been produced by polymerization of the lower olefins rather than by disproportionation of large alkyl radicals.

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The cluster integrals, b_l, in the condensation theory are expressible as a sum of products of irreducible integrals K_R. The coefficient of each member of the sum is derived in a simple manner.

IN their excellent text book, *Statistical Mechanics*, J. E. Mayer and M. G. Mayer[1] present a certain connection between the "cluster integrals" b_l and the "irreducible integrals" β_K. Their reasoning in establishing this connection is rather elementary and very complicated. Before I enter into an alternative analytical discussion of the subject, I want to generalize the notion of irreducible integrals which may be applied to any statistics, whereas Mayer's seem to be inseparably connected with the classical statistics and with the restricting assumption of binary interaction between the gas molecules. It concerns certain integrals of the form

$$N! I_N = \int^{(N)} \cdots \int W(1,2,\cdots,N) d1\, d2 \cdots dN$$

with

$$W(1,2,\cdots,N) = \exp(-\beta V(1,2,\cdots,N)).$$

Here $V(1,2,\cdots,N)$ is the energy of the configuration of the molecules $1,2,\cdots,N$ (numerals also represent the coordinates of the molecules), and $\beta = 1/KT$. W is symmetrical in its N arguments. In treating this multiple integral Ursell[2] devised a method of expansion which may be described according to Kahn and Uhlenbeck[3] as follows: We introduce successively new functions U by the scheme:

$$W(1) = U(1)$$
$$W(1,2) = U(1,2) + U(1)U(2)$$
$$W(1,2,3) = U(1,2,3) + U(1,2)U(3) + U(23)U(1)$$
$$\qquad\qquad + U(31)U(2) + U(1)U(2)U(3).$$

[1] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).
[2] H. D. Ursell, Proc. Cambridge Phil. Soc. **23**, 685 (1927).
[3] B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938).

Then the symmetrical functions U have the property that they vanish everywhere except at the points where the arguments are close to each other. This is a consequence of the assumed short range of interaction forces. In general, $W(1,2,\cdots,N)$ is of the form

$$W(1,\cdots,N)$$
$$= \sum_{\Sigma l m l = N} S\left\{ \overset{m_1}{\prod} U(i) \overset{m_2}{\prod} U(ik) \cdots \overset{m_l}{\prod} U(i_1\cdots i_l) \cdots \right\}.$$

The first summation S is the symmetrization of the U-products and the second summation $\sum$ extends over all partitions of the number N. The number of terms in S, each of which gives on integration the same values

$$\prod_{l=1}^{N} (l! J_l)^{m_l}$$

where

$$l! J_l \equiv \int^{(l)} \cdots \int U(1,2,\cdots,l) d1\, d2 \cdots dl \equiv V \cdot l! b_l,$$

is easily computed and is given by

$$\frac{N!}{\prod_l (l!)^{m_l} m_l!}$$

so that

$$I_N = \sum_{\Sigma l m l = N} \prod_l \frac{(J_l)^{m_l}}{m_l!}.$$

This is Ursell's development. In order to attain Mayer's development, we introduce another infinite set of func-

tions V defined by

$$U(1,2) = V_1(1,2)$$

$$U(1,2,3) = V_2(1,2,3) + V_1(12)V_1(23)$$
$$+ V_1(23)V_1(31) + V_1(31)V_1(12)$$

$$U(1,2,3,4) = V_3(1,2,3,4) + \sum_{12 \text{ terms}} V_2(123)V_1(34)$$
$$+ \sum_{12 \text{ terms}} V_1(12)V_1(23)V_1(34)$$
$$+ \sum_{3 \text{ terms}} V_1(12)V_1(13)V_1(14)$$

$$U(1,2,3,4,5) = V_4(12345) + \sum_{60 \text{ terms}} V_3(1234)V_1(45)$$
$$+ \sum_{15 \text{ terms}} V_2(123)V_2(345)$$
$$+ \sum_{60 \text{ terms}} V_1(12)V_1(23)V_1(34)V_1(45)$$
$$+ \sum_{60 \text{ terms}} V_1(12)V_1(23)V_1(24)V_1(45)$$
$$+ \sum_{5 \text{ terms}} V_1(12)V_1(13)V_1(14)V_1(15).$$

The method of construction is the following. U with l arguments is a sum of isobaric products ΠV_R with $\sum R = l-1$. In each product the variables are never separated in groups, so that the product is not factorized into factors with mutually foreign variables. But the two and more V's within a product contain one and only one common variable. Further the products are of such nature that, if a common variable is omitted, the product is factorized into several factors with mutually different variables. The V's are totally symmetric functions. The introduction of V's are based on the assumption that the mutual potential energy of the molecules is dependent only on their relative coordinates, not on their absolute position in space, so long as the influence of the gas enclosure is neglected.

Then the integral of the product of the V's are reducible to the product of integrals of the individual V's. For we have, e.g.,

$$\int V_2(123)V(3\cdots)\cdots d1d2d3\cdots$$
$$= \int V_2(123)d1d2 \cdot \int V(3\cdots)\cdots d3\cdots$$

since the first integral becomes independent on the common variable 3. The individual integrals

$$K_R = \int V_R(12\cdots R, R+1)d1d2\cdots dR$$

are just Mayer's irreducible integrals. Every product

of the form,

$$\overset{n_1}{\Pi V_1} \overset{n_2}{\Pi V_2} \cdots \overset{n_R}{\Pi V_R} \cdots \quad \left(\sum_R R n_R = l-1 \right),$$

with given numbers of factors $n_1, n_2, \cdots n_R, \cdots$ all give rise to one and the same integral, i.e.,

$$K_1{}^{n_1} K_2{}^{n_2} \cdots K_R{}^{n_R} \cdots \quad \cdot v,$$

where v is the volume of the gas enclosure. And the problem under our discussion is to determine the number $T(n_1 n_2, \cdots n_R \cdots)$ of different products with the above form in the representation of a given $U(12\cdots l)$. The numbers $T(n_1, 0, 0, 0, \cdots)$ have been subjects of many mathematicians since the time of Cayley, as the number of "trees" with given number l of the molecules. A modern method of obtaining $T(n_1, 0, 0, \cdots)$ has been given by G. Bol.[4] We want to generalize his method to our problem of $T(n_1 n_2 \cdots n_R \cdots)$.

The starting point is the establishment of a recursion formula. This is obtained if, in a given generalized tree

$$\overset{n_1}{\Pi V_1} \overset{n_2}{\Pi V_2} \cdots \overset{n_R+1}{\Pi V_R} \cdots,$$

a factor V_R is omitted. Then the tree is separated in general into $(R+1)$ trees. These may have $n_{h,m} V_h$'s $(m=1,2,\cdots,R,R+1)$.

We have of course $\sum_m n_{h,m} = n_h$. An elementary consideration will lead to the recursion formula

$$(n_R+1) \cdot (R+1)! \cdot T(n_1, n_2, \cdots, n_R+1, \cdots)$$
$$= \sum_{(n_h, m)} l! \prod_{m=1}^{R+1} \frac{l_m T(\cdots n_{hm} \cdots)}{l_m!}$$

$l_m = 1 + \sum_h h n_{h,m}$ is the number of molecules contained in the tree $\{\cdots, n_{h,m} \cdots\}$ and the above summation extends over all partitions $n_h = \sum n_{hm}$ of $n_h (h=1,2,\cdots, h=R$ inclusive).

In order to solve the recursion formula we introduce a generating function

$$F(x, y_1, y_2, \cdots) = \sum_{\substack{(n_R=0,1,\cdots,\infty) \\ l=1+\Sigma R n_R}} \frac{T(n_1 n_2 \cdots) x^l y_1{}^{n_1} y_2{}^{n_2} \cdots}{l!}.$$

It has a redundant variable $F(x, y_1, y_2, \cdots) = \lambda F(\lambda^{-1} x, \lambda y_1, \lambda^2 y_2, \cdots)$ and satisfies Euler's equation

$$x \frac{\partial F}{\partial x} = F + y_1 \frac{\partial F}{\partial y_1} + 2 y_2 \frac{\partial F}{\partial y_2} + \cdots.$$

The recursion equation becomes now

$$(R+1)! \frac{\partial F}{\partial y_R} = \left(x \frac{\partial F}{\partial x} \right)^{R+1}$$

[4] G. Bol, Abhandl. Math. Seminar Hansischen Univ. 12, 242 (1938). (I thank Mr. Kasuga for bringing my notice to the paper.)

which leads, combined with Euler's equation, to

$$x\frac{\partial F}{\partial x}=F+\sum_{R=1}\frac{Ry_R}{(R+1)!}\left(x\frac{\partial F}{\partial x}\right)^{R+1}.$$

This equation may be considered as an ordinary differential equation with fixed parameters y_R.

Let

$$G\equiv x\frac{\partial F}{\partial x}.$$

Then the equation becomes

$$G=F+\sum\frac{Ry_R}{(R+1)!}G^{R+1}.$$

or, after differentiatiation by G, considered as independent variable,

$$1=\frac{dF}{dG}+\sum\frac{y_R}{(R-1)!}G^R.$$

Since

$$\frac{dx}{x}=\frac{dF}{dG}\frac{dG}{G}$$

it gets the form

$$\frac{dx}{x}=\left\{1-\sum_R\frac{y_R}{(R-1)!}G^R\right\}\frac{dG}{G},$$

which integrates immediately to

$$x=G\exp\left\{-\sum_{R=1}\frac{y_R}{R!}G^R\right\}.$$

$T(n_1\cdots)$ will now be obtained as the coefficient of x^l in the power series of G times l. Cauchy's theorem now gives

$$\frac{1}{2\pi i}\oint\frac{Gdx}{x^{l+1}}$$

$$=\frac{1}{2\pi i}\oint\frac{\exp(l\sum y_RG^R/R!)}{G^{l-1}}\left(1-\sum\frac{y_R}{(R-1)!}G^R\right)\frac{dG}{G}$$

$$=\frac{1}{2\pi i}\oint\frac{1}{l}\frac{\exp(l\sum y_RG^R/R!)}{G^l}dG$$

$$=\frac{1}{l}\sum_{\Sigma hn_h=l-1}\prod_h\frac{1}{n_h!}\left(\frac{ly_h}{n!}\right)^{n_h},$$

and the final formula is obtained:

$$T(n_1n_2\cdots n_R\cdots)=\frac{l!}{\prod_R(R!)^{n_R}n_R!}l^{\Sigma n_R-2}.$$

As one sees the generating function F or G here introduced plays an important role in the further discussions of Mayer's condensation theory. In fact, if we put $y_R=K_R\equiv R!\beta_R$ in $F(x,y_1\cdots)$, we have

$$F(x,K_1,K_2,\cdots)=\sum b_lx^l\equiv X(x)$$

and $G=x(\partial F/\partial x)$, $x=G\exp(-\sum y_RG^R/R!)$ are equivalent to

$$y=xX'(x),\quad x=ye^{-\phi(y)},\quad \phi(y)\equiv\sum_{K=1}^{\infty}\beta_Ky^K$$

(for notation, see Kahn-Uhlenbeck[3]).

The theory of this report was formulated several years ago and printed in our book on quantum statistical mechanics in Japanese.[5] Mr. Y. Muto has successfully applied it to the theory of multi-component systems and the idea may be useful in a wider circle of statistical problems.

[5] K. Husimi, Ed., *Quantum Statistical Mechanics* (Kyoritu Syuppan K.K., 1948).