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THE THERMOELECTRIC MICRODETERMINATION OF MOLECULAR WEIGHT—III[1]

THEORETICAL

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Abstract—A method is described for the calculation of the steady state temperature difference between a drop of solvent and a drop of solution suspended in a solvent saturated atmosphere. The procedure is used to discuss the influence of different parameters on the performance of an apparatus for the thermoelectric routine determination of molecular weight.

INTRODUCTION

IN THE thermoelectric microdetermination of molecular weight[4] a drop of a solution and a drop of the solvent are suspended in an atmosphere saturated with the solvent vapour. The steady state temperature difference which is developed between the drops is measured. The temperature difference is linear with the solution strength,

$$\Delta T = d \,.\, m \tag{1}$$

where d = Constant [deg. kg g-mole^{-1}],
m = Solution molality [g-mole kg^{-1}],
ΔT = Temperature difference between drops [deg].

This relation is valid only for ideal solutions, d then being dependent solely upon the solvent.

A full understanding of the method depends upon evaluating d in terms of the apparatus and solvent constants and this is attempted in the present work. Once this relationship has been established, the optimum working conditions for the reproducibility of d with time and different apparatuses can be obtained. Hitherto d has been related empirically to the various constants,[5] little information thus being derived concerning cell design.

2. *Basis of the calculation*

At the steady state the drops are assumed to be of uniform and constant temperature. The thermistor[6] current is assumed zero in order to simplify the calculation. In

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[1] Part II: D. Wegmann, C. Tomlinson and W. Simon, *International Symposium on Microchemical Techniques Proceedings* 1961.

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[4] W. Simon and C. Tomlinson, *Chimia* **14**, 301 (1960).

[5] B. R. Y. Iyengar, *Rec. Trav. Chim.* **73**, 789 (1954).

[6] Thermistors are used normally to measure the temperature difference between the solvent and solution drop.

fact, the thermistor resistance changes by only 0·2% on replacing the solvent by a solution drop, this altering the electrical heating factor by a negligible amount. The only heat gain considered therefore is that due to condensation of solvent vapour onto the solution drop. At the steady state the rate of heat gain by this process must be balanced by the rate of heat loss by conduction and radiation. From the work of Langstroth *et al.*[7], it seems justifiable to neglect convective heat loss.

As rate controlling factors in the thermal balance the following are possible: (a) solvent evaporation from the cell reservoir, (b) thermal conduction through the drop, (c) diffusion of the solute through the solution drop, (d) diffusion of the solvent through the cell atmosphere. Higuchi *et al.*[8] demonstrated that under vacuum conditions (a) only became significant for solvents of low volatility. Factor (b) would lead to a strong dependence of d upon drop size, a fact which has not been observed.[4] Both the independence of d from the nature of the solute in dilute solution and the magnitude of solute diffusion coefficients suggest the insignificance of (c). The operative factor thus appears as (d), as assumed by previous workers.[9,10]

A suitable model for the pendant drop is required in order to investigate the variation of d with drop radius. The actual form is approximated in two ways: (i) the cylinder model, and (ii) the echelon model. In (i) the drop hangs from the cylindrical thermistor with a constant cross sectional area. In (ii) the conical form of the thermistor tip is approximated by eighteen short cylinders each of height 0·01 cm, the smallest having a diameter of 0·02 cm, the largest that of the thermistor. The lower eight cylinders are of solid glass, while the upper ten are hollow and have a glass wall thickness the same as that of the thermistor stem. The drop hangs in spherical form with its centre coincident with the tip of the thermistor.

While considering thermal factors concerning the drop, the cell and drop are assumed to be concentric spheres, the former being of equal area to the actual cell.[11] In dealing with the thermistor heat factors the cell and thermistor stem are considered to be coaxial cylinders. Thermal gains by the drop are considered positive, losses negative.

Further assumptions are: (a) the absorption of radiation by the cell atmosphere is neglected, (b) the dilution of the solution drop and any consequent additional thermal factor is neglected.

3. *Theoretical calculation*

3.1. *Positive heat factor.*

$$\dot{H} = L \, . \, \dot{m} \tag{2}$$

where $\dot{H}$ = Rate of heat gain through condensation [cal sec^{-1}],

L = Solvent latent heat of vaporization [cal g^{-1}],

$\dot{m}$ = Rate of solvent condensation [g sec^{-1}].

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[7] G. O. Langstroth, C. H. H. Diehl and E. J. Winhold, *Canad. J. Res.* **A28**, 580 (1950).

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[11] I. Langmuir, E. Q. Adams and G. S. Meikle, *Trans. Amer. Electr. Soc.* **24**, 53 (1914).

By diffusion theory,[12]

$$\dot{m} = \frac{S \,.\, M \,.\, D \,.\, Z \,.\, \Delta p}{R \,.\, T_0} \tag{3}$$

where S = Shape factor [cm],
M = Solvent molecular weight [g g-mole^{-1}],
D = Solvent vapour diffusion coefficient into air [cm^2 sec^{-1}],
Z = Units conversion factor [cal cm^{-3} Torr^{-1}],
R = General gas constant [cal g-mole^{-1} deg^{-1}],
T_0 = Absolute cell temperature [°K],
Δp = Solvent vapour pressure lowering by the solute [Torr].
From the work of Langmuir,[11]

$$S = \frac{4 \,.\, \pi \,.\, r_c' \,.\, r_d'}{(r_c' - r_d')} \tag{4}$$

where r_c' = Radius of a sphere of the cell inner surface area [cm],
r_d' = Radius of a sphere of the drop surface area [cm].
These radii are given by,

$$r_c' = \sqrt{\tfrac{1}{2} \,.\, r_c\,(r_c + l_c)} \tag{5}$$

$$r_d' = \sqrt{\tfrac{1}{2} \,.\, r_d(r_d + \sqrt{r_d^2 - r_t^2})} \tag{6}$$

where r_c = Cell radius [cm],
r_d = Drop radius [cm],
r_t = Thermistor stem radius [cm],
l_c = Cell length [cm].

By *Rauolt's Law* and the *Clausius–Clapeyron* equation,[10]

$$\Delta p = -\frac{M \,.\, L \,.\, p \,.\, \Delta T}{R \,.\, T_0^2} + m \,.\, M \,.\, 10^{-3} \,.\, p \tag{7}$$

where p = Solvent saturated vapour pressure at T_0 [Torr].
From Eqs (2), (3) and (7),

$$\dot{H} = \frac{S \,.\, M^2 \,.\, D \,.\, Z \,.\, L \,.\, p}{R \,.\, T_0}\left(\frac{m \,.\, 10^{-3}}{\Delta T} - \frac{L}{R \,.\, T_0^2}\right)\Delta T \tag{8}$$

3.2. *Negative heat factors.*

3.2.1. *Conduction through the gas phase.*

$$\dot{Q}_v = -S \,.\, k \,.\, \Delta T \tag{9}$$

where $\dot{Q}_v$ = Rate of heat loss from the drop [cal sec^{-1}],
k = Thermal conductivity of the cell atmosphere [cal cm^{-1} sec^{-1} deg^{-1}].

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[12] J. Stefan, *Sitz. Akad. Wien* **65**, 323 (1872).

3.2.2. *Radiation from the drop.*

$$\dot{Q}_r = -4 \,.\, \pi \,.\, r_d'^2 \,.\, \sigma \,.\, \epsilon_d(T_1^4 - T_0^4) \qquad (10)$$
$$= -16 \,.\, \pi \,.\, r_d'^2 \,.\, \sigma \,.\, \epsilon d \,.\, T_0^3 \,.\, \Delta T$$

where $\dot{Q}_r$ = Rate of heat loss from the drop [cal sec^{-1}],
T_1 = Solution drop temperature [°K],
T_0 = Cell temperature [°K],
σ = *Stefan–Boltzmann* constant [cal cm^{-2} sec^{-1} deg^{-4}],
ϵ_d = Drop surface emissivity.

3.2.3. *Conduction through the thermistor leads.* The electric current passes through the thermistor bead by way of two thin platinum wires welded to thick cunife wires at their upper ends. Because of the relative diameters the temperature gradient is assumed to be negligible in the cunife wires. Hence,

$$\dot{Q}_w = -\frac{2 \,.\, \pi \,.\, r_w^2 \,.\, k_w}{l_w} \Delta T \qquad (11)$$

where $\dot{Q}_w$ = Rate of heat loss through the platinum wires [cal sec^{-1}],
r_w = Platinum wire radius [cm],
l_w = Platinum wire length [cm],
k_w = Thermal conductivity of the platinum wires [cal cm^{-1} sec^{-1} deg^{-1}].

3.2.4. *Thermal losses through the thermistor stem.* Consider a small length dx of the thermistor stem, then

$$\dot{Q}_1 = -k_t \,.\, A_t \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_x \qquad (12)$$

where $\dot{Q}_1$ = Rate of heat gain by conduction by the element [cal sec^{-1}],
k_t = Thermal conductivity of the thermistor glass [cal sec^{-1} cm^{-1} deg^{-1}],
A_t = Thermistor glass cross sectional area [cm^2],
x = Co-ordinate along the thermistor stem from the drop [cm].

Similarly, the element loses heat by conduction along the thermistor stem,

$$\dot{Q}_2 = k_t \,.\, A_t \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{x+\mathrm{d}x} \qquad (13)$$

Heat loss also occurs by conduction through the gas phase. Consider a ring about the element dx of radius r, then,

$$\dot{Q}_3 = k \,.\, 2 \,.\, \pi \,.\, r \,.\, \mathrm{d}x \left(\frac{\mathrm{d}T}{\mathrm{d}r}\right)_r \qquad (14)$$

$$\dot{Q}_3 \int_{rt}^{rc} \frac{\mathrm{d}r}{r} = 2. \;\pi \,.\, k \,.\, \mathrm{d}x \int_{T}^{To} \mathrm{d}T$$

$$\dot{Q}_3 = -\frac{2 \,.\, \pi \,.\, k(T - T_0)\, \mathrm{d}x}{\ln (r_c/r_t)} \qquad (15)$$

where T = Temperature of the thermistor element [°K].

Radiation losses by the element are given by

$$\dot{Q}_4 = -8 . \pi . r_t . \sigma . \epsilon_t . T_0^3(T - T_0)\,\mathrm{d}x \tag{16}$$

where ϵ_t = Emissivity of the thermistor glass.

Since a steady state exists,

$$\dot{Q}_1 + \dot{Q}_2 + \dot{Q}_3 + \dot{Q}_4 = 0$$

$$k_t . A_t\left\{\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{x+\mathrm{d}x} - \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_x\right\} = \left(\frac{2 . \pi . k}{\ln r_c/r_t} + 8 . \pi . r_t . \sigma . \epsilon_t . T_0^3\right)(T - T_0)\,\mathrm{d}x$$

$$k_t . A_t\left(\frac{\mathrm{d}^2T}{\mathrm{d}x^2}\right) = \left(\frac{2 . \pi . k}{\ln r_c/r_t} + 8 . \pi . r_t . \sigma . \epsilon_t . T_0^3\right)(T - T_0) \tag{17}$$

This equation is of the form,

$$\frac{\mathrm{d}^2T}{\mathrm{d}x^2} - q^2 . T + q^2 . T_0 = 0$$

where

$$q^2 = \frac{\dfrac{2 . \pi . k}{\ln r_c/r_t} + 8 . \pi . r_t . \sigma . \epsilon_t . T_0^3}{k_t . A_t} \tag{18}$$

The general solution is,

$$T = T_0 + B_1 . e^{q.x} + B_2 . e^{-q.x} \tag{19}$$

where B_1, B_2 are constants.

With boundary conditions,

$$\left.\begin{array}{l} x = 0 \\ T = T_1 \end{array}\right\} T_1 = T_0 + B_1 + B_2 \tag{20}$$

$$\left.\begin{array}{l} x = 1 \\ T = T_0 \end{array}\right\} T_0 = T_0 + B_1.e^{q.l} + B_2.e^{-q.l} \tag{21}$$

where l = Length of exposed thermistor stem [cm].

From Eqs (20) and (21),

$$B_1 = -\frac{\Delta T . e^{-q.l}}{e^{q.l} - e^{-q.l}} \tag{22}$$

$$B_2 = \frac{\Delta T . e^{q.l}}{e^{q.l} - e^{-q.l}} \tag{23}$$

From equations (19), (22), and (23),

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{x=0} = B_1 . q - B_2 . q \tag{24}$$

$$= -q . \Delta T . \coth q . l$$

$$\dot{Q}_t = k_t . A_t\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)_{x=0}$$

$$\dot{Q}_t = -k_t . A_t . q . \Delta T . \coth q . l$$

where $\dot{Q}_t$ = Total rate of loss of heat along the thermistor stem [cal.sec^{-1}].

3.3. *General thermal balance of the solution drop.* At the steady state,

$$\dot{H} + \dot{Q}_v + \dot{Q}_r + \dot{Q}_w + \dot{Q}_t = 0 \tag{25}$$

By the following substitutions into Eqs (8), (9), (10), (11) and (24) and their substitution into equation (25) we have,

$$a = \frac{S \,.\, M^2 \,.\, D \,.\, Z \,.\, L \,.\, p}{R \,.\, T_0} \tag{26}$$

$$b = \frac{L}{R \,.\, T_0^2} = (10^3 \,.\, d_t)^{-1} \tag{27}$$

where d_t = Theoretical thermodynamic d value (measured theoretically on ideal solutions in the absence of all heat losses).

$$c_v = S \,.\, k \tag{28}$$

$$c_r = 16 \,.\, \pi \,.\, \sigma \,.\, \epsilon_d \,.\, r_d^2 \,.\, T_0^3 \tag{29}$$

$$c_w = \frac{2 \,.\, \pi \,.\, k_w \,.\, r_w^2}{l_w} \tag{30}$$

$$c_t = q \,.\, k_t \,.\, A_t \,.\, \coth q \,.\, l. \tag{31}$$

Hence,

$$d = \frac{\Delta T}{m} = \frac{a \,.\, 10^{-3}}{a \,.\, b + c_v + c_r + c_w + c_t} \tag{32}$$

$$\eta = \frac{d}{d_t} = \frac{a \,.\, b}{a \,.\, b + c_v + c_r + c_w + c_t} \tag{33}$$

where η = Efficiency of a given solvent.

The above equations express the required constants d and η in terms of the solvent and apparatus parameters and are the basis upon which the numerical calculations are made.

3.4. *Solvent thermistor influence.* The above calculation neglects the presence of the reference thermistor and solvent drop. This however will influence the solution drop in providing a short diffusion and heat loss path. Consequently the shape factor should be modified. An estimation of the effect may be made by assuming that the solvent drop increases the shape factor proportionally to the solid angle α which it subtends at the solution drop. The shape factor S' of the system with the cell as a sphere of radius $(y - r_d)$, concentric with solution thermistor drop is therefore given by,

$$S' = \frac{4 \,.\, \pi(y - r_d)r_d'}{y - r_d - r_d'} \tag{34}$$

where y = Distance between thermistor axes [cm].

$$\Delta S = \frac{\alpha}{4\,.\,\pi}(S' - S)$$

$$= \frac{\pi\,.\,r_d^2\,.\,r_d'^2(r_c' + r_d - y)}{y^2(y - r_d - r_d')(r_c' - r_d')} \tag{35}$$

where ΔS = Increase in S due to the presence of the other thermistor [cm].

4. *Constants*

4.1. *Apparatus constants*

TABLE 1. APPARATUS CONSTANTS

Constant	Value	Constant	Value
r_t	0·18 cm	l_c	3·50 cm
r_d	0·25 cm	l_w	0·85 cm
r_c	1·70 cm	y	0·75 cm
r_w	0·0025 cm	A_t	0·0704 cm^2
l	2·00 cm	T_0	302·0°K

4.2. *Solvent constants at* 302·0°K. (See Table 2) Latent heat values are obtained by linear extrapolation from literature values at other temperatures. Diffusion coefficients are calculated from D_0 (at 0°C) by the expression $D = D_0(T/T_0)^m$, where $m = 1{\cdot}75$ for water and 2·00 for all other solvents. Literature vapour pressure data are fitted to $\lg p = A + B/T$ where necessary. Thermal conductivity coefficients are calculated from the pure gas values by linear interpolation.

4.3. *General constants at* 302·0°K. (See Table 3)

5. *Numerical calculation*

A programmed computer (IBM 1620) was employed in the calculation of d and η values. The programme was arranged to yield values of relative heat losses,

$$h_i = 100\,.\,\frac{c_i}{\Sigma\, c_i}\,[\%] \tag{36}$$

where c_i = Appropriate heat loss factor (see Section 3.3), as well as the percentage change in d for any desired change of a constant.

6. *Results and discussion*

6.1. d *and* η. The calculated d and η values are compared in Table 4 with those experimentally determined.[1] The overall correspondence is good, especially considering the uncertainty of many of the constants used. It is significant that the correspondence deteriorates as this uncertainty increases.

The average contribution of the thermistor stem, vapour phase, radiation and thermistor wire heat losses are: 37·6, 37·8, 22·9 and 1·7% respectively. Little variation in these numbers is found from solvent to solvent and they indicate the importance of thermistor design upon the experimental efficiency. By making the

TABLE 2. SOLVENT CONSTANTS

Solvent	M	L	D	p	$k_{.} \cdot 10^5$
H_2O	18·02	580·0[13,14]	0·266[13,15–17]	29·8[13]	6·18[13]
MeOH	32·04	281·0[18]	0·163[13]	149·3[13,19]	5·76[20]
C_6H_6	78·11	102·0[13,21]	0·0987[15]	113·9[21,22]	5·68[20]
EtOAc	88·10	96·6[13]	0·0874[13,23]	115·3[24]	5·68[13]
Et_2O	74·12	86·7[13,25]	0·0951[13,33]	616·6[19]	3·99[20]
CCl_4	153·8	49·9[13]	0·0798[13,17,26]	135·4[13,27]	5·41[13]
CH_2Cl_2	84·94	81·8[28,29]	0·100[13]	485·3[13]	3·44[13]
$CHCl_3$	119·4	61·9[13]	0·111[30]	231·7[13,31,32]	4·88[13,20]

TABLE 3. GENERAL CONSTANTS

Constant	Value	Constant	Value
σ	$1{\cdot}355 \,.\, 10^{-12}$ cal cm^{-2} sec^{-1} deg^{-4}	Z	$3{\cdot}1854 \,.\, 10^{-5}$ cal cm^{-3} Torr^{-1}
k_{air}[34]	$6{\cdot}27 \,.\, 10^{-5}$ cal cm^{-1} sec^{-1} deg^{-1}	R	1·9865 cal g-mole^{-1} deg^{-1}
k_t	$1{\cdot}43 \,.\, 10^{-3}$ cal cm^{-1} sec^{-1} deg^{-1}	ϵ_t[35]	0·94
k_w	$1{\cdot}66 \,.\, 10^{-1}$ cal cm^{-1} sec^{-1} deg^{-1}	ϵ_d[35]	0·95

TABLE 4. RELATIVE HEAT LOSSES h_t
Calculated and experimentally determined d and η values

Solvent	d_{exp}	d_{calc}	η_{exp}	η_{calc}	h_v	h_r	h_w	h_t
H_2O	0·197	0·196	0·631	0·6286	41·92	20·71	1·50	35·85
MeOH	0·514	0·516	0·797	0·7997	40·49	21·46	1·56	36·49
C_6H_6	1·05	1·054	0·591	0·5931	40·20	21·61	1·57	36·62
EtOAc	1·12	1·123	0·597	0·5986	40·20	21·61	1·57	36·62
Et_2O	1·77	1·782	0·847	0·8529	33·13	25·36	1·84	39·68
CCl_4	1·97	2·076	0·543	0·5718	39·21	22·13	1·61	37·05
CH_2Cl_2	2·00	1·897	0·903	0·8563	30·28	26·88	1·95	40·88
$CHCl_3$	2·07	2·207	0·707	0·7540	37·12	23·23	1·68	37·96

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TABLE 5. CALCULATED INFLUENCE ON d OF VARIATIONS IN THE CONSTANTS

Constant varied	Variation %	Resulting change of d in ‰							
		H_2O	MeOH	C_6H_6	EtOAc	Et_2O	CCl_4	CH_2Cl_2	$CHCl_3$
Cell length	+1	−0·09	−0·05	−0·10	−0·10	−0·04	−0·10	−0·04	−0·06
Cell radius	+1	−0·01	−0·01	−0·02	−0·02	−0·02	−0·03	−0·03	−0·02
Cell radius	+400	−1·71	−1·36	−2·94	−2·91	−2·79	−3·76	−3·45	−2·99
Thermistor radius	+1	−2·78	−1·53	−3·11	−3·07	−1·24	−3·32	−1·25	−1·97
Thermistor, inner radius	−100	−28·30	−15·80	−31·62	−31·21	−12·80	−33·64	−12·95	−20·19
Thermistor length	+1	0·01	0·01	0·01	0·01	0·01	0·01	0·01	0·01
Thermistor length	−50	−7·34	−4·32	−8·85	−8·74	−4·59	−9·83	−5·08	−6·33
Wire length	−90	−50·38	−28·84	−57·13	−56·41	−25·12	−61·29	−25·99	−37·96
Glass conductivity	+1	−0·70	−0·39	−0·79	−0·78	−0·31	−0·84	−0·31	−0·50
Drop emissivity	+1	−0·73	−0·40	−0·83	−0·82	−0·35	−0·90	−0·36	−0·54
Thermistor emissivity	+1	−0·33	−0·19	−0·39	−0·38	−0·17	−0·42	−0·19	−0·26
Vapour pressure	+1	3·72	2·00	4·07	4·02	1·47	4·28	1·44	2·46
Heat of vaporization	+1	−2·54	−5·93	−1·83	−1·94	−6·99	−1·41	−7·05	−5·03
Diffusion coefficient	+1	3·72	2·00	4·07	4·02	1·47	4·28	1·44	2·46
Gas phase conductivity	+1	−1·90	−0·99	−2·00	−1·97	−0·60	−2·05	−0·54	−1·12
Shape factor	+1	2·15	1·18	2·42	2·39	0·97	2·59	0·99	1·53
Shape factor (ΔS)	+2·06	4·39	2·42	4·95	4·88	1·98	5·30	2·02	3·14

thermistor heat loss negligible, a maximum increase of 11% in efficiency can be gained with the most favourable solvent.

The effect of changes in the constants used in the calculation are shown in Table 5. Small variations in all constants can be considered to have a linear effect upon d. For large variations it must be considered whether the present model is adequate. In the light of Tables 4 and 5, the effect of errors in the solvent constants on the d_{calc} values can be discussed. For water, ether and benzene the constants are reliable (i.e. 1% accuracy) and excellent d value correspondence is observed. For methanol, the chosen L value may be 1% high[36] and the D_0 value up to 10% high.[37] d_{calc} may therefore be 1·4% high. Accurate determinations of the vapour pressure of ethyl acetate are lacking and the chosen value may be up to 4% high.[13,19] Thus d_{calc} may be high by 1·6%. The chlorinated solvents have been least accurately investigated and very divergent values for the same constant are reported. Thus D_0 for carbon tetrachloride varies[26,37] from 0·0700 to 0·1236 cm^2 sec^{-1}, and L for chloroform[38] from 62 to 66 cal g^{-1}. For methylene chloride no D_0 values are available and use has been made of Gilliland's equation.[23] This however in general yields values from 10 to 20% low.[39] The vapour pressure of methylene chloride is also uncertain, very few determinations having been made.

Such uncertainties, particularly in D_0, are reflected in the large scatter of d_{calc} about d_{exp} for these solvents, and improvements will only be made as more reliable constants become available. A further error involving all the solvents lies in the method of determining the thermal conductivity of the cell atmosphere. A simple linear interpolation method based on the partial pressure of the components has been used here, though the more laborious but accurate method of Lindsay *et al.*[40] would be preferable.

6.2. *η and* r_d. The variation of η with r_d is shown by Figs. 1 and 2. The two models show similar behaviour, η not varying significantly in the normal drop radius range. This confirms earlier less precise calculations[41] and numerous experimental observations.[4] For very small drops the present theory is inapplicable since dilution becomes significant here at the steady state. With the present thermistors ($r_t = 0{\cdot}18$ cm) a drop radius in the range 0·20–0·30 cm seems ideal, since maximum efficiency and minimum variation of η with r_d are obtained. By using thermistor clips[1] both the drop size and shape are reproducible and should lead to insignificant d value variations with time.

6.3. *Cell design.* Ideal cell dimensions should not be critical in their accuracy for d and η reproducibility, should be convenient practically, and should yield a high efficiency. Since η can be increased only by a few per cent by optimizing the cell geometry, reproducibility must have precedence over efficiency where the requirements are contradictory. The present apparatus approximates to the optimum conditions. Although η is increased by reducing cell size, reproducibility is affected (see below).

The most significant avoidable heat loss is that along the thermistor stem. For

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[36] E. F. Fiock, D. C. Ginnings and W. B. Holton, *J. Res. Nat. Bur. Stand.* **6**, 881 (1931).

[37] B. V. Deryagin, P. S. Prokhorov and A. D. Malkina, *Zhur. Fiz. Khim.* **24**, 503 (1950).

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solid thermistors of the same outer radius as a normal thermistor an average decrease in η of about 3 % is expected. The heat loss along the thermistor stem varies approximately as r_t not r_t^2, assuming solid stem thermistors. Therefore increases in η of 5 %

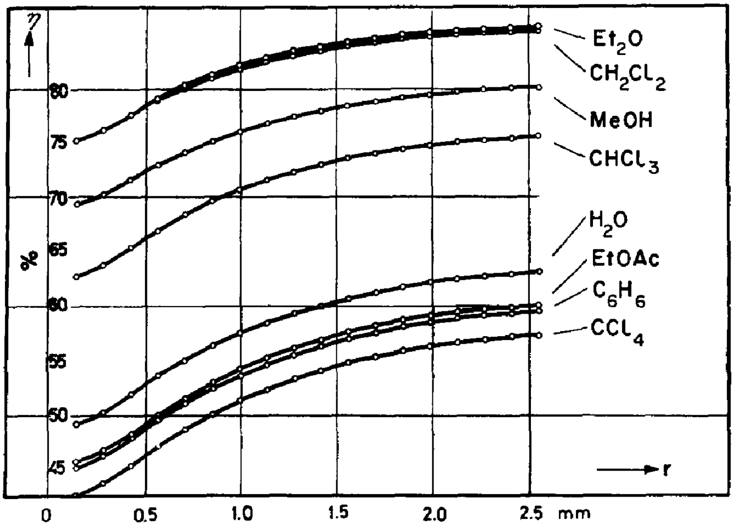

FIG. 1. Efficiency as a function of drop size (Echelon Model)

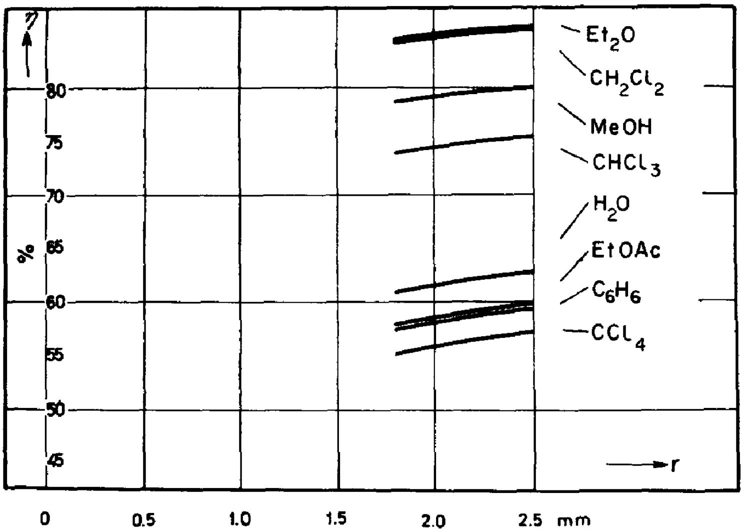

FIG. 2. Efficiency as a function of drop size (Cylinder Model)

only would result from reducing the thermistor radius to 0·05 cm, but such a thermistor would be very fragile. Heat losses through the vapour phase are only reduced by decreasing the thermal conductivity of the cell atmosphere e.g. by replacing air by another gas.

Utilizing the present thermistors (see Table 1) the cell dimensions can be altered little to increase η. In general, decreasing r_c and y leads to increased efficiency. In very small cells however small variations in drop size, reservoir level etc. will become increasingly significant and affect the reproducibility of d. A minimum value of y of 0·70 cm is suggested. Below this thermistor axis separation, S increases rapidly and is very sensitive to drop size variations. Cell radii below 0·7 cm are thus precluded and it is likely that d value reproducibility for radii below 1·0 cm is unsatisfactory. Heat losses along the thermistor stem for l_c values of less than approximately 2·0 cm may become more significant particularly if r_c is large.

Cells conforming to the above recommended dimensions should vary little in their efficiencies. Experience with six apparatuses of similar dimensions to that used in the present work agrees with the above results.

7. *Conclusions*

The accuracy of the predicted d and η values by the developed theory seems limited only by the reliability of the constants employed. However, rigorous tests of the theory by d value predictions on further solvents, with different cell inert gases, and on changing the temperature, are required. The latter effect is complex and will be considered in another place. Once the theory has been verified, the method will afford an accurate way of determining D_0 values, provided the necessary constants are known with sufficient precision.