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Received for review June 12, 1972. Accepted November 10, 1972. A NDEA Fellowship by the Office of Education and supplementary financial support by the National Science Foundation, Rice University, and the Monsanto Co. for G. F. Carruth are gratefully acknowledged.

Vapor Pressure and Sublimation Enthalpy of Anthraquinone and of 1,5- and 1,8-Dihydroxyanthraquinones

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The vapor pressure and the sublimation enthalpy of anthraquinone have been simultaneously determined by a microcalorimetric Knudsen effusion technique, utilizing a Calvet differential microcalorimeter:

$$\log p_{\text{torr}} = (11.94 \pm 0.08) - (5624 \pm 32)/T$$

$$\Delta H_{\text{sub}}°(T) = (30007 \pm 106) - (10.01 \pm 0.24)\text{T cal mol}^{-1}$$

The vapor pressure of the derivatives 1,5- and 1,8-dihydroxyanthraquinones has been determined, measuring the rates of mass loss in the Knudsen conditions, utilizing a SETARAM model B-60 Ugine Eyraud thermobalance:

1,5-dihydroxy anthraquinone: log p_{torr} =

$$(12.90 \pm 0.09) - (6435 \pm 38)/T$$

1,8-dihydroxy anthraquinone: log p_{torr} =

$$(13.14 \pm 0.06) - (6098 \pm 26)/T$$

The Gibbs energy functions of condensed anthraquinone have also been estimated.

Very few sets of vapor pressure and sublimation enthalpy data of anthraquinone and its 1,5- and 1,8-dihydroxy derivatives are reported in the literature. Hoyer and Peperle *(5)* determined the vapor pressure–temperature dependence for these substances by an effusion method, and Beynon and Nicholson *(2)* measured the sublimation enthalpy of these compounds by means of a radioactive ionization gage.

Previously, vapor pressure determinations for the anthraquinone were carried out by Inokuchi and Coll *(6)* and, in a range of higher pressures (>100 torr), by Nelson and Senseman *(13)*, utilizing the effusion and manometric methods, respectively. As for the sublimation enthalpy of the anthraquinone, only the value proposed by Magnus *(7)* and that recently determined by Beech and Lintonbon *(1)* with a scanning differential calorimeter are available.

The not very good agreement of the reported data led us to effect new determinations of the vapor pressure and sublimation enthalpy of these three compounds. Study of the anthraquinone was based on the differential calorimetry combined with the Knudsen effusion technique for simultaneous determinations of vapor pressures and sublimation enthalpies of the same sample *(8–10)*.

Due to the relative temperature ranges (too high for the employment of the apparatus used for anthraquinone), vapor pressures of the two derivatives, 1,5- and 1,8-dihydroxyanthraquinone, were determined by a thermobalance measuring the rate of mass loss in the Knudsen conditions.

Experimental and Results

Anthraquinone. The microcalorimetric measurements were made with a SETARAM Calvet differential microcalorimeter described elsewhere *(3, 11)*. The twin microcalorimeter elements were placed symmetrically in a Kanthal block, and the differential thermal flow was measured by two thermopiles in opposition, 396 Pt and Pt-Rh 10% thermocouples, connected with a galvanometer. The thermogram was a recording guided by the same galvanometer. The assembly and evaporation experiment were described in detail in previous works *(8–10)*.

The proportionality instrument constant (P/Δ) between the thermal power and galvanometer deflection was determined by Joule effect at each temperature of the experiment. Temperatures were measured by an iron constantan previously calibrated thermocouple placed in the center of the calorimetric block.

The simultaneous measurements of the sublimation enthalpy and vapor pressure of the same anthraquinone sample were carried out by the experimental procedure used in previous works *(8–10)*, measuring the area of the thermogram relative to the quantitative evaporation in the Knudsen conditions.

The relationships were secured by the well-known following expressions:

$$\Delta H_{\text{sub}}^{\circ}(T) = 1/4.184\ (M/m)(P/\Delta)(A/v) \qquad (1)$$

$$p_{(\text{torr})} = (2.256 \times 10^{-2} \times 760)/S(dm)/(dt)(T/M)^{1/2}\ (1/K) \qquad (2)$$

where

$\Delta H_{\text{sub}}^{\circ}$ (T) = sublimation enthalpy value at the abs temp T, cal mol^{-1}

p = vapor pressure, torr. (Throughout this paper torr = 1.333×10^{-3} bar.)

Table I. Sublimation Enthalpy and Vapor Pressure of Anthraquinone

T, K	$10^5\ (P/\Delta)$, W mm^{-1}	m, mg	A, mm^2	$\Delta H_{\text{sub}}^{\circ}\ (T)$, cal mol^{-1}	$10^6\ (dm/dt)$,[a] g sec^{-1}	p, torr
			Cell 1			
397	6.92	20.93	5292			
	6.95	22.45	5641	26075	1.780	5.90×10^{-3}
	6.95	19.17	4811			
403	6.98	35.55	8901			
	7.00	31.44	7832	26033	2.862	9.56×10^{-3}
	7.02	37.12	9202			
409	7.05	53.52	13163			
	7.04	47.28	11635	25869	4.409	1.48×10^{-2}
	7.06	49.65	12182			
415	7.18	75.92	18304			
	7.16	84.36	20371	25831	7.189	2.44×10^{-2}
	7.19	81.27	19566			
422	7.27	96.03	22820			
	7.27	89.17	21164	25767	11.430	3.91×10^{-2}
	7.26	94.44	22440			
426	7.35	141.45	33170			
	7.33	137.21	32297	25753	15.210	5.22×10^{-2}
	7.36	143.56	33673			
428	11.23	181.63	27853			
	11.25	176.15	26926	25701	18.800	6.48×10^{-2}
	11.21	183.30	28178			
431	11.27	249.99	38178			
	11.27	241.39	36829	25693	22.040	7.62×10^{-2}
	11.28	237.84	36324			
			Cell 2			
435	11.28	81.07	12332			
	11.30	75.19	11414	25625	11.530	1.18×10^{-1}
	11.32	83.00	12600			
443	11.35	176.93	26754			
	11.36	177.64	26796	25581	17.020	1.76×10^{-1}
	11.37	170.18	25608			
449	11.40	244.00	36594			
	11.39	237.24	35664	25543	23.780	2.47×10^{-1}
	11.42	231.65	34710			
452	11.43	273.56	40851			
	11.43	280.15	41754	25456	29.800	3.11×10^{-1}
	11.45	258.67	38524			
458	11.54	396.70	58560			
	11.52	388.42	57373	25432	41.320	4.34×10^{-1}
	11.57	391.20	57670			
464	11.59	518.41	76036			
	11.61	539.05	78912	25384	62.390	6.59×10^{-1}
	11.62	527.25	77212			
471	11.69	650.26	94300			
	11.70	633.42	91728	25313	94.240	1.00
	11.72	641.12	92843			

[a] For each temperature, the value of the rate of mass loss, dm/dt, is that calculated as mean of the three experimental values, practically coincident.

Cell 1, diameter of the effusion hole 1.0 mm, thickness of edges 0.1 mm, Clausing's correction factor 0.909.

Cell 2, diameter of the effusion hole 0.6 mm, thickness of edges 0.1 mm, Clausing's correction factor 0.857.

M = molar mass of the species
m = mass of the sample evaporated, grams
P/Δ = microcalorimeter constant, determined at each temperature, W mm^{-1}
A = area of the thermogram, mm^2
v = recording speed of the thermogram, equal to $^1/_{12}$ mm sec^{-1}
S = effusion hole area, cm^2
dm/dt = rate of mass loss, gr sec^{-1}
T = absolute temperature
K = Clausing's correction factor *(4)*

Samples of anthraquinone 99.5% pure (Fluka Co.) were vaporized from silver Knudsen cells with different effusion holes (Table I). To test the reproducibility of the obtained data, three quantitative vaporizations were carried out at each temperature and the corresponding mean values are reported and plotted in Table I and in Figure 1, respectively. The least-squares treatment of $\Delta H_{\text{sub}}(T)$ vs. T gives the equation:

$$\Delta H_{\text{sub}}°(T) = (30007 \pm 106) - (10.01 \pm 0.24)\, T \qquad (3)$$

The experimental average vapor pressure values of the anthraquinone are also reported in Table I. These values are plotted as function of $1/T$ in Figure 2 together with the representative slopes proposed by Hoyer *(5)* and Inokuchi *(6)*.

The relative equation obtained by least-squares treatment of our data is:

$$\log p_{\text{torr}} = (11.94 \pm 0.08) - (5624 \pm 32)/T \qquad (4)$$

The second-law value of the sublimation enthalpy of anthraquinone so obtained, $\Delta H_{\text{sub}}° = 25735 \pm 146$ cal mol^{-1}, is in good agreement with the calorimetric value at the mid-range temperature obtained by Equation 3, $\Delta H_{\text{sub}}°$ (434K) = 25663 ± 210 cal mol^{-1}. The associated errors are the standard deviations.

Even if our vapor pressure values reported in Figure 2 show a certain agreement with the tensimetric values proposed by Hoyer *(5)*, a critical comparison with previous works of the vapor pressure equation of the anthraquinone (Table II) shows a better agreement of our data with that of Inokuchi *(6)*. The examination of the sublimation enthalpy values at 298.15K (Table II) led us to propose an estimated average value of 27 ± 1 kcal mol^{-1}, taking into account the good agreement of the sublimation enthalpy values obtained in this work by two independent procedures.

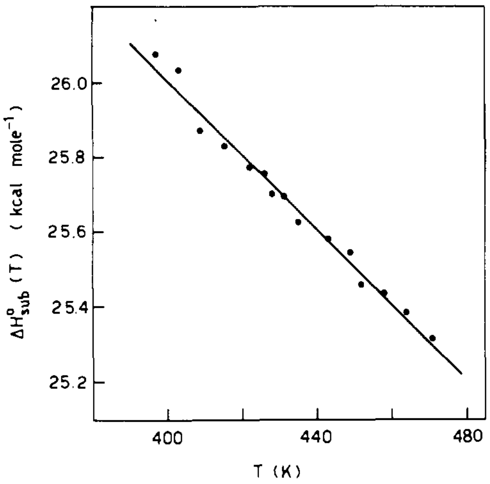

Figure 1. Sublimation enthalpy of anthraquinone

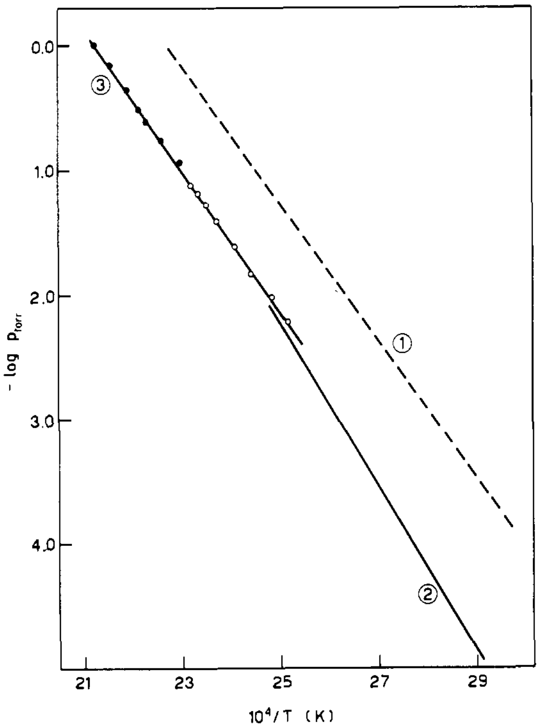

Figure 2. Vapor pressure of anthraquinone
1, Inokuchi *(6)*; 2, Hoyer *(5)*; 3, this work (○ cell 1, ● cell 2, see text)

Table II. Vapor Pressure and Sublimation Enthalpy of Anthraquinone

Author	Method	Temp or temp range, K	Vapor pressure equation, $\log p_{\text{torr}} = A\text{-}B/T$		Sublimation enthalpy, Kcal mol^{-1}	
			A	B	$\Delta H_{\text{sub}}°$ (T)	$\Delta H_{\text{sub}}°$ (298.15K)[a]
Inokuchi *(6)*	Effusion	376[b]	12.457	5475	25.0[c]	25.8
Hoyer *(5)*	Effusion	343 to 403	14.31	6604	29.4	30.2
Magnus *(7)*		298.15				26.8[d]
Beynon *(2)*	Radioactive ioniz. gage	430[b]			25.4	26.5 ± 0.2[d]
Beech *(1)*	Scanning calorimetry	470 to 590			30.35 ± 0.72	32.65 ± 0.72
This work	Effusion	397 to 471	11.94 ± 0.08	5624 ± 32	25.8 ± 0.2[c]	27.1 ± 0.2
	Calorimetric	434			25.7 ± 0.2	27.0 ± 0.2

[a] The values of $\Delta H(T)$ have been reported to 298.15K using the $(\Delta H°_T - H°_{298.15})$ values obtained from the Eq. 3 (see text). [b] The authors report the mean temperatures of their measurements. [c] Second-law value. [d] Value reported by the authors.

The third-law calculation of the $\Delta H_{sub}°$ (298.15K) has not been possible because no Gibbs energy function values of the condensed phase were available. An estimation of the Gibbs energy functions $(G_T° - H_{298.15}°)/T$ for the condensed anthraquinone has been made using the well-known third-law expression in the form:

$$[(G_T° - H_{298.15}°)/T]_{cond} = \Delta H_{sub}°(298.15K)/T + R \ln p_{atm} + [(G_T° - H_{298.15}°)/T]_{gas} \quad (5)$$

The experimental vapor pressures determined in this work, the proposed $\Delta H_{sub}°$ (298.15K) = 27 ± 1 kcal mol^{-1} and the Gibbs energy function values for the gaseous anthraquinone proposed by Nath Singh et al. *(12)* have been used in this calculation. The Gibbs energy function values determined at each experimental temperature are plotted in Figure 3 with those of the gaseous molecule.

1,5 and 1,8-Dihydroxyanthraquinones. The rate of mass loss in the Knudsen conditions of samples 98% pure of 1,5- and 1,8-dihydroxyanthraquinone has been measured by a null Ugine-Eyraud Model B.60 SETARAM microbalance. In this experiment, the reaction chamber, a silica glass tube 60 cm high and 17 mm in internal di-

Table III. Vapor Pressure of 1,5- and 1,8-Dihydroxyanthraquinone

1,5-Dihydroxyanthraquinone			1,8-Dihydroxyanthraquinone		
T, K	10^6 (*dm/dt*), g sec^{-1}	*p*, torr	*T*, K	10^6 (*dm/dt*), g sec^{-1}	*p*, torr
Cell 1			Cell 3		
410	0.559	1.75×10^{-3}	373	0.476	6.14×10^{-4}
411	0.539	1.69×10^{-3}	376	0.616	7.98×10^{-4}
418	1.075	3.41×10^{-3}	379	0.769	1.00×10^{-3}
422	1.344	4.28×10^{-3}	381	1.028	1.34×10^{-3}
423	1.536	4.90×10^{-3}	383	1.267	1.66×10^{-3}
429	2.475	7.95×10^{-3}	385	1.457	1.91×10^{-3}
432	3.264	1.05×10^{-2}	387	1.864	2.45×10^{-3}
434	3.456	1.12×10^{-2}	390	2.325	3.07×10^{-3}
438	5.376	1.74×10^{-2}	396	4.596	6.11×10^{-3}
439	4.762	1.55×10^{-2}	401	6.440	8.62×10^{-3}
445	9.257	3.03×10^{-2}	407	9.225	1.24×10^{-2}
449	8.966	2.95×10^{-2}			
451	13.229	4.36×10^{-2}	Cell 4		
456	18.205	6.03×10^{-2}	392	1.398	4.29×10^{-3}
461	23.976	7.98×10^{-2}	399	2.151	6.66×10^{-3}
466	35.860	1.20×10^{-1}	404	3.994	1.24×10^{-2}
472	49.171	1.66×10^{-1}	406	4.265	1.33×10^{-2}
			412	7.079	2.23×10^{-2}
Cell 2			416	10.680	3.34×10^{-2}
450	2.939	4.22×10^{-2}	418	10.600	3.36×10^{-2}
457	4.852	7.02×10^{-2}	422	16.360	5.21×10^{-2}
462	7.505	1.09×10^{-1}	427	22.350	7.16×10^{-2}
467	10.332	1.51×10^{-1}	432	33.333	1.07×10^{-1}
469	10.337	1.51×10^{-1}	437	47.930	1.55×10^{-1}
473	13.060	1.92×10^{-1}			
478	19.890	2.94×10^{-1}	Cell 5		
484	27.150	4.04×10^{-1}	429	6.204	8.69×10^{-2}
488	51.050	5.11×10^{-1}	435	8.755	1.24×10^{-1}
495	56.440	8.49×10^{-1}	441	14.047	1.99×10^{-1}
503	67.510	1.02	446	19.590	2.80×10^{-1}
			451	28.800	4.14×10^{-1}
			456	38.330	5.54×10^{-1}

Cells 1 and 4: Diameter of the effusion hole 1.0 mm, thickness edge 0.1 mm, Clausing's correction factor 0.909.

Cells 2 and 5: Diameter of the effusion hole 0.5 mm, thickness edge 0.1 mm, Clausing's correction factor 0.833.

Cell 3: Diameter of the effusion hole 1.5 mm, thickness edge 0.1 mm, Clausing's correction factor 0.9375.

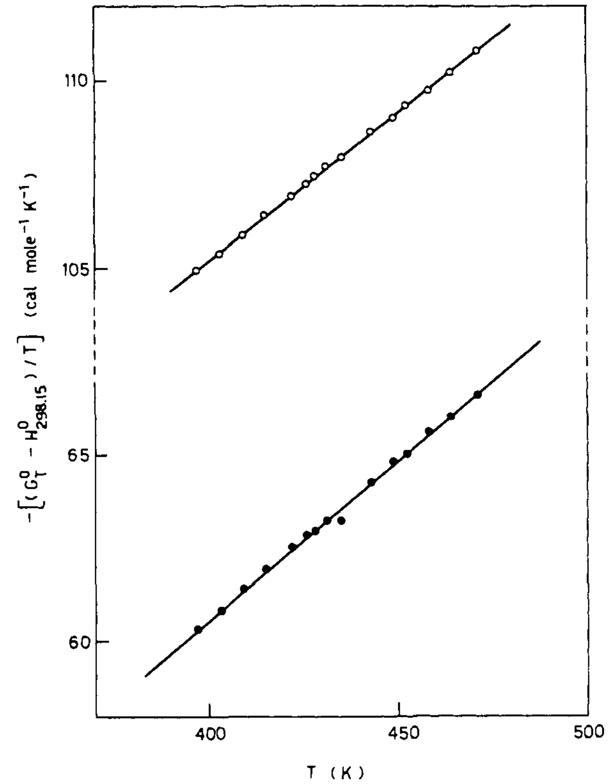

Figure 3. Gibbs energy function values of solid anthraquinone (●) estimated in this work and of gaseous anthraquinone (O) taken from Nath Singh *(12)*

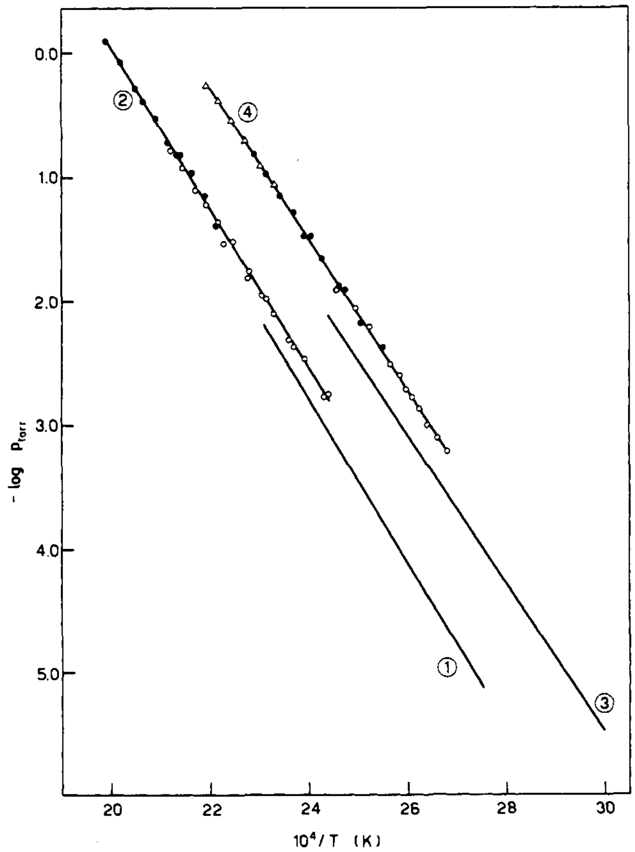

Figure 4. Vapor pressure of 1,5-dihydroxyanthraquinone (1,5-DA) and of 1,8-dihydroxyanthraquinone (1,8-DA)

1,5-DA: 1, Hoyer *(5)*; 2, this work (O cell 1, ● cell 2, see text). 1,8-DA: 3, Hoyer *(5)*; 4, this work (O cell 3, ● cell 4, △ cell 5, see text)

Table IV. Vapor Pressure and Sublimation Enthalpy of 1,5-Dihydroxyanthraquinone (1,5-DA) and 1,8-Dihydroxyanthraquinone (1,8-DA)

Compound	Author	Method	Mean temp	Vapor pressure equation, $\lg p_{\text{torr}} = A - B/T$		Sublimation enthalpy, Kcal mol^{-1}	
				A	B	$\Delta H_{\text{sub}}°$ (T)	$\Delta H_{\text{sub}}°$ (298.15K)
1,5-DA	Hoyer *(5)*	Effusion	398	13.10	6619	29.5	30.3[a]
	Beynon *(2)*	Radioactive ioniz. gage	456	–	–	26.6 ± 1.1	28.2 ± 1.1
	This work	Effusion	457	12.90 ± 0.09	6435 ± 38	29.5 ± 0.2	31.2 ± 0.2[a]
1,8-DA	Hoyer *(5)*	Effusion	368	13.82	6422	28.6	29.1[a]
	Beynon *(2)*	Radioactive ioniz. gage	404	–	–	25.3 ± 0.2	26.2 ± 0.2
	This work	Effusion	415	13.14 ± 0.06	6098 ± 26	27.9 ± 0.1	29.0 ± 0.1[a]

[a] The $\Delta H_{\text{sub}}°$ (T) have been reduced to 298.15K using the heat content estimated by Beynon *(2)*.

ameter, was heated along its whole length by a cylindrical coaxial graphite resistance. Silver Knudsen cells with different effusion holes (Table III) containing the samples were suspended from the balance beam and placed in the center of the isothermal zone of the reaction chamber (about 15 cm long), determined in a previous experiment.

The mass losses of the samples were recorded at temperatures maintained constant within ±1°C by means of an efficient thermoregulation device. The temperature of the effusion cell was measured with a previously calibrated iron constantan thermocouple inserted in an identical cell placed immediately beneath the one and recorded simultaneously to the sample mass loss. A differential pumping system for the reaction chamber, balance housing, and furnace allowed the achievement of an operative vacuum better than 1×10^{-5}torr.

The vapor pressure of 1,5- and 1,8-dihydroxyanthraquinones have been determined by Equation 2. The 1,5-dihydroxyanthraquinone (1,5-DA) has been investigated in the temperature range 410–503K. The relative vapor pressure data are reported in Table III and plotted in Figure 4. A least-squares treatment of the data gives a pressure-temperature relationship as

$$\log p_{\text{torr}} = (12.90 \pm 0.09) - (6435 \pm 38)/T \qquad (6)$$

The resulting second-law value of the sublimation enthalpy of 1,5-DA is $\Delta H_{\text{sub}}°$ (475K) = 29.5 ± 0.2 kcal mol^{-1}.

The vapor pressure of 1,8-dihydroxyanthraquinone (1,8-DA) has been measured in the temperature range 373–456K, and the relative values are reported in Table III and plotted in Figure 4. The relative least-square pressure-temperature relationship is:

$$\log p_{\text{torr}} = (13.14 \pm 0.06) - (6098 \pm 26)/T \qquad (7)$$

and the resulting second-law value for the sublimation enthalpy is $\Delta H_{\text{sub}}°$ (415K) = 27.9 ± 0.1 kcal mol^{-1}. For both substances the errors associated with the $\Delta H_{\text{sub}}°$ values are the standard deviations.

A comparison with the results reported in the literature is given in Table IV and Figure 4. There is good agreement between the values of vapor pressure and sublimation enthalpy determined in this work for 1,5-DA and 1,8-DA with those reported by Hoyer *(5)*. Therefore respective values of 30.5 ± 1.0 and 29.0 ± 0.5 kcal mol^{-1} for the sublimation enthalpy of 1,5-DA and 1,8-DA are proposed.

Acknowledgment

We express our gratitude to Giovanni De Maria for helpful discussions and to C. N. R. Centro di Termodinamica Chimica alle Alte Temperature for the support of this work.

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Received for review September 19, 1972. Accepted January 19, 1973. Work supported by C. N. R. Centro di Termodinamica Chimica alle Alte Temperature.