

# Estimation of Molar Heat Capacities in Solution from Gas Chromatographic Data

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## Abstract

The temperature dependence of retention data (retention or capacity factors) is measured for 35 aliphatic ketones and aldehydes as model compounds on a dimethylpolysiloxane stationary phase. A novel model is derived to determine the heat of solution and the solution molar heat capacities from the fits of the log natural of the difference of the retention factor and the column temperature (T) versus  $1/T$  and the temperature arrangement. The convex curvature present in the residual plots of a former defined equation of ours disappears when applying a newly defined model. A detailed statistical analysis clearly shows the superiority of the refined model to the earlier one in a broader temperature range. The validation of this model is made through a comparison of heat capacity values taken from literature determined by different methods. The molar heat capacity of a pure liquid oxo compound is similar to that of when the same compound is solvated in a stationary phase.

## Introduction

The temperature dependence of retention data has attracted large interest in the past couple of decades (1–5), and the most discussed question has been the temperature dependence of the retention index (1). Finally, the scientific community agreed that the dependence of retention indices on column temperature could be correctly described by an Antoine-type hyperbolic curve (1,2). However, it should be emphasized that the Antoine equation can process a wide linear range on apolar phases. Retention indices of nonpolar substances on nonpolar stationary phases show an almost complete linear dependence on the isotherm column temperature (1). The linear approximation can provide excellent results within this range without using the Antoine equation (2).

Pacáková and Feltl have attributed thermodynamic significance to the equation constants of the Antoine equation (3). They neglected the changes of standard molar enthalpy and entropy of sorption to temperature. However, some problems

have arisen when using Kováts indices to determine thermodynamic quantities (i.e., the distribution function of Kováts indices is not normal) (4). Perhaps, this has been the reason why new methods have been elaborated to determine the specific retention volume ( $V_g$ ) using other chromatographic parameters (5,6).

The slopes of the logarithm of  $V_g$  or the corrected retention time versus the lines of the inverse column temperature ( $1/T$ ) contain the molar heat of vaporization in gas–liquid chromatography (molar heat of adsorption in gas solid chromatography) (7–10). The excess enthalpy ( $\Delta H^E$ , the change of enthalpy during the transfer of 1 mol of pure liquid solute into 1 mol of infinitely diluted solution) is a quantity of essential importance in the characterization of solute–stationary phase interactions. It can be determined either from the enthalpy of vaporization ( $\Delta_{\text{vap}}H$ ), the temperature dependence of the activity coefficient ( $\gamma$ ) (11–14), or calorimetrically (9). The enthalpy of vaporization can be calculated using the following equation:

$$\Delta H^E = -\Delta_{\text{vap}}H + \Delta_{\text{sol}}H \quad \text{Eq. 1}$$

where  $\Delta_{\text{sol}}H$  is the change of enthalpy during the dissolution of 1 mol of the solute from the gas phase into the liquid stationary phase.

The disadvantage of the enthalpy of vaporization method defined in equation 1 is that the values of  $\Delta_{\text{sol}}H$  and  $\Delta_{\text{vap}}H$  are of a similar order of magnitude, hence very accurate  $\Delta_{\text{vap}}H$  measurements are needed. This can be achieved in some cases (15). The excess enthalpy changes with temperature similar to other enthalpy terms. This effect was characterized by an additive term ( $C_p^E \times \ln T$ ) in an equation describing the temperature dependence of  $\gamma$  (13,14). The excess heat capacity ( $\Delta C_p^E$ ) was observed to depend on the type of stationary phase used when analyzing hydrocarbons.

Castells et al. (16) have tested the equation of Clarke and Glew (17) under gas chromatographic (GC) conditions. This method describes the temperature dependence of the equilibrium constant in a larger temperature range and improves the accuracy of the thermodynamic quantities determined. A correction was used in the determination of the thermodynamic properties of the solutions of hydrocarbons—the general Gibbs free energy ( $\Delta G$ ), the change in enthalpy ( $\Delta H$ ), and the molar heat capacity

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difference of the solute in the solvated and gas state at a constant pressure ( $\Delta C_p$ )—in the polar and apolar stationary phases for packed columns using the temperature dependence of specific retention volumes by a three-parameter equation (16). The regression of this equation resulted in a small error in the determination of the thermodynamic quantities.

Nevertheless, the measurement of  $V_g$  is relatively easy for packed columns only. There are some difficulties connected to the determination of  $V_g$  for capillary columns such as the mass of the stationary phase being uncertain (the film thickness is not uniform) and the measurement of the carrier flow rate at low speed being similarly dubious (18).

Because of the extended usage of capillary columns with relatively inert walls, the solution phenomenon of the new bonded phases became the target of investigations. Instead of  $V_g$ , the retention factor ( $k$ ) was more suitable to determine the thermodynamic parameters using its temperature dependence. Recently, we have suggested using  $\ln k/T$  versus  $1/T$  lines to obtain the molar heat of solutions from the slope (19) in a temperature range of 323 to 383 K. This method provides precise

results for *n*-alkanes and oxo compounds. Although the points are very well described by a line (correlation coefficients are in the range of 0.9987 to 0.99996), a characteristic convex curve can be seen in the residuals even in this narrow temperature range. This fact suggests that this model is not completely adequate. We have failed to notice earlier the convex curve in the fit of  $\ln k$  (or  $\ln V_g$ ) versus  $1/T$ . Therefore, our aim was to elaborate a new adequate equation having thermodynamic significance to increase the precision of the descriptive equations for retention factors and the thermodynamic quantities determined.

Ketones and aldehydes were selected as model compounds. As it will be shown, the theory and derived equations are general; they are not limited solely to oxo compounds. Studies testing the equations using other compounds are currently under way and will be reported in due course.

## Experimental

Formerly, we have deduced an equation for the determination

**Table I. Temperature Dependence of Retention Factors for Oxo Compounds on a Dimethylpolysiloxane Stationary Phase**

Temperature (°C)	20	30	40	50	60	70	90	110
Acetone	1.000	0.720	0.530	0.399	0.313	0.253	0.168	0.117
Buta-2-one	2.986	2.024	1.398	1.012	0.751	0.574	0.367	0.239
Pentan-2-one		4.894	3.225	2.221	1.635	1.168	0.694	0.432
Pentan-3-one		5.385		2.424		1.256	0.742	0.449
3-Methyl butan-2-one		3.870		1.853		1.002	0.588	0.374
Hexan-2-one		13.074	8.352	5.457	3.702	2.607	1.384	0.800
Hexan-3-one		12.858		5.538		2.597	1.369	0.788
4-Methyl pentan-2-one		8.302		3.676		1.834	1.013	0.609
2,2-Dimethyl butan-3-one		6.312		2.880		1.500	0.846	0.520
3-Methyl pentan-2-one		9.435		4.102		2.043	1.119	0.662
Heptan-2-one				13.302		5.664	2.746	1.468
Heptan-3-one				12.696		5.443	2.673	1.446
Heptan-4-one				11.777		5.062	2.497	1.342
5-Methyl hexan-2-one				10.239		4.467	2.310	1.235
2,4-Dimethyl pentan-3-one		14.339		5.903		2.838	1.510	0.871
5-Methyl heptan-3-one				21.073		8.566	3.992	2.087
2-Methyl heptan-3-one				20.451		8.329	3.885	2.032
Octan-3-one				31.767		12.095	5.271	2.656
Nonan-5-one				65.868		23.227	9.465	4.485
Acetaldehyde	0.3057	0.2351	0.1900	0.1569	0.1305	0.1095	0.0850	0.0643
Propanal	1.0290	0.7145	0.5453	0.4243	0.3226	0.2616	0.1817	0.1332
Acrolein				0.3850		0.2453	0.1690	0.1228
Isobutanal	2.0440	1.4670		0.7620		0.4464	0.2883	0.1966
Butanal	2.8285	1.9767		0.9948		0.5706	0.3568	0.2412
Isovaleraldehyde		3.6256		1.7067		0.9314	0.5722	0.3657
2-Methyl butanal		4.0328		1.9332		1.0125	0.5981	0.3903
<i>trans</i> -Butenal				1.5756		0.8546	0.5149	0.3344
Valeraldehyde		5.3685		2.4776		1.2530	0.7430	0.4622
Trimethyl acetaldehyde		2.1900		1.0975		0.6206	0.3875	0.2595
Hexanal		14.3427		5.9028		2.8680	1.5085	0.8400
2-Ethyl butanal		10.2220		4.4070		2.1855	1.1965	0.7049
3,3-Dimethyl butanal		6.0585		2.8223		1.4583	0.8422	0.5180
Heptanal				14.2743		6.1535	2.9770	1.5783
Octanal				34.3043		13.1530	5.8630	2.9335
2-Ethyl hexanal				23.3983		9.4250	4.3754	2.2685

of the enthalpy of solutions from GC data (model 1) (19):

$$\ln\left(\frac{k}{T}\right) = -\frac{\mathcal{Q}_{\text{sol}}H^\circ}{RT} + \frac{\mathcal{Q}_{\text{sol}}S^\circ}{R} + C' \quad \text{Eq. 2}$$

where  $\mathcal{Q}_{\text{sol}}H^\circ$  is the standard enthalpy of the solution,  $R$  is the universal gas constant, and  $\mathcal{Q}_{\text{sol}}S^\circ$  is the standard entropy of the solution.

The parameters of equation 2 have been determined from the linear least-squares fit of  $\ln(k/T) = -A/T + C$  with a slope of  $\Delta_{\text{sol}}H/R$ . The equation is valid only for a limited range of temperature in which  $\Delta_{\text{sol}}H^\circ$  and  $\Delta_{\text{sol}}S^\circ$  are considered to be independent from the temperature. The effect of heat capacity on the enthalpy and entropy terms cannot be neglected in order to obtain more exact data in an extended temperature range (60°C–80°C).

The Kirchoff law and the third law of thermodynamics describes the effect of temperature on enthalpy and entropy:

$$\Delta_{\text{sol}}H_T^\circ = \Delta_{\text{sol}}H_{T_0}^\circ + \int_{T_0}^T \Delta C_p dT \quad \text{Eq. 3}$$

$$\Delta_{\text{sol}}S_T^\circ = \Delta_{\text{sol}}S_{T_0}^\circ + \int_{T_0}^T \Delta C_p d \ln T \quad \text{Eq. 4}$$

where  $\mathcal{Q}_{\text{sol}}H^\circ_{T_0}$  and  $\mathcal{Q}_{\text{sol}}S^\circ_{T_0}$  are the standard enthalpy and entropy differences at a reference temperature ( $T_0$ ) measured in Kelvin (possibly at 298 K), respectively, and  $\Delta C_p$  is the molar heat capacity difference of the solute in the solvated state,  $C_p(\text{sol})$ , and the gas phase,  $C_p(\text{g})$ :

$$\Delta C_p = C_p(\text{sol}) - C_p(\text{g}) \quad \text{Eq. 5}$$

The heat capacity is also temperature dependent in a broader

**Table II. Comparison of Two- and Three-Parameter Fits for Ketones (Models 1 and 2)**

Solute (ketone)	Model	R	F	s	Cor C <sup>11</sup>	A	B
Acetone	1	0.99958040	7145	0.02548	-15.95	3000	
	2	0.99993908	20518	0.01063	-56.57	3213	5.962
Butan-2-one	1	0.99933063	4477	0.03726	-16.48	3474	
	2	0.99993815	20209	0.01241	-77.71	3794	8.985
Pentan-2-one	1	0.99955193	5576	0.03061	-16.86	3847	
	2	0.99991952	12424	0.01451	-76.74	4214	8.766
Pentan-3-one	1	0.99960051	3753	0.03493	-17.02	3928	
	2	0.99991953	6213	0.01920	-74.67	4280	8.439
3-Methyl butan-2-one	1	0.99980381	7643	0.02326	-16.70	3733	
	2	0.99999758	206400	0.00317	-59.40	3994	6.250
Hexan-2-one	1	0.99980822	13032	0.02290	-17.68	4398	
	2	0.99999573	234300	0.00382	-66.57	4698	7.157
Hexan-3-one	1	0.99992199	19227	0.01731	-17.71	4407	
	2	0.99998100	26317	0.01046	-45.52	4577	4.071
4-Methyl pentane-2-one	1	0.99982913	8777	0.02405	-17.26	4136	
	2	0.99999981	2668000	0.00098	-61.67	4407	6.500
2,2-Dimethyl butan-3-one	1	0.99983650	9172	0.02254	-16.97	3964	
	2	0.99999441	89482	0.00510	-57.89	4214	5.991
3-Methyl pentane-2-one	1	0.99984627	9755	0.02313	-17.33	4194	
	2	0.99999558	113200	0.00480	-59.43	4451	6.163
Heptan-2-one	1	0.99987882	8250	0.01950	-18.37	4900	
	2	0.99999904	259900	0.00246	-76.94	5354	8.535
Heptan-3-one	1	0.99983746	6151	0.02228	-18.21	4834	
	2	0.99999753	101100	0.00389	-84.89	5350	9.716
Heptan-4-one	1	0.99987292	7868	0.01968	-18.27	4830	
	2	0.99999198	31181	0.00699	-75.73	5275	8.372
5-Methyl hexan-2-one	1	0.99980729	5188	0.02355	-17.99	4694	
	2	0.99987899	2066	0.02640	-61.33	5029	6.314
2,4-Dimethyl pentane-3-one	1	0.99977781	6749	0.02918	-17.60	4400	
	2	0.99999010	50504	0.00754	-70.28	4722	7.711
5-Methyl heptan-3-one	1	0.99981927	5532	0.02491	-18.61	5127	
	2	0.99999998	10480000	0.00040	-93.76	5709	10.95
2-Methyl heptan-3-one	1	0.99982495	5711	0.02449	-18.62	5120	
	2	0.99999996	6808000	0.00050	-92.47	5692	10.76
Octan-3-one	1	0.99976043	4173	0.03068	-19.31	5484	
	2	0.99999153	29525	0.00816	-110.21	6188	13.25
Nonan-5-one	1	0.99979544	4887	0.03054	-19.89	5907	
	2	0.99999370	39688	0.00758	-110.58	6609	13.21

temperature range ( $C_p = A + BT + CT^2 + \dots$ ). However, it is not always possible to obtain reliable retention data over a temperature range of 100°C in GC. The introduction of new parameters (a, b, and c) would make the evaluation rather uncertain. Hence, we neglected the temperature dependence of the  $C_p$  of the solute in the gas and solvated states. After the integration of  $\Delta_{\text{sol}}H^\circ$  and  $\Delta_{\text{sol}}S^\circ$  (equations 3 and 4) and their substitution into equation 2, we obtain:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta_{\text{sol}}H^\circ_{T_0}}{RT} + \frac{\Delta_{\text{sol}}S^\circ_{T_0}}{R} + \frac{\Delta C_p}{R} \frac{(T_0 - T)}{T} + \frac{\Delta C_p}{R} (\ln T - \ln T_0) + C' \quad \text{Eq. 6}$$

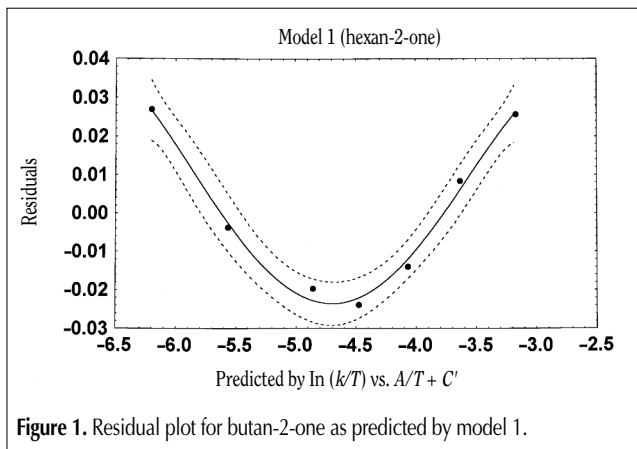


Figure 1. Residual plot for butan-2-one as predicted by model 1.

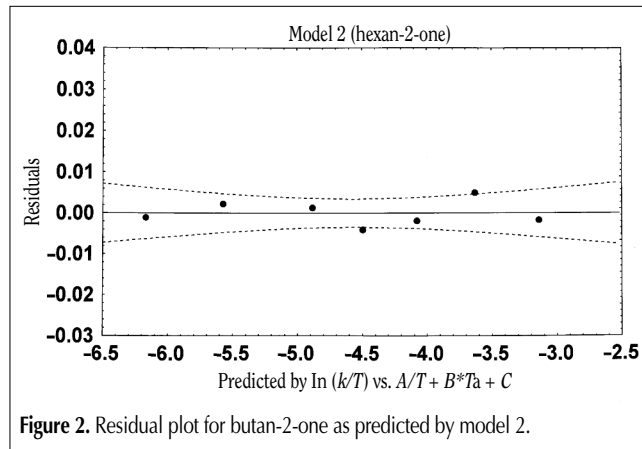


Figure 2. Residual plot for butan-2-one as predicted by model 2.

Table III. Comparison of Two- and Three-Parameter Fits for Aldehydes (Models 1 and 2)

Solute (ketone)	Model	R	F	s	C or C''	A	B
Acetaldehyde	1	0.99928627	4199	0.02496	-14.59	2253	
	2	0.99977372	5522	0.01539	-50.15	2439	5.220
Propanal	1	0.99873439	2366	0.04241	-15.52	2874	
	2	0.99984723	8181	0.01614	-84.09	3233	10.064
Acrolein	1	0.99979718	4929	0.01394	-15.13	2709	
	2	0.99999594	61585	0.00279	-56.76	3031	6.067
Isobutanal	1	0.99963777	5518	0.03077	-16.16	3278	
	2	0.99994724	14213	0.01356	-61.42	3511	6.643
Butanal	1	0.99959756	4967	0.03392	-16.36	3428	
	2	0.99997088	25759	0.01054	-68.36	3697	7.632
Isovaleraldehyde	1	0.99938751	2447	0.04025	-16.52	3655	
	2	0.99993783	8041	0.01571	-86.99	4085	10.320
2-Methyl butanal	1	0.99950925	3054	0.03695	-16.71	3749	
	2	0.99996182	13094	0.01262	-82.26	4149	9.595
<i>trans</i> -Butenal	1	0.99975092	4013	0.02025	-16.32	3550	
	2	0.99999745	97966	0.00290	-77.10	4021	8.856
Valeraldehyde	1	0.99952131	3131	0.03800	-16.94	3904	
	2	0.99994651	9346	0.01556	-83.09	4307	9.683
Trimethyl acetaldehyde	1	0.99949645	2977	0.03431	-16.30	3436	
	2	0.99999742	193400	0.00301	-79.51	3822	9.253
Hexanal	1	0.99990032	15046	0.01972	-17.72	4440	
	2	0.99995041	10082	0.01703	-43.54	4598	3.779
2-Ethyl butanal	1	0.99982504	8571	0.02481	-17.33	4217	
	2	0.99999274	68878	0.00619	-62.20	4491	6.568
3,3-Dimethyl butanal	1	0.99983609	9149	0.02227	-16.83	3911	
	2	0.99999405	84058	0.00520	-57.23	4158	5.913
Heptanal	1	0.99995309	21317	0.01212	-18.28	4896	
	2	0.99999979	1218000	0.00113	-54.76	5179	5.315
Octanal	1	0.99982022	5561	0.02630	-19.06	5427	
	2	0.99999932	369300	0.00228	-98.25	6041	11.54
2-Ethyl hexanal	1	0.99982442	5694	0.02476	-18.64	5169	
	2	0.99999956	569000	0.00175	-93.22	5746	10.87

Rearranging the equation and separating the temperature-independent terms ( $C''$ ), we obtain:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta_{\text{sol}}H_{T_0}^{\circ}}{RT} + \frac{\Delta C_p}{R}\left[\frac{T_0}{T} + \ln T\right] + C'' \quad \text{Eq. 7}$$

Another equation (model 2) can be formulated by the introduction of a new variable called temperature arrangement ( $T_a$ ):

$$\ln\left(\frac{k}{T}\right) = A\frac{1}{T}BT_a + C'' \quad \text{Eq. 8}$$

where:

$$A = -\frac{\Delta_{\text{sol}}H_{T_0}^{\circ}}{R} \quad \text{Eq. 9}$$

$$B = \frac{\Delta C_p}{R} \quad \text{Eq. 10}$$

$$C'' = C' + \frac{\Delta_{\text{sol}}S_{T_0}^{\circ}}{R} - \frac{\Delta C_p}{R} - \frac{\Delta C_p}{R} \ln T_0 \quad \text{Eq. 11}$$

$$T_a = \frac{T_0}{T} + \ln T \quad \text{Eq. 12}$$

Then, it is possible to search the solution as a two-variable ( $1/T$  and  $T_a$ ) three-parameter fit (Figure 2).

Aliphatic ketones and aldehydes were chosen as model compounds. They were purchased from Fluka AG and Aldrich and were used without further purification. The length of the column was 50 m, the inner diameter 0.32 mm, and the film thickness 1.05  $\mu\text{m}$ . The stationary phase was dimethylpolysiloxane (HP-1) (Hewlett-Packard, Palo Alto, CA). The measurements were performed with a 5890 HP Series II GC with an HP 3365 ChemStation. Further details of analysis have been given in an earlier work (19).

The  $k$  values were measured at temperatures of 50°C, 70°C, 90°C, and 110°C, making at least three injections at each temperature. In some cases, the measurements were also done at 20°C, 30°C, 40°C, and 60°C.

Table I lists the averages of multiple determinations of the  $k$  values measured with HP-1 as the stationary phase.

## Results and Discussion

In order to compare the two models—which are based either on temperature independent  $\Delta_{\text{sol}}H^{\circ}$  and  $\Delta_{\text{sol}}S^{\circ}$  (model 1) or the consideration of their temperature dependence (model 2)—we

**Table IV. Estimation of the Standard Enthalpy of Solution and the Solution Molar Heat Capacities for Ketones on the Dimethylpolysiloxane Stationary Phase at 298 K**

Solute	$\Delta_{\text{sol}}H_{T_0}^{\circ}$	$\Delta C_p$	$C_p(\text{g})$	$C_p(\text{g})$ (Benson)*	$C_p(\text{g})$ (Yoneda)†	$C_p(\text{l})$	$C_p(\text{sol})$	$C_p(\text{sol})^*$	$C_p(\text{sol})^\ddagger$
Acetone	26.71	49.6	74.70 <sup>‡</sup>	74.7	53.7	123.8**	124.3	124.3	103.3
Butan-2-one	31.54	74.7	102.7 <sup>‡</sup>	102.5	98.8	159.2 <sup>††</sup>	177.4	177.2	173.5
Pentan-2-one	35.03	72.9	120.9 <sup>‡</sup>	122	121.7	185.5 <sup>††</sup>	193.8	194.9	194.6
Pentan-3-one	35.58	70.2		115.4	121.7	190.1 <sup>††</sup>		185.6	191.9
Butan-2-one-3-me	33.20	52.0		112	128.5	180.0 <sup>§§</sup>		164.0	180.5
Hexan-2-one	39.06	59.5		144.8	144.8	214.8 <sup>††</sup>		204.3	204.3
Hexan-3-one	38.05	33.8		146.9	144.7	216.9 <sup>***</sup>		180.7	178.5
Pentane-2-one-4-methyl	36.64	54.0	138.2 <sup>§</sup>	144.7	144.8	211.9 <sup>†††</sup>	192.2	198.7	198.8
Butane-2-one-3,3-dimethyl	35.03	49.8	154.8 <sup>§</sup>	135.1	128.5	206.9 <sup>***</sup>	204.6	184.9	178.3
Pentane-2-one-3-methyl	37.00	51.2	149.4 <sup>§</sup>	122	121.7		200.6	173.2	172.9
Heptan-2-one	44.51	71.0		167.5	167.6	243.6 <sup>††</sup>		238.5	238.6
Heptan-3-one	44.48	80.8		169.6	167.6			250.4	248.4
Heptan-4-one	43.85	69.6		169.6	169.6	246.3 <sup>††</sup>		239.2	239.2
Hexan-2-one-5-methyl	41.81	52.5		167.7	167.7			220.2	220.2
Pentane-3-one-2,4-dimethyl	39.25	64.1		149.6	171.9	235.4 <sup>***</sup>		213.7	236.0
Heptane-3-one-5-methyl	47.46	91.0		192.3	190.7			283.3	281.7
Heptane-3-one-2-methyl	47.32	89.5		182.3	197.3			271.8	286.8
Octan-3-one	51.44	110.2		192.4	190.6			302.6	300.8
Nonane-3-one	54.95	109.8		215.1	213.5			324.9	323.3

\* Calculated according to Benson's additivity rule by the THERGAS computer code (31,32).

† Calculated according to Yoneda's successive substitution method by the THERGAS computer code (32).

‡ Obtained from reference 23.

§ Obtained from reference 24.

\*\* Obtained from reference 25.

†† Obtained from reference 26.

††† Obtained from reference 27.

§§ Obtained from reference 28.

\*\*\* Obtained from reference 29.

†††† Obtained from reference 30.

have made two linear fits (a two- and three-parameter fit according to equations 2 and 8, respectively). The results are shown in Tables II and III.

As it can be seen from the tables, model 2 (equation 8) is superior to model 1 (equation 2) in all cases. The following statistical properties were used to characterize the goodness of description: the multiple correction coefficient (R), the overall Fisher statistics (F), and the residual error (s). Their definitions can be found in standard books of regression (20). The definition of F is of relevance in this study:

$$F = \frac{\sum (\hat{y} - \bar{y})^2 / (p - 1)}{\sum_{i=1}^n (y - \hat{y})^2 / (n - p)} \quad \text{Eq. 13}$$

where  $y$  is the measured value (here the retention factor),  $\hat{y}$  is the predicted value,  $\bar{y}$  is the average value,  $p$  is the number of parameters in the model or models, and  $n$  is the number of measured points (in this case, different isotherm temperatures). In other words, the null hypothesis was tested by the following procedure: parameters  $A$  or  $A$  and  $B$  in the models (excluding  $C$  and  $C''$ ) were zero against the alternative hypothesis and at least one of the parameters  $A$  or  $A$  and  $B$  (excluding  $C$  and  $C''$ ) was not zero. We compared the calculated F value using equation 13 with a critical F value from the table of the Fisher distribution at  $p - 1$  and  $n - p$  degrees of freedom. If the calculated F value surpassed the critical one, the null hypothesis had to be rejected. The parameters in the models were significant in such cases.

The larger the F and R values, the better was the description. However, small residual errors indicated good fits. When analyzing the data of tables, it can be concluded that large correlation coefficients, large values of F, and small  $s$  values indicate the goodness of fits and adequacy of model 2. It should be emphasized that these findings do not invalidate earlier results. It is possible to reliably estimate solution heat values from model 1 (equation 2). Model 2, however, is more exact and makes it possible to determine molar heat capacity differences and  $\Delta_{\text{sol}}H^\circ$  at 298 K.

In order to illustrate the difference in precision for the two models, butan-2-one was chosen as a test compound. It can be seen that the residuals (i.e., the difference between the measured and predicted  $k$  values for butan-2-one) versus the predicted values by model 1 shows a characteristic convex curve. This convex curve is clearly observable despite some dispersion (Figure 1).

However, Figure 2 (the plot of residuals against predicted values by model 2) suggests a smaller range of residuals and no curvature at all. Similar figures can be obtained for all oxo compounds, which suggests the superiority of model 2.

In some cases (such as 5-methyl hexan-2-one and heptan-4-one), the inclusion of the temperature arrangement in the model is not significant even at a 10% significance level. This is most probably because of the small degree of freedom (i.e., four temperature points only). Nevertheless, model 2 with its two variables ( $1/T$  and  $T_a$ ) is highly significant in these cases and provides a reliable description of the temperature dependence.

The difference in the intercepts ( $C'$  and  $C''$ ) of the two fits can be explained by the new constants included into  $C''$ . Parameter  $A$

and hence  $\Delta_{\text{sol}}H^\circ_{T_0}$  in model 2 differ only slightly from those published earlier (19), because now the temperature range is larger (the average temperature is lower) for compounds with higher volatility.

The  $\Delta_{\text{sol}}H^\circ$  is determined mainly by equation 1 in which the excess enthalpy is not higher than 10% for  $\Delta_{\text{vap}}H^\circ$  in the same stationary phase (19). The standard enthalpy of vaporization increases with the decreasing temperature according to equation 3, because  $C_p(g) - C_p(l)$  is negative and approximately  $-50$  kJ/mol (21). The value of parameter  $A$  in model 2 is approximately 2–5 kJ/mol higher than that of  $A$  in model 1, which is in agreement with the former arguments.

The molar heat capacity difference  $C_p(\text{sol}) - C_p(g)$  is an exclusive parameter of model 2. The estimated values are given in Table IV for ketones and Table V for aldehydes.

No direct method is available for the estimation of the  $\Delta C_p$  value. The reality of  $\Delta_{\text{sol}}H^\circ$  can be controlled by the derived quantity of  $\Delta H^{E,0}$  or  $\Delta_{\text{vap}}H^\circ$  (19). We could not find any calorimetric experiments on the determination of  $\Delta H^{E,0}$  or  $\Delta C_p$  in GC stationary phases. Nevertheless, the  $\Delta C_p$  values that were determined resemble those of hydrocarbons in phthalate stationary phases (14).

The  $C_p(g)$  values are available from the literature or can be estimated theoretically by the group additivity method, and  $C_p(\text{sol})$  can be calculated from equation 5 (Tables IV and V). There are several additivity schemes that can be used to estimate thermodynamic characteristics. They differ in how the molecules are cut into small pieces and how the increments take into account the neighboring atoms or molecule parts. The best known and used method is without any doubt that of Benson (31). However, the solute molecules can be considered derivations of successive substitutions of methane as well. If the increments of the substituents are well-determined (as in the case of noncyclic compounds), then there is an additional tool that can be used to estimate the thermodynamic properties (Yoneda method) (32). The  $C_p(g)$  values were estimated by group additivity (Benson) and successive-substitution methods (Yoneda) (31,32). Unfortunately, both methods can sometimes provide very imprecise results, as can be seen from the comparison with literature values (Tables IV and V).

Reliable  $C_p(g)$  and  $C_p(l)$  data are available for acetone. The comparison suggests that a  $\Delta C_p(g)$  calculated by the additivity rule of Benson is much more acceptable than the value obtained by the Yoneda method. On the contrary to this, only the Yoneda method provides acceptable results for 2-methyl butan-2-one.

Comparison of the  $C_p(l)$  and  $C_p(\text{sol})$  data showed that the solvated state resembled the pure liquid state with a low value of excess molar heat capacity. Calorimetric measurements for the dissolution of ketones in apolar solvents show that  $\Delta C_p^{E,0}$  is near zero in very diluted solutions (26).

In summary, a comparison with literature data suggests that, with the exception of some cases, model 2 is able to estimate molar heat capacities at or above the precision and accuracy levels common in the literature.

During the derivation of model 2, we never used any special features of oxo compounds. Hence, it can be expected that model 2 is applicable to other compound classes as well, although the validation or the examples in this study exclusively concern the oxo compounds.

**Table V. Estimation of the Standard Enthalpy of Solution and the Molar Heat Capacities for Aldehydes on the Dimethyl-Polysiloxane Stationary Phase at 298 K**

Solute	$\Delta_{\text{sol}}H^\circ_{T_0}$	$\Delta C_p$	$C_p(\text{g})^\ddagger$	$C_p(\text{g})$ (Benson)*	$C_p(\text{g})$ (Yoneda) <sup>†</sup>	$C_p(\text{l})$	$C_p(\text{sol})$	$C_p(\text{sol})^*$	$C_p(\text{sol})^\ddagger$
Acetaldehyde	20.27	43.4	54.6	55.0	33.1	96.2 <sup>§</sup>	98.0	98.4	76.5
Propanal	26.87	83.7	78.6	79.3	79.2	137.2 <sup>**</sup>	162.3	163.0	162.9
Acrolein	25.20	50.4		60.8	69.2			111.2	119.6
Isobutanal	29.19	55.2		92.0	99.7			147.2	154.9
Butanal	30.73	63.4	100.9	102.0	102.1	164.7 <sup>††</sup>	164.3	165.4	165.5
Isovaleraldehyde	33.96	85.8		124.7	125.2			210.5	211.0
Butanal-2-methyl	34.49	79.8		114.8	122.6			194.6	202.4
<i>trans</i> -Butenal	33.43	73.6		83.8	93.5			157.4	167.1
Valeraldehyde	35.81	80.5	123.5	124.7	125.1	189.2 <sup>**</sup>	204.0	205.2	205.6
Trimethyl acetaldehyde	31.77	76.9		115.1	99.7	186.2 <sup>**</sup>		192.0	176.6
Hexanal	38.22	31.4	148.0	147.5	148.0	210.4 <sup>††</sup>	179.4	178.9	179.4
Butanal-2-ethyl	37.33	54.6		137.5	145.5			192.1	200.1
Butanal-3,3-dimethyl	34.56	49.2		146.9	125.2			196.1	174.4
Heptanal	43.05	44.2	170.9	170.2	171.0		215.1	214.4	215.2
Octanal	50.22	95.9	193.7	193.0	194.0		289.6	288.9	289.9
Hexanal-2-ethyl	47.77	90.4		183.0	191.5			273.4	281.9

\* Calculated according to Benson's additivity rule by the THERGAS computer code (30,31).

<sup>†</sup> Calculated according to Yoneda's successive substitution method by the THERGAS computer code (31).<sup>‡</sup> Obtained from references 22 and 23.<sup>§</sup> Obtained from reference 33.<sup>\*\*</sup> Obtained from reference 27.<sup>††</sup> Obtained from reference 34.<sup>†††</sup> Obtained from reference 35.

## Conclusions

By the introduction of a new variable ( $T_a$ ), a new model was derived that takes into account the temperature dependence of thermodynamic quantities. The method presented here provided reliable heat of solution and heat capacity values. The validation of results was made by a comparison with heat capacity values taken from the literature and seemed to be an easy and applicable method for the determination of thermodynamic quantities for polymeric stationary phases.

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