

HEAT CAPACITIES ESTIMATION FOR AROMATIC SUBSTANCES BASED ON SPECTROSCOPIC DATA

Saad H. M. Al-Saadi ,

Electrochemical Engineering Department , Engineering College , Babylon University

Abstract

For Benzene, Ethylbenzene, Toluene and three Xylenes , values of heat capacity based on spectroscopic data have been estimated over relatively large range of temperature (from 100 to 1100 K) , using the statistical thermodynamic method based on a rigid-rotor, harmonic- oscillator model. The calculated heat capacities from spectroscopic data have been expressed in fitted form. The heat capacity values estimated from spectroscopic data in the present work, and for the predicting heat capacities from present work fitted equation are identical to those reported by A.P.I. project 44 at high temperature range .

Introduction

Heat capacities are not of great practical use but also of real theoretical interest in many cases . The change with temperature of the heat of a chemical reaction is determined by the heat capacities of the reactants and products . The heat capacity tells us much about the thermal motion of atoms and molecules . Theoretical evaluation based upon the detailed properties of atoms , molecules , or crystals now contribute reliable heat capacity value in favorable cases [1] .

For the purpose of these calculations the statistical thermodynamic method based on a rigid-rotor , harmonic- oscillator model was used for six aromatic substances {Benzene, Ethylbenzene, Toluene and three Xylenes}. This model enable the contributions from translational, overall and internal rotation and vibration to be evaluated .For the translational rotation contributions estimation the substances were considered as symmetrical tops attached to a rigid frame, except Ethylbenzene which was considered as a methylene group with a symmetrical methyl group and a balanced , but unsymmetrical phenyl group attached . The calculations were extended to the high temperature range , in order to check that , the present calculations agreed in this range with those carried in connection with A.P.I. Project 44 [2] .

Theoretical Evaluation of Vapor Heat Capacities from Spectroscopic Data

This method of evaluating heat capacities may be said to have its origin partly in the kinetic theory of gases and partly in the work of Einstein [3] .

According to the kinetic theory of gases the heat capacities of a monatomic gas should be $(3/2R)$, a contribution of $(1/2 R)$ arising from each degree of freedom. According to the quantum theory the heat capacity should become zero at 0 K. However, the results that $C_V = (3/2 R)$ is observed for monatomic gases down to about 3 K. For a diatomic gases , energy may be taken up by the molecules not only in the form of kinetic energy , but also as rotational kinetic energy and as oscillatory energy due to intramolecular vibrations. At sufficiently high temperatures the contribution to the heat capacity arising from rigid rotation is also $(1/2 R)$ per degree of freedom. For linear molecules there are two degree of rotational freedom so the contribution to the heat capacity arising from rigid rotation is in this case (R) . The quantum theory predicts that, at 0K the contribution from this case will be zero . In

practice , however , the full contribute (1/2 R) per degree of freedom will be fully taken up at temperatures down to 85 K [3] .

The contribution to the heat capacity arising from intramolecular vibration cannot be calculated so easily. At sufficiently high temperatures the contribution for this cause tend to (R) per vibrational mode. At temperature normally of interest, however, the contribution will be less than this, at 0K it is zero. Unlike the contributions from translation and rotation this contribution does not rise sharply to a steady value at temperatures above a few degree K, but arises much more slowly. The equation used to evaluate the contribution from this case was taken over from Einstein's work on solids, which Einstein considered to consist of set harmonic oscillators . The only modification that was necessary was to consider only a single vibrational mode at a time . According to Einstein's equation as applied to gases,

$$C_{vib} = \left[\frac{u^2 e^u}{(e^u - 1)^2} R \right] \text{-----} (1)$$

Where C_{vib} is the contribution to the heat capacity arising from vibrational mode of frequencies (ω_i),

$$u = \frac{h\nu}{kT} = \frac{hc\omega_i}{kT} = 1.4386 \frac{\omega_i}{T} \text{-----}(2)$$

(ω_i = frequencies in cm^{-1} , T = temperature in K , R = universal constant)

To summaries, the heat capacity for a diatomic gas at temperatures above a few degree (K) is given by,

$$C = \left[\left(\frac{3}{2} R \right) + \frac{n_r R}{2} + \sum C_{vib} \right] \text{-----}(3)$$

Where n_r is the number of rotational degree of freedom (2 in this case) and C_{vib} for each mode is given by equation (1) .

Following the work outlined above , developments in the theory of heat capacities have been continued , and very reliable calculations may now be made in the ideal gas state provided spectroscopic data (giving the intramolecular energy levels are available).When applied to complex molecules it is necessary to add further terms to equation (3). In addition to the basic terms, giving the contribution arising from the translational, over all rotational and vibrational degrees of freedom , allowance is made for internal rotation, that is, the rotation of one portion of molecule about a valance bond joining that portion to the rest of the molecule .

In order to evaluate this term it is convenient to set up a model to represent the molecules under consideration. For example Pitzer and Gwinn [4] took as their model as symmetrical top attached to a rigid frame , for which they presented a general treatment. They used this model to calculate heat capacities for a series of alkylbenzene. It enabled the contributions to the heat capacity and other thermodynamic functions arising from the hindered rotation of alkyl group, or groups, to be evaluated .

This treatment in turn led to other investigation giving rise to further improvements in the prediction of vibrational spectra, moments of inertia, anharmonic corrections, and free energies for Si2 through Si5 clustering [5]. The translational contribution is based on the ideal gas limit . The rotation contribution is approximated using a classical rigid rotor. Vibrational modes are determined from the dynamical matrix in the harmonic approximation . Corrections due to the anharmonicity and coupling between rotational and vibrational modes are fitted from the molecular dynamics simulation .

Calculation of the Heat Capacities for some Aromatic Substances

- Vibrational Contributions

The vibrational frequencies for Benzene, Toluene and three Xylenes were taken from assignments of Pitzer and Scott [6], while the vibrational frequencies of Ethylbenzene were assigned on semi-empirical basis by Pitzer and his co-workers [7], their procedure involved detailed considerations of only the lowest frequencies of vibration of the benzene ring and also of the frequencies associated with vibration of ethyl group . The remaining frequencies were taken from the assignment for Toluene of Pitzer and Scott [6] .Some practical values of the vibrational spectrum based on infrared spectroscopy for aromatic substances are used [8], in the present work . For example ,the frequencies and also the resulting vibrational contributions to the heat capacity for Benzene and o-Xylene which are calculated from Einstein's equation (1) are listed in tables (1) and (2) at a few representative temperatures . In order to establish the heat capacity behavior of aromatic substances , calculations were carried out at intervals of (5 K) from 100 K up to 1100 K , based on computer program written in FORTRAN 90 .

The total vibrational contributions estimated from Einstein's equation for the vibrational heat capacities are plotted against temperature at intervals of (20 K) from 100 K up to 1000 K in figure (1) .

- Translational And Over – All Rotation Contributions :

The three translational and three rotational degree of freedom each contribute (R/2) cal/mole. K to the heat capacity . The total translational and over – all rotation contributions to the heat capacity thus amount to (3 R) .

- Internal Rotation Contributions :

To evaluate the translational rotation contributions for aromatic substances {Benzene, Ethylbenzene, Toluene and three Xylenes }we used the model suggested by Pitzer and Gwinn [4]. The substances were considered as symmetrical tops attached to a rigid frame , except Ethylbenzene which was considered as a methylene group with a symmetrical methyl group and a balanced, but unsymmetrical phenyl group attached . By term "balanced", it is meant that the center of gravity of the phenyl group is on the axis of rotation but that the two moment of the phenyl group perpendicular to the axis of rotation are not equal .

These contributions were obtained from the table given by Pitzer and Gwinn [4] and reproduced by Lewis and Randall [9]. This table gives the internal rotational contribution to the heat capacity as a function of the partition function ($1/Q_f$) and the quantity (V/RT), where (V) is the potential barrier for restricted rotation (it would be zero for free rotation) . The partition function is therefore ,

$$Q_f = \frac{2.7935}{n_1} (10^{38} I_r T)^{1/2} \text{ ----- (4)}$$

Where n_1 = symmetry number .

I_r = reduced moment of inertia .

T = temperature in K .

The values of constants such as symmetry number, reduced moment of inertia and potential barrier are given by Pitzer *et al* [6] and listed in table (3). Using Pitzer and Gwinn tables and the above constants {in table (3)} values of the internal rotational contribution to the heat capacity were calculated using computer program in FORTRAN 90 at intervals of (5 K) from 100 K up to 1100 K the results found at a few representative temperature are given in table (4) .

- Calculation of Total Heat Capacity :

The heat capacity arising from contributions from all above sources was calculated from the equation ,

$$C_P = [R + 3R + C_{vib} + C_{ROT}] \text{ ----- (5)}$$

The first term on the right hand side is the usual ideal gas relationship to convert (C_V) to (C_P) . The second term ($3R$) is the combined contribution to the heat capacity arising from translational and over – all rotational degree of freedom . The third and fourth terms are the contributions from the vibrational and restricted rotation respectively . These contributions are listed in table (4) . The parameters used in the calculation of (C_{ROT}) are given in table (3). The contribution (C_{vib}) was evaluated by applying Einstein's equation to each vibrational mode while (C_{ROT}) was obtained from the table given by Pitzer and Gwinn [4] and reproduced by Lewis and Randall [9] . The above calculations and the subsequent fitting for heat capacity (C_P^0) equation were carried out using the computer program written in FORTRAN 90 . The Lewis and Randall table was input in the computer for this purpose.

The calculation could not be extended to temperatures below 100 K , since the term (V/RT) for the internal rotation for methyl group then rose near (20) or above this value which is the highest value considered in the Lewis and Randall table [9] .

Heat Capacity Equation

The temperature dependence of heat capacities is complex , and there is no reliable equation that express the data . The heat capacity may be represented as follows :

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2} \text{ ----- (6)}$$

The above expression from combination of two simplest expressions of practical value are :

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2 \text{ ----- (7)}$$

and

$$\frac{C_P}{R} = a + bT + cT^{-2} \text{ ----- (8)}$$

Where α, β and γ and a, b and c are constants characteristics of the particular substance, the ratio $\frac{C_P}{R}$ is dimensionless , the units of C_P governed by the choice of (R) [10] .

Yaws *et al* [11] represented the heat capacities of 700 compounds in the temperature range from 298 to 1000 K using the following form of equation ,

$$C_P = A + BT + CT^2 + DT^3 \text{ ----- (9)}$$

Baily and Gallaway [12] used the following form of the heat capacity equation in their work for producing and extending heat capacity and other thermal data for paraffins,

$$C_P = a + bT + cT^2 + dT^3 + eT^4 + fT^5 \text{ ----- (10)}$$

The NASA polynomial have the form ,

$$CP = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \text{ ----- (11)}$$

Based on the two types of the numerical constants supplied in NASA thermodynamics files, the first type of coefficients for the high temperature range (above 1000 K), while the second type of coefficients for the low temperature range (below 1000 K) . The coefficient of equation (11) have been obtained based on thermodynamic and transport properties of individual species by McBride *et al* [13] .

In the present work the heat capacity of six aromatic substances {Benzene , Ethylbenzene, Toluene and three Xylenes} in the temperature range of 100 up to 1100 K was fitted to same fourth order polynomial equation as that used by NASA . The coefficients in the equation ,

$$C_P = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 \text{-----} (12)$$

were fitted by method of least squares to heat capacities calculated at the temperature range from 100 up to 1100 K . The coefficient values for present work equation (12) listed in table (5) .

Discussion

As part of the work of the American Petroleum Institute , values have been calculated for heat capacity based on quantum and statistical mechanics , but detailed knowledge of structure and spectra is necessary to obtain numerical values . These calculations do not extended to temperatures below 25 C⁰ , in the present work the heat capacity calculations for some aromatic substances have been extended to lower temperatures (the calculations for the temperature range from 100 up to 1100 K) . There seemed to be no reason why the method described by A.P.I. should not be applicable at lower temperatures , also the calculations were extended to high temperatures , in order to check that the present results agreed in this range with those carried in connection with A. P. I. project [2] .

The molecule is assumed to be a rigid rotator and the vibration to be harmonic, the atoms displaced from equilibrium are acted upon by resorting forces proportional to the displacement . The vibrational contributions was evaluated from Einstein's equation (1) to each vibrational mode . These calculated values of the total vibrational contribution were plotted against temperature are shown in figure (1), it seems that as the temperature increased the vibrations become more violent , and when the temperature decrease to 100 K it has become near zero and that is behavior for the vibrational contribution of aromatic substances seems to be in a good agreement with Einstein's model. The absolute deviations for the calculated vibrational contributions from the experimental results were : 0.105 % , 0.065 % and 0.018 % for o-Xylene , 1.046 % , 0.283 % and 0.05 % for m-Xylene and 0.004 % , 0.003 % and 0.012 % for p-Xylene for the temperatures 300 , 500 and 1000 K respectively . The agreements are reasonably very good , as shown in table (6), and the maximum absolute deviation was 1.046 % at 300 K for p-Xylene .

Many researchers have been used the group-contribution method to estimate heat capacities . The most accurate method of Rihani and Doraiswamy [14] , which is applicable to large variety of compounds . The mean absolute deviations for the present work heat capacities values calculated using spectroscopic data were:0.01225%, 0.41325 % , 0.10725 % and 0.3015 % for Benzene , Ethylbenzene, o-Xylene and m-Xylene from the experimental results. While the absolute deviation values for the heat capacity values calculated based on group-contribution method of Rihani and Doraiswamy [14] were : 0.5525 % , 0.8145 % , 2.3735 % and 0.7395 % for the same aromatic substances for the temperatures 298.16, 500, 700 and 1000 K . The accuracy level are somewhat less when predicting heat capacities at temperature below about 500 K when using Rihani and Doraiswamy [14] , for example the absolute deviation values were : 0.615 % , 0.782 % , 6.021 % and 1.544 % for Benzene , Ethylbenzene , o-Xylene and m-Xylene from the experimental results at 298.16 K. For the same aromatic substances the absolute deviations were: 0.025 % , 0.006% , 0.266% and 0.877 % for the present work calculations based on spectroscopic data at 298.16 K .

For computational purposes the calculated heat capacities from spectroscopic data have been expressed in fitted form (equation12), which can be used in the temperature range from

100 to 1100 K . The mean absolute deviations for the fitted equation values over the temperature values given in table (8) were: 0.5927%, 0.7477%, 0.4493 %, 0.2475 %, 0.4643 % and 0.3553 % for Benzene, Ethylbenzene, Toluene, and Three Xylenes from the experimental results. The mean absolute deviations for the heat capacities values estimated from equation (6) {which is cited in reference [10]} were: 2.9635%, 1.8169% and 1.7851 % for Benzene , Ethylbenzene, and Toluene from the experimental results. At certain heat capacity values the absolute deviation rise to 5 % from the experimental results when using equation (6). The temperature range for using this from 298 to 1500 K .

The suggested form by Yaws *et al* [11] more convenient for heat capacities estimation for temperature range 298 to 1000 K . The mean absolute deviation were: 0.0634 % , 0.8 % , 1.1258 % , 0.0863 % , 0.1014 % and 0.1164 % for Benzene, Ethylbenzene , Toluene , and three Xylenes from the experimental results .

It may be seen , that the results in the temperature range from 298.16 to 1000 K for heat capacities from spectroscopic data in the present work , and for the heat capacities from present work fitted equation are identical to those reported by A.P. I. [2] and those calculated from more accurate form by Yaws *et al* [11] .

Table (1): Vibrational contributions to the heat capacity of Benzene calculated from Einstein equation at T=300 K. Number of vibrational frequencies = 3 x N - 6

NO.	Frequency ω_i (cm^{-1})	$u = 1.4386 \omega_i / T$	Einstein equation** $C/R = u^2 \text{EXP}(u) / [\text{EXP}(u) - 1]^2$
1	992	4.756970	1.978016E-01
2	3062	14.683310	9.052480E-05
3	1298	6.224342	7.703915E-02
4	685	3.284803	4.361124E-01
5	1016	4.872058	1.845839E-01
6	606	2.905972	5.168825E-01
7	606	2.905972	5.168825E-01
8	3047	14.611380	9.632552E-05
9	3047	14.611380	9.632552E-05
10	1596	7.653352	2.781679E-02
11	1596	7.653352	2.781679E-02
12	1178	5.648902	1.131632E-01
13	1178	5.648902	1.131632E-01
14	849	4.071238	2.926034E-01
15	849	4.071238	2.926034E-01
16	671	3.217669	4.499540E-01
17	1011	4.848082	1.872770E-01
18	3046	14.606580	9.672499E-05
19	1693	8.118499	1.965129E-02
20	1170	5.610540	1.160291E-01
21	400	1.918133	7.425121E-01
22	400	1.918133	7.425121E-01
23	985	4.723403	2.017967E-01
24	985	4.723403	2.017967E-01
25	1037	4.972761	1.736151E-01
26	1037	4.972761	1.736151E-01
27	1485	7.121070	4.103469E-02
28	1485	7.121070	4.103469E-02
29	3080	14.769630	8.401801E-05
30	3080	14.769630	8.401801E-05
			Total = 5.887845

** present work (based on spectroscopic data) .

Table (2) : Vibrational contributions to the heat capacity of p -Xylene calculated from Einstein equation at T = 273.15 K .

Number of vibrational frequencies = 3 x N - 6

NO.	Frequency ω_i (cm^{-1})	$u = 1.4386 \omega_i / T$	Einstein equation** $C/R = u^2 \text{EXP}(u) / [\text{EXP}(u) - 1]^2$
1	826	4.350297	2.506156E-01
2	3062	16.12665	2.578546E-05
3	460	2.422683	6.267534E-01
4	1204	6.341111	7.111371E-02
5	1616	8.510992	1.458338E-02
6	1182	6.225243	7.699179E-02
7	811	4.271297	2.620192E-01
8	697	3.670892	3.611521E-01
9	959	5.050768	1.654911E-01
10	313	1.648478	8.012846E-01
11	1200	6.320044	7.215139E-02
12	644	3.391757	4.145328E-01
13	3047	16.04765	2.763241E-05
14	1575	8.295057	1.719326E-02
15	313	1.648478	8.012846E-01
16	400	2.106681	6.997348E-01
17	971	5.113969	1.591423E-01
18	720	3.792026	3.393887E-01
19	3046	16.04238	2.776013E-05
20	1030	5.424704	1.308184E-01
21	1525	8.031722	2.097815E-02
22	1200	6.320044	7.215139E-02
23	1640	8.637393	1.323571E-02
24	1100	5.793374	1.029163E-01
25	232	1.221875	8.843496E-01
26	1450	7.636720	2.816097E-02
27	3080	16.22145	2.372986E-01
28	170	8.953395E-01	9.357919E-01
29	389	2.048748	7.129801E-01
30	800	4.213363	2.706236E-01
31	1377	7.252250	3.732063E-02
32	2950	15.53677	4.317043E-05
33	1152	6.067242	8.570936E-02
34	1451	7.641986	2.805155E-02
35	2950	15.536770	4.317043E-05
36	1152	6.067242	8.570936E-02
37	1451	7.641986	2.805155E-02
38	2950	15.53677	4.317043E-05
39	1380	7.268050	3.689503E-02
40	2950	15.53677	4.317043E-05
41	1100	5.793374	1.029163E-01
42	1450	7.636720	2.816097E-02
43	2950	15.53677	4.317043E-05

Continued Table (2) : Vibrational contributions to the heat capacity of p - Xylene calculated from Einstein equation at T = 273.15 K .

Number of vibrational frequencies = 3 x N - 6

NO.	Frequency ω_i (cm ⁻¹)	$u = 1.4386 \omega_i / T$	Einstein equation** $C/R = u^2 \text{EXP}(u) / [\text{EXP}(u) - 1]^2$
44	1100	5.793374	1.029163E-01
45	1450	7.636720	2.816097E-02
46	2950	15.53677	4.317043E-05
47	Internal frequency	-	-
48	Internal frequency	-	-
			Total = 8.869694

** present work (based on spectroscopic data) .

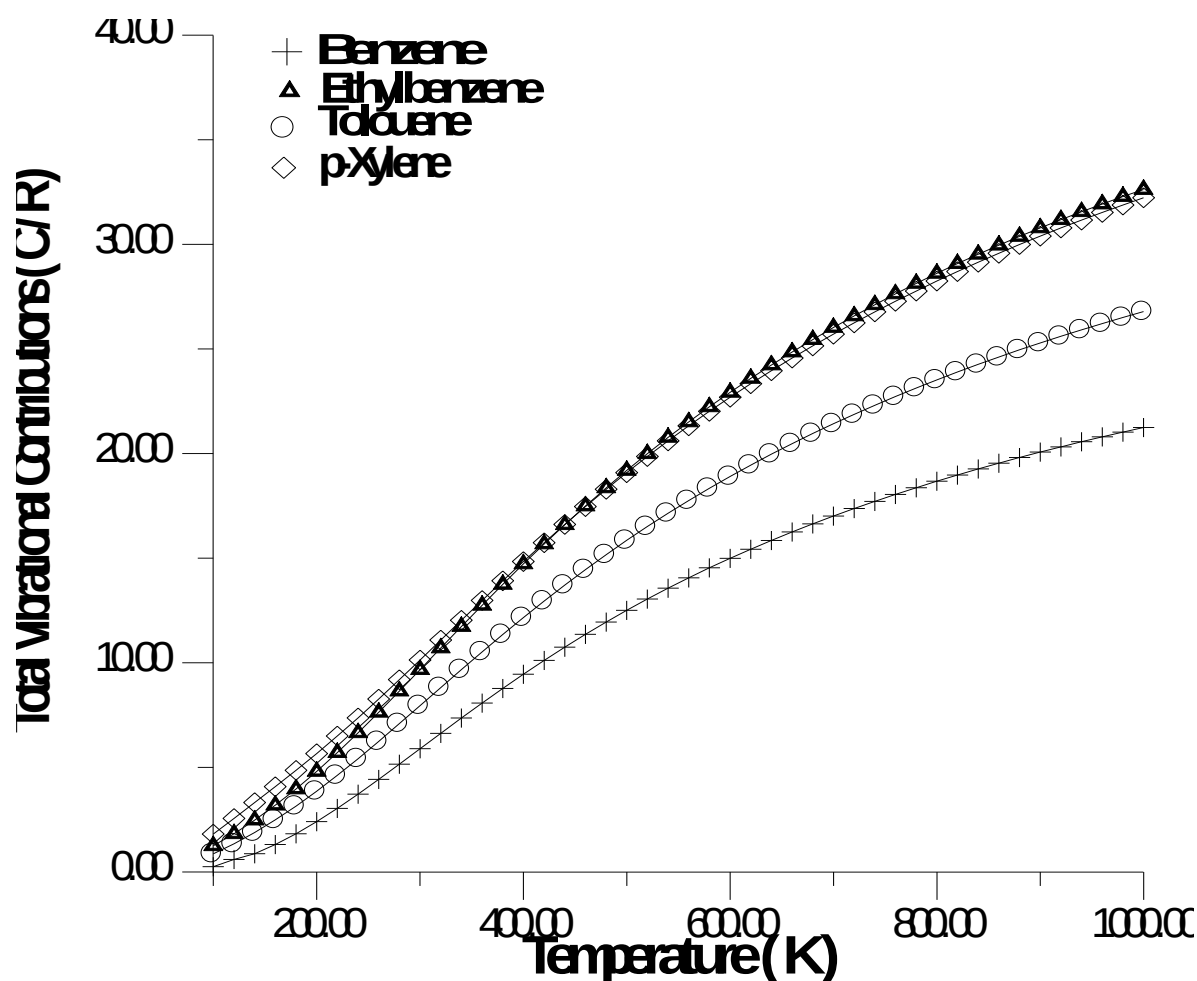


Figure (1) : Total Vibrational Contributions for (Some Aromatic Substances) as a Function of Absolute Temperature .

Table (3) : Constants for the calculation of the internal rotational contributions to the heat capacity :

Substance	Group	Potential barrier in cal / mole (V)	Symmetry number (n_1)	Reduced moment of inertia in gm cm ²
Benzene	Methyl	750	0	0
Ethylbenzene	Methyl	3400	3	5.18×10^{-40}
	Ethyl	1080	2	33.5×10^{-40}
Toluene	Methyl	750	6	5.32×10^{-40}
o-Xylene	Methyl	750	3	5.41×10^{-40}
m-Xylene	Methyl	750	6	5.41×10^{-40}
p-Xylene	Methyl	750	6	5.32×10^{-40}

Table (4): Calculated vibrational contributions, restricted rotational contributions and total Heat capacities of some aromatic substances:

Substance	Temperature (K)	Vibrational contribution (C_{vib})**	Restricted rotation contribution (C_{ROT})++		Total heat capacity (cal / mole K)**
			Methyl group	Ethyl group	
Benzene	200	4.777807	1.626490		12.727010
	300	11.700910	1.339233		19.650110
	400	18.786230	1.198601		26.735430
	500	24.853650	1.129169		32.802850
	600	29.788560	1.089291		37.737760
	700	33.801630	1.065706		41.750840
	800	37.111490	1.049768		45.060690
	900	39.879330	1.037371		47.828530
	1000	42.217490	1.029489		50.166700
Ethylbenzene	200	9.552189	1.772994	1.986296	21.260680
	300	19.214130	2.115462	1.599317	30.878110
	400	29.259400	2.193329	1.382985	40.784910
	500	38.135210	2.119598	1.258707	49.462720
	600	45.554660	1.987347	1.183166	56.674370
	700	51.711930	1.851742	1.135582	62.648450
	800	56.854000	1.726159	1.105016	67.634380
	900	61.179220	1.623408	1.081227	71.833050
	1000	64.837550	1.535546	1.066714	75.389020
Toluene	200	7.665689	1.306831		16.921720
	300	15.793500	1.209143		24.951850
	400	24.164490	1.137084		33.250770
	500	31.495250	1.092544		40.537000
	600	37.566620	1.065065		46.580880
	700	42.570760	1.047999		51.567960
	800	46.738350	1.036535		55.724080
	900	50.246990	1.027298		59.223490
	1000	53.224360	1.021285		62.194850

** Present work (based on spectroscopic data) .

++ Present work (restricted rotation contributions calculations based on potential barrier values in table (3)).

Continued Table (4): Calculated vibrational contributions, restricted rotational contributions and total Heat capacities of some aromatic substances :

Substance	Temperature (K)	Vibrational contribution (C_{vib})**	Restricted rotation contribution (C_{ROT})++		Total heat capacity (cal / mole K)**
			Methyl group	Ethyl group	
o-Xylene	200	10.883160	2.066404		22.965160
	300	19.859190	2.091450		31.991290
	400	29.266200	1.895382		41.006160
	500	37.735470	1.699792		49.084260
	600	44.908680	1.547672		55.953220
	700	50.916760	1.433624		61.733210
	800	55.974960	1.352507		66.629170
	900	60.263340	1.289027		70.790590
	1000	63.918280	1.237728		74.342930
m-Xylene	200	11.359790	1.310968		21.930930
	300	20.512360	1.210913		30.883390
	400	29.966060	1.137964		40.191180
	500	38.408570	1.093000		48.543770
	600	45.518070	1.065356		55.597980
	700	51.453080	1.048218		61.498710
	800	56.441970	1.036739		66.464650
	900	60.669220	1.027464		70.673360
	1000	64.271900	1.021334		74.263770
p-Xylene	200	11.247360	1.306831		21.810230
	300	20.130830	1.209143		30.498320
	400	29.480670	1.137084		39.704040
	500	37.928970	1.092544		48.063260
	600	45.086970	1.065065		55.166300
	700	51.079570	1.047999		61.124760
	800	56.122330	1.036535		66.144590
	900	60.396090	1.027298		70.399880
	1000	64.037640	1.021285		74.029410

** Present work (based on spectroscopic data) .

++ Present work (restricted rotation contributions calculations based on potential barrier values in table (3)) .

Table (5): Coefficients for use in equation (12) for the heat capacity estimation of six aromatic substances, at the temperature range from 100 K up to 1100 K : ($C_P = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$) **

Substance	a_0	$a_1 \times 10^2$	$a_2 \times 10^4$	$a_3 \times 10^7$	$a_4 \times 10^{11}$
Benzene	3.92057	2.20104	1.64177	-2.34171	9.39905
Ethylbenzene	6.74245	4.80713	1.80021	-2.65659	10.5962
Toluene	5.34485	3.53257	1.64372	-2.37626	9.45535
o-Xylene	6.70415	6.80486	0.998347	-1.67833	6.74436
m-Xylene	7.25758	5.26611	1.47095	-2.19535	8.65987
p-Xylene	8.01608	4.5889	1.59568	-2.2836	8.87352

** present work fitted equation .

Table (6): Comparison of experimental and calculated vibrational contributions from spectroscopic data for some aromatic substances : (absolute % deviation from experimental results are shown in brackets)

Substance	Temperature (K)	Experimental vibrational contribution (C_{vib}) [2]	Vibrational contribution (C_{vib})**
o-Xylene	300	19.88	19.85919 (0.105)
	500	37.76	37.73547 (0.065)
	1000	63.93	63.91828 (0.018)
m-Xylene	300	20.30	20.51236 (1.046)
	500	38.30	38.40857 (0.283)
	1000	64.24	64.27190 (0.050)
p-Xylene	300	20.13	20.13083 (0.004)
	500	37.93	37.92897 (0.003)
	1000	64.03	64.03764 (0.012)

** Present work (based on spectroscopic data) .

Table (7): Comparison of experimental and calculated heat capacities from spectroscopic data for some aromatic substances : (absolute % deviation from experimental results are shown in brackets)

Substances	Temperature (K)	Experimental heat capacity (cal / mole K) [2]	Calculated heat capacity from spectroscopic data** (cal / mole K)	Calculated heat capacity from spectroscopic data [14] (cal / mole K)
Benzene	298.16	19.52	19.51518 (0.025)	19.40 (0.615)
	500	32.80	32.80285 (0.009)	32.45 (1.067)
	700	41.75	41.75084 (0.002)	41.58 (0.407)
	1000	50.16	50.16670 (0.013)	50.10 (0.120)
Mean absolute deviation			(0.01225)	(0.5525)
Ethylbenzene	298.16	30.69	30.69188 (0.006)	30.45 (0.782)
	500	49.35	49.46272 (0.228)	48.70 (1.317)
	700	62.28	62.64845 (0.592)	61.75 (0.851)
	1000	74.77	75.38902 (0.827)	74.54 (0.308)
Mean absolute deviation			(0.41325)	(0.8145)
O – Xylene	298.16	31.89	31.80506 (0.266)	29.97 (6.021)
	500	49.13	49.08426 (0.093)	48.00 (2.300)
	700	61.77	61.73321 (0.060)	61.17 (0.971)
	1000	74.35	74.34293 (0.010)	74.20 (0.202)
Mean absolute deviation			(0.10725)	(2.3735)
M -Xylene	298.16	30.44	30.71007 (0.877)	29.97 (1.544)
	500	48.44	48.54377 (0.214)	48.00 (0.908)
	700	61.44	61.49871 (0.096)	61.17 (0.439)
	1000	74.25	74.26377 (0.019)	74.20 (0.067)
Mean absolute deviation			(0.3015)	(0.7395)

** Present work (based on spectroscopic data) .

Table (8): Comparison of experimental and calculated heat capacities from fitted equations for aromatic substances : (absolute % deviation from experimental results are shown in brackets)

Substances	Temperature (K)	Experimental heat capacity (cal / mole K) [2]	Calculated heat capacity from fitted equation (12)** (cal / mole K)	Calculated heat capacity from equation(6) [10] (cal / mole K)	Calculated heat capacity from equation(9) [11] (cal/mole K)
Benzene	298.16	19.52	19.61425 (0.483)	19.87964 (1.842)	19.50765 (0.063)
	300	19.65	19.73833 (0.450)	19.99056 (1.733)	19.65105 (0.005)
	400	26.74	26.41226 (1.226)	25.75615 (3.679)	26.80688 (0.250)
	500	32.80	32.57305 (0.692)	31.00625 (5.469)	32.77247 (0.084)
	600	37.74	37.83076 (0.240)	35.74086 (5.297)	37.70793 (0.085)
	700	41.75	42.02105 (0.649)	39.95997 (4.287)	41.75908 (0.022)
	800	45.06	45.20513 (0.322)	43.66359 (3.099)	45.08365 (0.052)
	900	47.83	47.66981 (0.335)	46.85172 (2.045)	47.83222 (0.005)
	1000	50.16	49.92747 (0.464)	49.52435 (1.267)	50.15774 (0.005)
	1100	52.16	52.71607 (1.066)	51.68149 (0.917)	-
Mean absolute deviation			(0.5927)	(2.9635)	(0.0639)
Ethylbenzene	298.16	30.69	30.87495 (0.603)	31.78407 (3.565)	30.67161 (0.060)
	300	30.83	31.05123 (0.718)	31.94617 (3.620)	30.86998 (0.130)
	400	40.76	40.48478 (0.675)	40.38162 (0.928)	40.86520 (0.258)
	500	49.35	49.19860 (0.307)	48.08272 (2.568)	49.30688 (0.087)
	600	56.44	56.74312 (0.537)	55.04948 (2.464)	56.38145 (0.104)
	700	62.28	62.92309 (1.033)	61.28189 (1.603)	62.27772 (0.004)
	800	67.15	67.79756 (0.964)	66.77996 (0.551)	67.17973 (0.044)
	900	71.27	71.67989 (0.575)	71.54367 (0.384)	71.27390 (0.005)
	1000	74.77	75.13775 (0.492)	75.57304 (1.074)	74.74904 (0.028)
	1100	77.77	78.99313 (1.573)	78.86807 (1.412)	-
Mean absolute deviation			(0.7477)	(1.8169)	(0.0800)
Toluene	298.16	24.80	24.93882 (0.560)	25.67966 (3.547)	24.75143 (0.196)
	300	24.95	25.08602 (0.545)	25.81733 (3.476)	24.92352 (0.106)
	400	33.25	32.98716 (0.791)	32.98171 (0.807)	33.58987 (1.022)
	500	40.54	40.30704 (0.575)	39.52144 (2.512)	40.94407 (0.997)
	600	46.58	46.64111 (0.131)	45.43651 (2.455)	47.13671 (1.195)
	700	51.57	51.8117 (0.469)	50.72695 (1.635)	52.31836 (1.451)
	800	55.72	55.86809 (0.266)	55.39273 (0.587)	56.63958 (1.650)
	900	59.22	59.0865 (0.225)	59.43386 (0.361)	60.24857 (1.737)
	1000	62.19	61.97005 (0.354)	62.85035 (1.062)	63.29589 (1.778)
	1100	64.73	65.24881 (0.802)	65.64219 (1.409)	-
Mean absolute deviation			(0.4493)	(1.7851)	(1.1258)
o-Xylene	298.16	31.85	31.95316 (0.324)	-	31.82600 (0.075)
	300	32.02	32.11866 (0.308)	-	32.00526 (0.046)
	400	41.03	40.88239 (0.360)	-	41.14962 (0.292)
	500	49.11	48.92323 (0.380)	-	49.08222 (0.057)
	600	55.98	55.96256 (0.031)	-	55.90822 (0.128)
	700	61.76	61.88366 (0.200)	-	61.73757 (0.036)
	800	66.64	66.73164 (0.138)	-	66.67543 (0.053)
	900	70.80	70.71349 (0.122)	-	70.83413 (0.048)
	1000	74.35	74.19805 (0.204)	-	74.31883 (0.042)
	1100	77.40	77.71605 (0.408)	-	-
Mean absolute deviation			(0.2475)	-	(0.0863)

** present work equation { coefficients used in equation are listed in table (5) } .

Continued table (8): Comparison of experimental and calculated heat capacities from fitted equations for aromatic substances : (absolute% deviation from experimental results are shown in brackets)

Substances	Temperature (K)	Experimental heat capacity (cal / mole K) [2]	Calculated heat capacity from fitted equation (12)** (cal / mole K)	Calculated heat capacity from equation(6) [10] (cal / mole K)	Calculated heat capacity from equation(9) [11] (cal / mole K)
m-Xylene	298.16	30.49	30.90102 (1.348)	-	30.45889 (0.102)
	300	30.66	31.06846 (1.332)	-	30.64532 (0.048)
	400	40.03	40.02391 (0.015)	-	40.17208 (0.355)
	500	48.43	48.33242 (0.201)	-	48.39388 (0.075)
	600	55.51	55.61207 (0.184)	-	55.43260 (0.139)
	700	61.43	61.68874 (0.421)	-	61.41013 (0.032)
	800	66.41	66.59617 (0.280)	-	66.44837 (0.058)
	900	70.63	70.57591 (0.077)	-	70.67161 (0.059)
	1000	74.23	74.07738 (0.206)	-	74.19694 (0.045)
	1100	77.31	77.75781 (0.579)	-	-
Mean absolute deviation			(0.4643)	-	(0.1014)
p -Xylene	298.16	30.32	30.53216 (0.695)	-	30.28681 (0.109)
	300	30.49	30.69694 (0.674)	-	30.47084 (0.063)
	400	39.70	39.55914 (0.356)	-	39.85899 (0.400)
	500	48.06	47.85353 (0.431)	-	48.02820 (0.066)
	600	55.16	55.16828 (0.015)	-	55.07170 (0.160)
	700	61.12	61.30454 (0.301)	-	61.09226 (0.045)
	800	66.14	66.27642 (0.206)	-	66.18547 (0.069)
	900	70.39	70.31098 (0.112)	-	70.44933 (0.084)
	1000	74.02	73.84828 (0.233)	-	73.98184 (0.052)
	1100	77.13	77.54131 (0.530)	-	-
Mean absolute deviation			(0.3553)	-	(0.1164)

** present work equation { coefficients used in equation are listed in table (5) } .

References

- 1- Al-Saadi , S.H.M., "Prediction of Latent Heat of Vaporization for some Chemical Substances by Using Three Parameters Law of Corresponding States", *M. Sc. Thesis* , University of Saddam , Baghdad , Iraq (1994) .
- 2- American Petroleum Institute Research Project 44, Thermodynamic Research Center, Department of Chemistry, "Selected Values of Properties of Hydrocarbons and Related Compounds " , Texas University (1970) .
- 3- Stull , D.R., Westrum , Jr.E.F. and Sinke , G.C., "The Chemical Thermodynamics of Organic Compounds " , Wiley , New York (1969) .
- 4- Pitzer , K. S. and Gwinn , W. D. , *J. Chem. Phys.* , **10** , 428 (1942) .
- 5- Dean , D.W. and Chelikowsky , J R., "First principles calculations of the thermodynamic properties of silicon clusters", Department of chemical engineering and material science, Minnesota supercomputer institute, university of Minnesota (1997) .
- 6- Pitzer , K. S. and Scott , D.W. , *J. Am. Chem. Soc.* , **65** , 803 (1943) .
- 7- Pitzer , K. S. , Taylor , W. J. , Wagman , D. D. , Williams , M.G. and Rossin , F. D. , *J. Res. Natn. Bur. Stand.* , **37** , 95 (1946) .

- 8- John C. , "Interpretation of Infrared Spectra, a Practical Approach", Encyclopedia of Analytical Chemistry , pp.10815–10837, John Wiley & Sons Ltd, Chichester, (2000) .
- 9- Lewis , G. N. and Randall , M. , " Thermodynamics " , Revised by K. S. Pitzer and L. Brewer , 2nd Edition , McGraw-Hill , New York (1961) .
- 10- 10-Smith , J. M. , Van Ness , H. C. and Abbott , M. M. , "Introduction to Chemical Engineering Thermodynamics " , Fifth Edition , McGraw-Hill , New York (1996) .
- 11-Yaws , C. L., Ni, H.M. and Chang , P.Y. , "Heat Capacities for 700 Compounds" , Chemical Engineering , **91** (1988) .
- 12- Baily , J.E. and Gallaway , T.R., "Toward Automated a Priori Calculation of Thermophysical Properties " , **490** , Chem. Tech. , August (1972) .
- 13- McBride , B.J., Gordon, S. and Reno, M.A., "Coefficients for Calculating Thermodynamic and Transport Properties of Individual Species", NASA Report TM-4513 , October (1993) .
- 14- Rihani , D. N. and Doraiswamy , L. K. , *Ind. Eng. Chem. Fundamentals* , **4** , **17** (1965)

إستخدام البيانات الطيفية لحساب السعة الحرارية لبعض المركبات الأروماتية

الخلاصة

تضمن البحث حساب السعة الحرارية بثبوت الضغط لستة من المركبات (العطرية) الأروماتية و هي [البنزين (البنزول) ، أثيل-البنزين (أثيل - البنزول) ، التولوين، والزاييلينات (أورثو- زاييلين، ميتا- زاييلين، و بارا- زاييلين)] بالإعتماد على قيم البيانات الطيفية لهذه المركبات و بإستخدام النموذج التذبذبي المتوافق . تم التعبير عن القيم المحسوبة كدالة لدرجة الحرارة و لمدى حراري واسع من (100 K) و لغاية (1100 K) ، و بمقارنة القيم المحسوبة بالإعتماد على البيانات الطيفية و القيم الناتجة من المعادلات التي تعبر عن السعة الحرارية كدالة لدرجة الحرارة (إعتماداً على البيانات الطيفية أيضاً)، مع القيم العملية كانت النتائج مقاربة جداً .