Calculation of Enthalpy and Entropy of Gases by Modified R.K. Equation of State

Article *in* Hungarian Journal of Industry and Chemistry · January 1981

3 authors, including:

Andjelka N. Mihajlov
University of Novi Sad
122 PUBLICATIONS   **321** CITATIONS

Some of the authors of this publication are also working on these related projects:

Project   Serbia Sustainable Development & Green Economy (Rio+20/SDGs) View project

Project   Environmental Listening View project

CALCULATION OF ENTHALPY AND ENTROPY OF GASES BY MODIFIED REDLICH–KWONG EQUATION OF STATE

A. Mihajlov*, B. Djordjević and A. Tasić

(Department of Chemical Engineering, Faculty of Technology
and Metallurgy, University of Belgrade, 1100 Belgrade,
Karnegieva 4, Yugoslavia and *Faculty of Technology,
University of Novi Sad, 21000 Novi Sad, Vlejka Vlahovića 2,
Yugoslavia)

Enthalpy and entropy of pure nonpolar, slightly polar and polar gases (carbon monoxide, propylene, hydrogen sulphide and ammonia) were calculated by two different procedures. One of them is based on the original Redlich–Kwong (RK) equation of state and the other on the RK equation with optimal parameters (for each isotherm separately — Ω_{cal}, and as temperature dependent values — Ω_{cor}).

2063 P-v-T data points of 124 isotherms were used to compute enthalpy and entropy of four investigated substances, with respect to the ideal gas reference state. Values of the properties, calculated by two procedures, were compared with experimental and smoothed results.

Introduction

Reliable thermodynamic properties of fluids are necessary for the appropriate design and rational operation of chemical processes. Since these data are not often readily available, especially for polar substances, considerable effort has been expended to increase the accuracy of the methods used for their analytical prediction.

Values of enthalpy and entropy are used in making equilibrium calculations and heat balances in reactors, separation equipment, heat exchangers, and power cycles, etc. These thermodynamic properties are becoming of increasing interest in geothermal, coal and other related technology. In this sense, the development of predictive methods for the properties mentioned above is of particular significance. The use of an equation of state, among which Redlich–Kwong's and their modifications represent a very popular two-parameter model, is one of the most suitable approaches.

In previous papers the capability of the Redlich–Kwong (RK) equation of state for correlating and predicting the thermodynamic properties was

demonstrated, such as compressibility factors [1, 2], heat capacities [3, 4] and second virial coefficients [5] of various substances using optimal values of the constants obtained for each available isotherm of P-v-T data. In this work the study of evaluation of thermodynamic properties is continued and attention is focused on the calculation of enthalpy and entropy of some nonpolar, slightly polar and polar gases.

Data reduction

The ability of the RK equation to predict volumetric, phase equilibrium and other properties was considered [7–10].

The RK equation of state (6) is as follows:

$$Z = \frac{v}{v-b} - \frac{a}{RT^{1.5}(v+b)} \tag{1}$$

where the constants a and b are related to the critical proterties by:

$$a = \Omega_a R^2 T_c^{2.5}/P_c \tag{2}$$

$$b = \Omega_b RT_c/P_c \tag{3}$$

REDLICH and KWONG recommended two universal dimensionless constants for Ω_a and Ω_b which are valid for all temperatures and pressures. For the conditions of critical point $(\partial P/\partial v)_{Tc} = (\partial^2 P/\partial v^2)_{Tc} = 0$ they obtained $\Omega_a = 0.4275$ and $\Omega_b = 0.08664$. However, it is now generally accepted that these parameters are temperature dependent and vary from substances to substances.

The method used in this study was proposed previously [1–3] as follows. Parameters Ω_a and Ω_b of RK equation were determined from P-v-T data of gases at each available isotherm separately (Ω_{cal}). For each temperature, the optimal values of these dimensionless parameters were found. The NEWTON-RAPHSON procedure [11] was used to minimize the objective function F defined by:

$$F = \sum_{i=1}^{n} (Z_{exp} - Z_{cal})_i^2 \tag{4}$$

where Z_{exp} stands for the values of factor compressibility obtained from P-v-T data, and Z_{cal} stands for the right hand side of Eq. (1). As shown in the cited articles, in all cases the proposed method was to be preferred to the results of other applied modifications of RK equation.

Enthalpy and entropy of investigated gases were evaluated by two different procedures. One of them was based on the original RK equation with constants which require the critical data of compounds (Eq. 2 and 3) and the other one with optimal parameters for each available isotherm. Enthalpy and entropy were estimated according to the original RK equation by:

$$H_{RK} = H_0 + \frac{1.5a}{T^{0.5}b} \ln \frac{v}{v+b} + RTZ + \frac{1.5a}{T^{0.5}b} \ln \frac{v_0+b}{v_0} - RTZ_0 \tag{5}$$

$$S_{RK} = S_0 + Rln \frac{v-b}{v_0-b} + \frac{0.5a}{T^{1.5}b} \ln \frac{v(v_0+b)}{v_0(v+b)} \tag{6}$$

Enthalpy and entropy obtained with optimal parameters were calculated by:

$$H = H_{RK} + FH$$
$$S = S_{RK} + FS \tag{7}$$

where FH and FS are as follows:

$$FH = -RT^2 (\partial b / \partial T) \left(\frac{1}{v-b} - \frac{1}{v_0 - b} \right) - \frac{T^{0.5}}{b} (\partial a / \partial T) \ln \frac{v(v_0 + b)}{v_0(v + b)} +$$

$$+ \frac{aT^{0.5}}{b^2} (\partial b / \partial T) \left(\ln \frac{v(v_0 + b)}{v_0(v + b)} + \frac{b}{v+b} - \frac{b}{v_0 + b} \right) \tag{9}$$

$$FS = -RT (\partial b / \partial T) \left(\frac{1}{v-b} - \frac{1}{v_0 - b} \right) - \frac{1}{bT^{0.5}} (\partial a / \partial T) \ln \frac{v(v_0 + b)}{v_0(v + b)} +$$

$$+ \frac{a}{b^2 T^{0.5}} (\partial b / \partial T) \left(\ln \frac{v(v_0 + b)}{v_0(v + b)} + \frac{b}{v+b} - \frac{b}{v_0 + b} \right) \tag{10}$$

In these expressions, H_0 and S_0 are given with respect to the ideal gas reference state. To calculate H and S by means of the modified method, the parameters Ω_a and Ω_b were considered two way: as established values at available isothermal conditions — for each isotherm separately (Ω_{cal}), and as temperature dependent parameters given by corresponding temperature correlations (Ω_{cor}).

The functions Ω_{cor} depend on $T_R (T_R = T/T_c)$. For each gas individually, in therms of two ranges of temperature ($T_R < 1$ and $T_R \geq 1$), the following empirical fitting of Ω_{cor} applied on the Ω_a and Ω_b:*

$$\Omega = C_0 T_R + C_1 T_R^2 + C_2 T_R^3 + C_3 T_R^6 \tag{11}$$

$$\Omega = C_0 + (C_1 / T_R) + (C_2 / T_R^2) + (C_3 / T_R^3) \tag{12}$$

$$\Omega = \frac{C_0}{T_R} + \frac{C_1}{T_R^2} + \frac{C_2}{T_R^3} + \frac{C_3}{T_R^6} \tag{13}$$

$$\Omega = C_0 + \frac{C_1}{1 - T_R} + \frac{C_2}{(1 - T_R)^2} + \frac{C_3}{(1 - T_R)^3} \tag{14}$$

$$\Omega = C_0 + C_1(1 - T_R) + C_2(1 - T_R)^{1/3} + C_3(1 - T_R)^{2/3} \tag{15}$$

$$\Omega = C_0 + C_1 \left(1 - \frac{1}{T_R} \right) + C_2 \left(1 - \frac{1}{T_R} \right)^{1/3} + C_3 \left(1 - \frac{1}{T_R} \right)^{2/3} \tag{16}$$

$$\Omega = T_R^{1.5} \left(\frac{C_0}{T_R} + \frac{C_1}{T_R^2} + \frac{C_2}{T_R^3} + \frac{C_3}{T_R^6} \right) \tag{17}$$

The coefficients C_0, C_1, C_2 and C_3 were determined by means of the least squares method. For tested gases: carbon monoxide, propylene, hydrogen sulphide and ammonia their values are listed in *Table 1*. The P-v-T data are collected from literature [12–15].

---

* In this consideration, the following correlations are included for comparison purposes: $\Omega = C_0 + C_1 T_R + C_2 T_R^2 + C_3 T_R^5$ and $\Omega = C_0(1 - T_R) + C_1(1 - T_R)^2 + C_2(1 - T_R)^3 + C_3(1 - T_R)^6$. However, in all cases these relations did not give satisfactory results.

Table 1.

Coefficients of equations (11)—(17)

SUBSTANCE	μ (debyes)	Number of data points	Number of isotherms	Ref.	$T_R<1$ Ω_a $^{(a)}$	$T_R<1$ Ω_a $C_j^{(c)}$	$T_R<1$ Ω_b $^{(a)}$	$T_R<1$ Ω_b $C_j^{(c)}$	$T_R=1$ Ω_a $^{(a)}$	$T_R=1$ Ω_a $C_j^{(c)}$	$T_R=1$ Ω_b $^{(a)}$	$T_R=1$ Ω_b $C_j^{(c)}$
Carbon-monoxide	0.10	496	22	12	(15)^b 0.21×10^{-2}	0.428 191	(14) 0.41×10^{-6}	0.084 702 25	(13) 0.54×10^{-4}	−1.190 624	(16) 0.41×10^{-6}	0.086 732 32
						5.684 563		0.002 556 05		6.414 374		−0.044 792 46
						1.943 668		−0.000 821 6		−5.917 375		−0.041 359 11
						−6.486 775		0.000 072 7		1.123 073		0.088 609 38
Propylene	0.35	737	50	13	(16) 0.25×10^{-2}	−6.524 891	(13) 0.83×10^{-2}	−1.413 908	(16) 0.61×10^{-3}	−6.524 891	(12) 0.15×10^{-4}	0.093 057 86
						24.491 15		2.281 383		24.491 15		0.000 434 66
						−21.101 12		−0.773 392 6		−21.101 12		0.000 015 626
						3.566 014		−0.029 555 1		3.566 014		0.000 000 07
Hydrogen sulphide	0.93	436	58	14,15	(17) 0.43×10^{-3}	6.392 852	(13) 0.13×10^{-2}	3.869 417	(12) 0.28×10^{-2}	2.579 578	(14) 0.54×10^{-8}	0.086 686 5
						−13.652 54		−8.751 409		−9.059 434		0.000 005 2
						8.175 424		5.335 808		13.143 69		0.000 002 37
						−0.495 5399		−0.373 809 8		−6.248 141		0.000 000 14
Ammonia	1.46	493	14	12	(11) 0.49×10^{-3}	28.268 77	(14) 0.58×10^{-3}	0.090 129 47	(16) 0.19×10^{-4}	0.427 8759	(16) 0.11×10^{-6}	0.086 641 71
						−77.014 49		−0.005 647 11		−0.695 8895		−0.151 073 1
						57.153 91		0.000 503 18		−0.422 5502		−0.116 093 8
						−7.974 042		−0.000 005 8		0.930 0377		0.234 312 6

$(a) = \sum_{i=1}^{n}(\Omega_{cal}-\Omega_{cor})_i^2$, (b) = all brackets refer to the correlation equations $(11)\div(17)$, $(c)=C_j$, $j=0, 1, 2, 3$ coefficients of equations $(11)-(17)$

Table 2.

Mean absolute deviation in enthalpy and entropy for four investigated gases

Substance	T_R min	T_R max	$\delta H(\%)$ RK	$\delta H(\%)$ SB	$\delta H(\%)$ OhAR	$\delta H(\%)$ RK (Ω_{cal})	$\delta H(\%)$ RK (Ω_{cor})	$\delta S(\%)$ RK	$\delta S(\%)$ SB	$\delta S(\%)$ OhAR	$\delta S(\%)$ RK (Ω_{cal})	$\delta S(\%)$ RK (Ω_{cor})
Carbonmonoxide	0.62	5.06	0.56	1.3	1.3	1.296	1.182	0.61	0.60	0.61	0.554	0.562
Propylene	0.91	1.43	0.48	0.49	0.51	0.486	0.492	0.20	0.23	0.29	0.213	0.306
Hydrogen sulphide	0.92	2.62	0.67	0.77	0.89	0.982	0.988	0.23	0.24	0.49	0.591	0.583
Ammonia	0.74	1.43	3.6	3.3	3.6	3.467	2.110	1.5	0.91	1.5	0.908	0.917

Results and discussion

The Ω_{cal} and Ω_{cor} were used to evaluate the enthalpy and entropy. The calculated results were compared with the original RK equation, where constants a and b were treated as universal values. The results for gases mentioned above are summarized in *Table 2*. In addition to these treatments, the SIMONET and BEHAR [16] and CHAUDRON, ASSELINEAU and RENON [17] modifications were also included in the analysis. All comparisons in this *Table* were realized for the same arbitrarily selected isotherms of volumetric and enthalpy and entropy data.

Table 2 indicates that all procedures give good agreement between the calculated and observed values of enthalpy and entropy. Howeveer, as indicated in the previous paper [1], factor compressibilities of some substances calculated by the original RK, SB and ChAR equations were considerably worse than those obtained by this method. Consequently these poor results were not reflected in the enthalpy and entropy calculations. Total mean absolute percentage deviation between calulated and experimental results was 1.14 and 0.56 for enthalpy and entropy respectively, when original RK parameters were used. When the properties were calculated employing optimal RK parameters (Ω_{cal}), the corresponding deviations for enthalpy and entropy were 1.16 and 0.51. Deviations for enthalpy and entropy using Ω_{cor} were 1.07 and 0.51 respectively. In the case of the SB and ChAR equations, the errors in H were
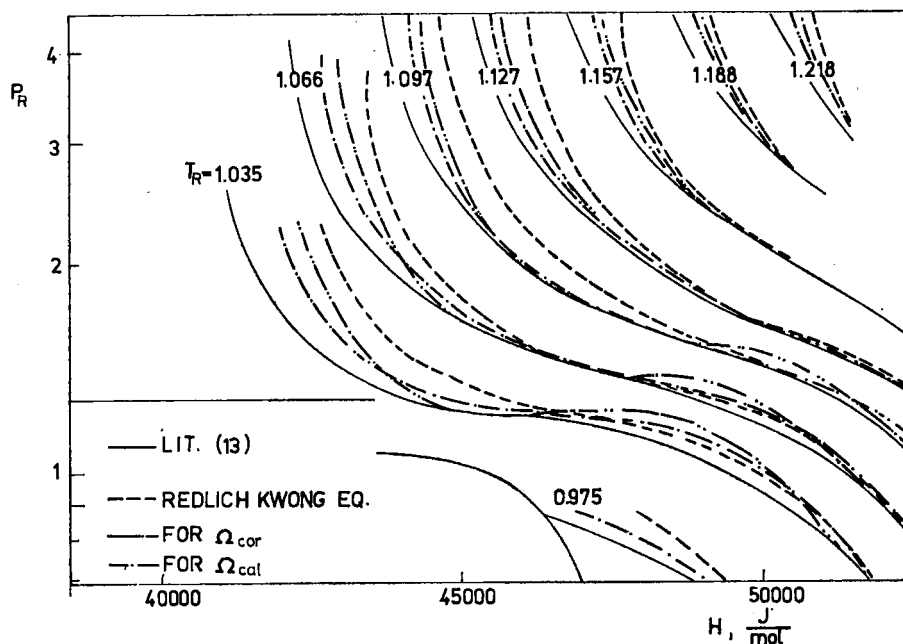

Fig. 1.

Enthalpy of Propylene. ———— denotes literature values [13]

1.46% and 1.56% respectively. Deviations for S were 0.50% and 0.73%, respectively.

In order to illustrate the validity of the proposed methods the predicted values of enthalpy and entropy are graphically given in *Fig. 1–3.*

From the results obtained for enthalpy and entropy of nonpolar and slightly polar gases, it could be concluded that this method does not improve its

Table 3.

Absolute deviation in enthalpy and entropy for isotherms in the vicinity
of the critical point up to $P_{R_{max}}$

Substance[a]	T_R	$P_{R_{max}}$	$\delta H(\%)$		$\delta S(\%)$	
			RK	RK (Ω_{cal})	RK	RK (Ω_{cal})
Carbon monoxide	1.002	5.794	6.212	1.206	0.537	0.967
Propylene	1.035	2.643	2.940	2.281	0.711	0.964
Ammonia	0.995	1.714	47.664	6.775	3.701	2.702

(a) Available pressure of Hydrogen sulphide is not sufficiently high.
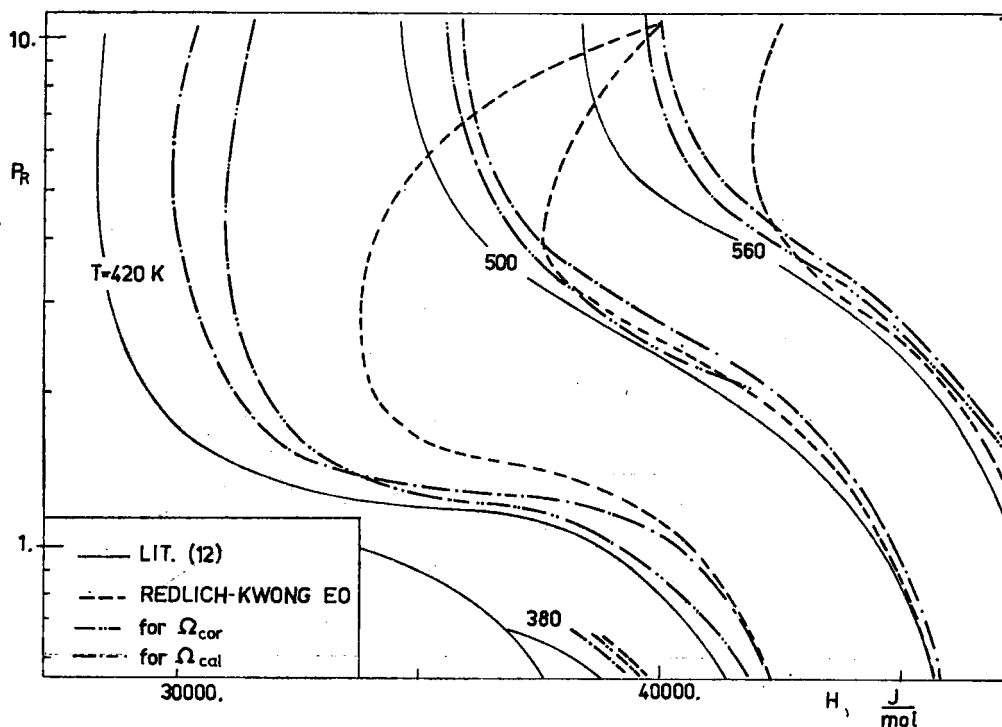
Fig. 2.

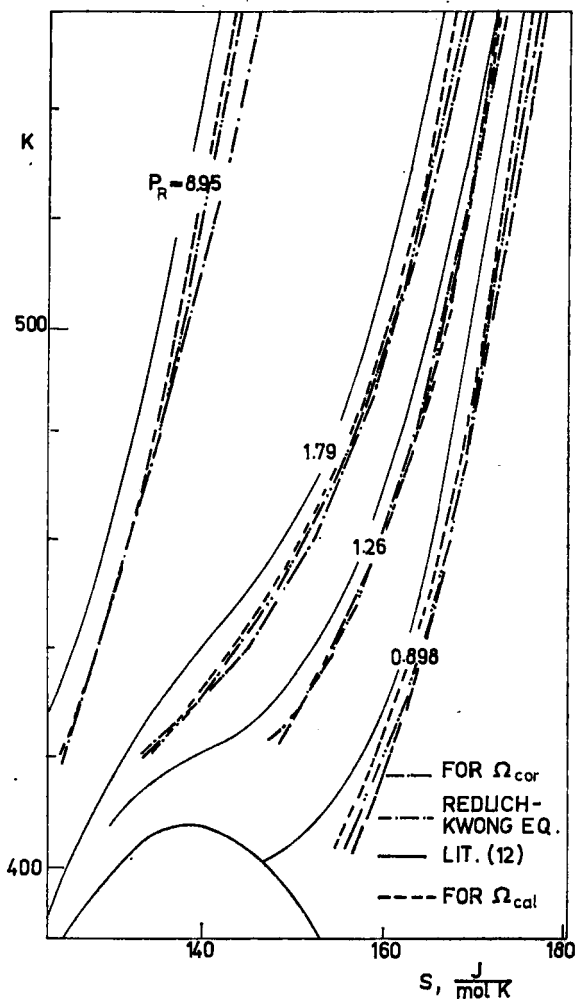Enthalpy of Ammonia. ———— denotes literature values [12]

Fig. 3.

Entropy of Ammonia. ———— denotes literature values [12]

capability over the original form of RK equation. The exception is ammonia which is a polar compound.

Although the calculated results for enthalpy are not represented in detail, from *Table 3* it can be noticed that this procedure with calculated parameters (Ω_{cal}) is preferred to the results of the original RK equation at high pressures and in the critical, very sensitive region. When the calculated entropy, obtained on the basis of Ω_{cal} values, were compared with those evaluated by the original RK equation, the results were comparable and satisfactory.

On the other hand, when this procedure with correlated parameters (Ω_{cor}) was applied to the temperature in the vicinity of the critical point, in some

cases (for CO, $T_R = 0.926$ and 1.002 and for NH_3, $T_R = 0.986$) the results obtained indicated that the derivatives of the dimensionless parameters with respect to temperature were too sensitive for the evaluation of enthalpy and entropy. For this reason, these isotherms were excluded from consideration.

Conclusions

The REDLICH–KWONG equation of state is suitable for enthalpy and entropy calculations of nonpolar, slightly polar and polar gases, regardless of whether original or modified form with optimal temperature dependent parameters are applied. However, for a highly polar compound, such as ammonia, better results are obtained with the modified form.

The procedure used in this work for correlation equations of the dimensionless parameter Ω_a and Ω_b in function of T_R produces only a small loss of accuracy in the calculation of thermodynamic properties mentioned above.

SYMBOLS

a, b parameters of REDLICH–KWONG equation of state
C_0, C_1, C_2, C_3 coefficients of Equations (11)—(17)
F objective function
H enthalpy
n number of data points
P pressure
R universal gas constant
S entropy
T temperature
v molar volume
Z compressibility factor

Greek symbols

Ω_a, Ω_b — dimensionless parameters of the REDLICH-KWONG equation

Subscripts

c critical property
o property given with respect to the ideal gas reference state
R   reduced property
RK   property given with respect to the original REDLICH-KWONG equation of state

REFERENCES

1. DJORDJEVIĆ, B. D., MIHAJLOV, A. N., GROZDANIĆ, D. K. TASIĆ, A. Ž. and HORVATH, A. L.: Chem. Eng. Sci., *1977*, 32, 1103.
2. MIHAJLOV, A. N.: Evaluation on Modified Constants in the Redlich–Kwong Equation of State. Correlation of P-v-T Data of Pure Nonpolar and Polar Gases. M.S. thesis, Faculty of Technology and Metallurgy, University of Beograd, 1977.
3. DJORDJEVIĆ, B. D., MIHAJLOV-DUDUKOVIĆ, A. N. and TASIĆ, A. Ž.: Chem. Eng. Sci., *1980*, 35, 752.

4. DJORDJEVIĆ, B. D., MIHAJLOV-DUDUKOVIĆ, A. N., JOVANOVIĆ, S. DJ. and TASIĆ, A. Ž.: Applicability of the RK Equation of State with Temperature Dependent Parameters to the Evaluation of Heat Capacity of Gaseous Ammonia and Carbon Monoxide, 2nd Yugoslav–Italian–Austrian Chemical Engineering Conference, Bled (Yugoslavia), 1980. Proc. Symp., u. 29–35.
5. DJORDJEVIĆ, B. D., MIHAJLOV-DUDUKOVIĆ, A. N. and TASIĆ, A. Ž.: A.I.Ch.E. Journal, *1980*, 26, 858.
6. REDLICH, O. and KWONG, J. N. S.: Chem. Rev., *1949*, 44, 233.
7. DJORDJEVIĆ, B. D., MIHAJLOV, A. N., GROZDANIĆ, D. K., TASIĆ, A. Ž. and MALIĆ, D.: Chem. Ind (Beograd), *1975*, 29, 291.
8. TSONOPOULOS, C. and PRAUSNITZ, J. M.: Cryogenics, *1969*, 9, 315.
9. HORVATH, A. L.: Chem. Eng. Sci., *1974*, 29, 1334.
10. MIHAJLOV-DUDUKOVIĆ, A. N., DJORDJEVIĆ, B. D. and TASIĆ, A. Ž.: Calculations of the Thermodynamic Properties of Real Gases and Liquids by Modified RK Equation of State, Advances in Separation Science, Trieste (Italy), 1978. Proc. Symp., p. 200–209.
11. ROSENBROOK, H. H. and STOREY, C.: Computational Techniques for Chemical Engineers. Pergamon Press, Oxford. 1966.
12. DIN, F.: Thermodynamic Functions of Gases, Butterworths, London. 1956.
13. VAUGHAN, W. E., GRAVES, N. R.: Ind. Eng. Chem., *1940*, 32, 1252.
14. REAMER, H. T., SAGE, B. H. and LACEY, W. N.: Ind. Ent. Chem., *1950*, 42, 140.
15. WEST, J. R.: Chem. Eng. Progr., *1948*, 44, 287.
16. SIMONET, R. and BEHAR, E.: Chem. Eng. Sci., *1976*, 31, 37.
17. CHAUDRON, J. ASSELINEAU, L. and RENON, H.: Chem. Eng. Sci., *1972*, 38, 839.

РЕЗЮМЕ

В сообщении описаны различные методы расчета энтальпии и энтропии чисто неполярных менее шплярных и полярных газов/двуокись углерода, пропилен, сероводород и аммония). Первый метод основан на оригинальном уравнении состояния РЕДЛИХА—КВОНГ-а (РК), а второй метод на уравнении РК с оптимальными параметрами/значения-Ω_{cal} для всех изотерм, а значения-Ω_{cor} зависящие от температуры).

Для расчета энтальпии и энтропии четырех исследованных газов использованы 2063 p-V-T данных 124 изотерм.

BIOCIDES FROM HALOGENATED BENZENES. I.

SOME NEW SUBSTITUTED ANALIDES OF DICHLOROBENZENE SULPHONIC ACIDS AND THEIR BIOCIDAL ACTIVITIES

A. Marei,* M. M. A. El-Sukkary,** F. I. El-Dib**
and O. H. El-Sayed***

(* Chem. Dept., Riyadh University, Riyadh, Saudi Arabia,
** Petrochem. Dept., Petroleum Research Institute, Cairo, Egypt.
and *** Chem. of Microorganisms Lab., National Research
Centre, Cairo, Egypt.)

Six different substituted anilides from every dichlorobenzene sulpho-
nyl chloride isomer were prepared and their bactericidal and fungicidal
activities were screened. The relation between their toxicity and their
chemical structure was investigated.

Introduction

It was established that toxicity to bacteria and fungi can result from two aryl
groups linked by —SO_2—NH— bridge [1–3]. In the present investigation,
it was planned to synthesize a number of such compounds, to screen their
toxicity towards microorganisms and to study their variation with the chemi-
cal structure.

Experimental

Preparation of 2,3-dichlorobenzene sulphonyl chloride

2,3-Dichloronitrobenzene was prepared according to [4, 5]. It was reduced to
2,3-dichloroaniline [6] which was diazotized and its diazonium compound was
treated with a saturated solution of SO_2 in glacial acetic acid containing
$CuCl_2$ [7] to produce the title compound, b.p. 124 °C/15 mm Hg, n_D^{20} 1.5919.
$C_6H_3O_2Cl_3S$, Calculated: C 29.35; H 1.23; Cl 43.32; S 13.06
          Found: C 30.05; H 1.11; Cl 43.71; S 13.12
IR absorption: (wave length im cm^{-1}) 1,460 for 1,2,3-trisubstituted aromatic
nucleus, 840 for C—Cl, 1,185 and 1,360 for SO_2—Cl.

Preparation of 3,4-,2,5 and 2,4-dichlorobenzene sulphonyl chlorides

These were prepared as in [8]. The starting materials (*a*), solvent (*b*), reaction temp. and time (*c & d*) and the products (*e*) are:

(a)	(b)	(c)	(d)	(e)
1,2-dichlorobenzene	CHCl₃	180 °C	16 hrs	3,4-dichlorobenzene sulphonylchloride
1,4-dichlorobenzene	CHCl₃	150 °C	1 hrs	2,5-dichlorobenzene sulphonylchloride
1,3-dichlorobenzene	CHCl₃	18 °C	4 hrs	2,4-dichlorobenzene sulphonylchloride

Preparation of 2,6-dichlorobenzene sulphonylchloride

2,6-Dichloroaniline was prepared from sulphanilamide according to [9]. It was then diazotized and converted into 2,6-dichlorobenzene sulphonyl chloride as given in [7].

Preparation of 3,5-dichlorobenzene sulphonyl chloride

3,5-dichlorobenzene sulphonamide was prepared according to [7] and on treating with ClSO₃H and SOCl₂, 3,5-dichlorobenzene sulphonyl chloride was obtained.

Preparation of N-substituted dichlorobenzene sulphonamides

Equimolecular amounts (0.05 mol.) of each dichlorobenzene sulphonyl chloride isomer and the used amine (*o, m, p*-anisidenes, *o, m, p*-phenetedines) were mixed and heated with vigorous stirring at 60–70 °C; NaOH solution (0.05 mol., 0.7 N) was then added dropwise over a period of $^1/_2$ hour. Heating and stirring were continued for a further $^1/_2$ hour. On cooling, a solid product separated, it was filtered, washed with dilute HCL and with water, dried and finally crystallized from aqueous ethanol, *Tables 1–6.*

Antibacterial and antifungal activities of the prepared compounds

The cup-plate method (10) was adopted with some modification:

a) The spore suspension of the test organism was prepared in inoculating flasks; each contained 50 ml of sporulating medium of the following composition (g/1): peptone, 3.0, meat extract, 3.0 and distilled water 1,000 ml.

The flasks were incubated for 6 days at 30 °C on a rotary shaker, then pasteurized at 80 °C for 10 minutes, this can be used for any spore forming bacteria, but in the case of nonsporulating bacteria, this technique can also be allowed without pasteurization after the sixth day of incubation.

b) A solid medium containing the following ingredients (g/1); peptone 6.0; yeast extract 3.0; meat extract 1.5; glucose 1.0; and agar 15.0 was sterilized and divided while hot (50–60 °C) in 15 ml portions among sterile petri-dishes of 9 cm diameter.

c) One ml of the spore suspension was placed on the surface of the cold solid medium in the petri-dishes and spread over the surface.

Table 1.

No. of comp.	Nomenclature	M.P. °C
I_1	N-o-anisyl-2,4-dichloro-benzene sulphonamide	122-3
I_2	N-m-anisyl-2,3-dichloro-benzene sulphonamide	133-4
I_3	N-p-anisyl-2,3-dichloro-benzene sulphonamide	145-6
I_4	N-o-phenetyl-2,3-dichloro-benzene sulphonamide	124-5
I_5	N-m-phenetyl-2,3-dichloro-benzene sulphonamide	120-1
I_6	N-p-phenetyl-2,3-dichloro-benzene sulphonamide	118-9

Table 2.

No. of comp.	Momenclature	M.P. °C
II_1	N-o-anisyl-3,4-dichloro-benzene sulphonamide	94-5
II_2	N-m-anisyl-3,4-dichloro-benzene sulphonamide	164-5
II_3	N-p-anisyl-3,4-dichloro-benzene sulphonamide	87-8
II_4	N-o-phenetyl-3,4-dichloro-benzene sulhponamide	82-3
II_5	N-m-phenetyl-3,4-dichloro-benzene sulphonamide	72-3
II_6	N-p-phenetyl-3,4-dichloro-benzene sulphonamide	110-1

Table 3.

No. of comp.	Nomenclature	M.P. °C
III_1	N-o-anisyl-2,5-dichloro-benzene sulphonamide	111-2
III_2	N-m-anisyl-2,5-dichloro-benzene sulphonamide	110-1
III_3	N-p-anisyl-2,5-dichloro-benzene sulphonamide	96-7
III_4	N-o-phenetyl-2,5-dichloro-benzne sulphonamide	136-7
III_5	N-m-phenetyl-2,5-dichloro-benzene sulphonamide	128-9
III_6	N-p-phenetyl-2,5-dichloro-benzene sulphonamide	109-10

Table 4.

No. of comp.	Nomenclature	M.P. °C
IV_1	N-o-anisyl-2,4-dichloro-benzene sulphonamide	112-3
IV_2	N-m-anisyl-2,4-dichloro-benzene sulphonamide	111-2
IV_3	N-p-anisyl-2,4-dichloro-benzene sulphonamide	98
IV_4	N-o-phenetyl-2,4-dichloro-benzene sulphonamide	137
IV_5	N-m-phenetyl-2,4-dichloro-benzene sulphonamide	129
IV_6	N-p-phenetyl-2,4-dichloro-benzene sulphonamide	110-11

Table 5.

No. of comp.	Nomenclature	M.P. °C
V_1	N-o-anisyl-2,6-dichloro-benzene sulphonamide	145-6
V_2	N-m-anisyl-2,6-dichloro-benzene sulphonamide	118-9
V_3	N-p-anisyl-2,6-dichloro-benzene sulphonamide	116-7
V_4	N-o-phenetyl-2,6-dichloro-benzene sulphonamide	97-8
V_5	N-m-phenetyl-2,6-dichloro-benzene sulphonamide	134-5
V_6	N-p-phenetyl-2,6-dichloro-benzene sulphonamide	106-7

Table 6.

No. of comp.	Nomenclature	M.P. °C
VI_1	N-o-anisyl-3,5-dichloro-benzene sulphonamide	77-8
VI_2	N-m-anisyl-3,5-dichloro-benzene sulphonamide	121-2
VI_3	N-p-anisyl-3,5-dichloro-benzene sulphonamide	78-9
VI_4	N-o-phenetyl-3,5-dichloro-benzene sulphonamide	102-3
VI_5	N-m-phenetyl-3,5-dichloro-benzene sulphonamide	117-8
VI_6	N-p-phenetyl-3,5-dichloro-benzene sulphonamide	149-50

d) The test substances were dissolved in a few drops of acetone, then completed to the appropriate volume with distilled water to make colloidal suspensions of different concentrations which were 50, 100, 200, 500, 1,000 and 2,000 μg/ml.

e) In a petri-dish containing the culture of one of the chosen microorganisms seven small pits were made in positions widely separated from each other. These were marked on the bottom of the dish. One of these pits was filled with acetone and water mixture as a blank test and the other pits were filled with the solutions of the test substances with different concentrations. The petri-dishes were incubated at 5 °C for 1–2 hours to permit good diffusion and then trasferred to an incubator at 28 °C for 4–8 hours. Methylene blue was added to the medium before solidification to give more definite and restricted zones. The inhibition zone is transparent blue, in contrast to the background, which is opaque due to the thin or thick growth of the organism. The zone of inhibition was well defined and the margin between it and the bacterial growth was sharp, allowing easy measuring of the diameter.

The activity of each of the prepared substances against four microorganisms representing gram + ve and − ve bacteria, fungus and yeast (Bacillus subtilis, Escherichia coli, Aspergillus niger and Candida albicans respectively) was first investigated. The activity of the test substances at different concentrations towards any test organism was expressed as follows:

$$+ + + \text{at concentration of} \quad 50 \quad \text{μg/ml}$$
$$+ + \text{at concentration of} \quad 100-500 \quad \text{μg/ml}$$
$$+ \text{at concentration of} \quad 1,000-2,000 \quad \text{μg/ml}$$

If no activity was noticed with a solution of 2,000 μg/ml concentration, the substance was considered inactive and this inactivity was expressed with −. The substances with activity of the order + + + or + + towards any of these four organisms (Tables 7–10) were then screened with the other six species of bacteria and yeast in the same manner *(Tables 11–16)*.

Discussion

The six isomers of dichlorobenzene sulphonyl chlorides were prepared. Each sulphonyl chloride was converted to six anilides with the following structure:

$R_1 = o\text{-}$ or $m\text{-}$ or $p\text{-OMe}$; $o\text{-}$ or $m\text{-}$ or $p\text{-OEt}$
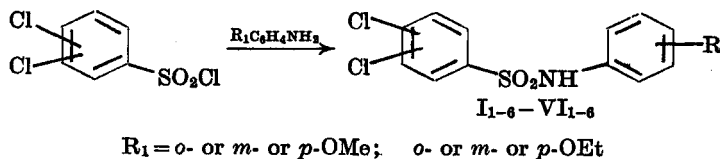
The chemical structure of the prepared new compounds was elucidated by microanalysis and infrared light absorption measurement. The compounds which have analogous structure, absorbed this light at nearly the same wave lengths. The following results were obtained from some compounds which can be considered as representatives of their classes in the present work.

Table 7.

Toxicity to B. subtilis

$R_1 =$

Position of Cl_2		o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3-	I	–	–	–	–	–	–
3.4-	II	–	–	+++	+	+++	–
2.5-	III	–	–	+	–	–	–
2.4-	IV	–	+	–	–	–	–
2.6-	V	–	–	–	–	–	–
3.5-	VI	–	++	+	–	+++	–

Table 8.

Toxicity to Escherichia coli

$R_1 =$

Position of Cl_2		o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3-	I	–	–	–	–	–	–
3.4-	II	–	–	–	–	–	–
2.5-	III	–	–	–	–	–	–
2.4-	IV	–	–	–	–	–	–
2.6-	V	++	–	–	–	–	–
3.5-	VI	–	–	+	–	++	–

Table 9.

Toxicity to Aspergillus niger

$R_1 =$

Position of Cl_2		o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3-	I	–	–	–	–	–	–
3.4-	II	–	–	–	+	–	–
2.5-	III	–	–	–	–	–	–
2.4-	IV	–	–	–	–	–	–
2.6-	V	–	–	–	–	–	–
3.5-	VI	–	–	–	–	+	–

These two tables show that Cl_2 is inactive in all positions.

a) The Table indicates that Cl_2 is active in the positions 3,4- & 3,5-.

b) Comparison of VI2 with VI5 shows m-OEt > m-OMe inactivity.

Table 10.

	Toxicity to Candida albicans $R_1 =$					
Position of Cl_2	o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3- I	—	—	—	—	—	—
3.4- II	—	—	—	—	—	—
2.5- III	—	—	—	—	—	—
2.4- IV	—	—	—	—	—	—
2.6- V	—	—	—	—	—	—
3.5- VI	—	—	—	—	—	—

All compounds were found non-toxic to this organism.

Table 11.

	Toxicity to Bacillus cereus $R_1 =$					
Position of Cl_2	o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3- I						
3.4- II			+++		+++	
2.5- III						
2.4- IV						
2.6- V	—					
3.5- VI		++			+++	

Table 12.

	Toxicity to Microccus sp. $R_1 =$					
Position of Cl_2	o-OMe 1	m-OMe 2	p-OMe 3	o-OEt 4	m-OEt 5	p-OEt 6
2.3- I						
3.4- II			+++	+	++	
2.5- III						
2.4- IV						
2.6- V	++					
3.5- VI		++			+++	

From these two Tables it can be seen that

a) Cl_2 is active in positions 3,4- and 3,5-
b) Vi_2 and Vi_5 show m-OEt > m-OMe inactivity.