Determination of Henry's Law Constants of Organics in Dilute Aqueous Solutions

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Henry's law constants of 15 volatile organic compounds in dilute aqueous solutions were measured by the procedure of equilibrium partitioning in a closed system. The method is based upon the measurement of the headspace concentration by gas chromatography. The compounds investigated included six halogenated hydrocarbons, four aromatic hydrocarbons, and five alkanes. The measurements were made at three temperatures between 25 and 45 °C. The measured Henry's law constants compared well with the literature data of some liquids. The temperature dependence of Henry's law constant was also studied from the van't Hoff relation.

Introduction

Accurate knowledge of Henry's law constants, H, or air/water partitioning coefficients are required to predict the behavior of organic compounds in the environment. In particular, when the compounds are relatively volatile and exhibit low solubility in water, air stripping may be a viable method for above-ground treatment. Compounds which exhibit these characteristics are certain chlorinated and methylated hydrocarbons, commonly used as solvents, which also tend to be responsible for some pervasive ground water contamination problems (*1*). However, accurate measurements of Henry's law constants for some of these compounds are rare in the literature.

Henry's law constants have been calculated from vapor pressure and solubility data (*2–4*) or determined experimentally (*2, 5, 6*). However, most commonly, these are also determined by equilibrating an aqueous solute across an air/water interface in either a static (*5*) or a dynamic system (*6*). In the latter category, an innovative static headspace method referred to as equilibrium partitioning in closed systems (EPICS) has been used (*7, 8*) frequently to measure the Henry's law constants of volatile organic compounds. The EPICS method is based on a comparison of the headspace concentration of a volatile compound in two systems at equilibrium which are identical in the mass of the compound but not identical in the volumes of the gas and liquid phases. Henry's law constants can thus be derived from the ratio of headspace concentrations and volumetric data (*7, 8*). In the present paper, we report the experimental measurements for 15 organics from halogenated compounds to hydrocarbons including both aromatic and saturated aliphatic compounds.

Experimental Section

Aldrich HPLC grade chemicals were of guaranteed reagent grade and were used directly from fresh bottles without further purification. The certified minimum purities of these chemicals were 99+ mol %. A gas chromatographic analysis of them showed major peak areas of more than 99.9%. Water was deionized and distilled in an all-glass distillation unit prior to use.

A saturated stock solution for each individual compound was prepared by adding the compound in an amount in excess of its solubility to distilled water in amber glass septum bottles. All stock solutions were allowed to equilibrate for at least two weeks before use to ensure complete equilibration. For compounds less dense than water the stock solution was transferred to a 250-mL separatory funnel at least 48 h before use. Aliquots were then withdrawn from the bottom of the separatory funnel for preparation of the EPICS samples. However, for compounds more dense than water, the aliquots of the solution were withdrawn directly from bottles.

To prepare EPICS samples, three pairs of 250-mL amber glass bottles were filled with 20 and 200 mL of distilled water, respectively. The same volume of saturated stock solution was then added to each of the six bottles. To ensure that the concentration range of the EPICS samples was within the region where Henry's law is applicable (i.e., dilute solutions of approximately 10 mg/L in the 200-mL system), a general rule was used to control the volume added (*9*). For high-concentration stock solutions, 1 mL was chosen as the lower limit for addition to the EPICS bottles. For low-concentration stock solutions, 10 mL was chosen as the upper limit to be added. The following equation was used:

$$V \cong 2000/S \qquad (1)$$

where V is the volume of stock solution to be added (mL) and S is the aqueous solubility of the chemical (mg/L). For example, the solubility of heptane is 50 mg/L at 25 °C; then according to eq 1, 40 mL of the stock solution should be used to make the EPICS sample. However, applying the rule mentioned above, only 10 mL of the stock solution, i.e., the upper limit, was used to make the EPICS samples of heptane.

The bottles were sealed with a silicone rubber septum cap with a Teflon liner facing toward the bottle headspace. These liners were used only once to prevent adsorption of the test compound into the silicone rubber once the liner had been pierced. The loaded bottles were shaken vigorously and then placed in a constant temperature water bath for at least 48 h, during which time the bottles were shaken periodically. After equilibration, headspace samples were withdrrawn from the bottles by using a gas-tight syringe and injected into a Varian 3300 gas chromatograph. The GC conditions were so controlled that the retention time for most of the compounds was within 0.5–1 min. From the observed peak areas of the GC experiments, the dimensionless Henry's law constants,

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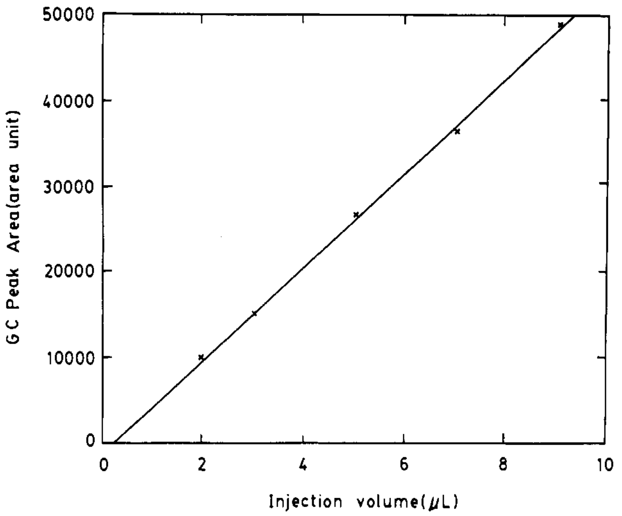

Figure 1. GC detector response linearity check for *trans*-1,2-dichloroethylene at 25 °C.

H_c (m^3 of liquid/m^3 of gas), were calculated as (*7, 8*)

$$H_c = \frac{(C_{g1}/C_{g2})V_{l1} - V_{l2}}{V_{g2} - (C_{g1}/C_{g2}) - V_{g1}} \quad (2)$$

where the symbols C and V represent, respectively, the concentration of the organic compound present and the volume of the gas (g) or liquid (l) phase. The subscripts 1 and 2 identify the two closed systems, namely, bottles containing EPICS samples with 20 and 200 mL of water, respectively. The only experimental information needed to determine H_c is, therefore, the ratio of gas-phase concentrations (C_{g1}/C_{g2}) in the two systems, and the values of absolute concentrations are not necessary because any proportional measure of concentration (such as GC peak areas) yields the desired headspace concentration ratio in eq 2.

The principle requirement for a successful application of the method is that the instrument response must be linear throughout the concentration range of interest. Therefore, the instrument response was examined in the beginning of the experiment with three compounds, namely, *trans*-1,2-dichloroethylene, toluene, and cyclohexane. These compounds were chosen because they represent the types of compounds selected, namely, halogenated compounds, aromatics, and alkanes. The linearity of the detector response was confirmed using a sample with a constant headspace concentration and then injecting varying volumes of samples. The detector response was found to be linear with respect to the volume injected as shown in Figures 1–3 with a correlation coefficient of better than 0.95 in all cases.

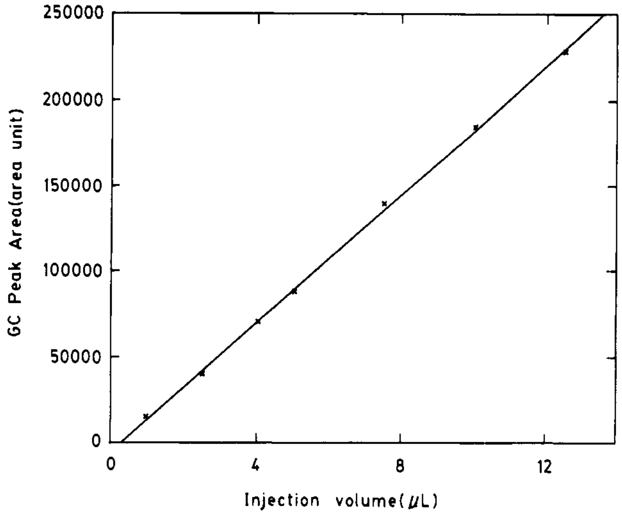

Figure 2. Same as in Figure 1 for cyclohexane at 25 °C.

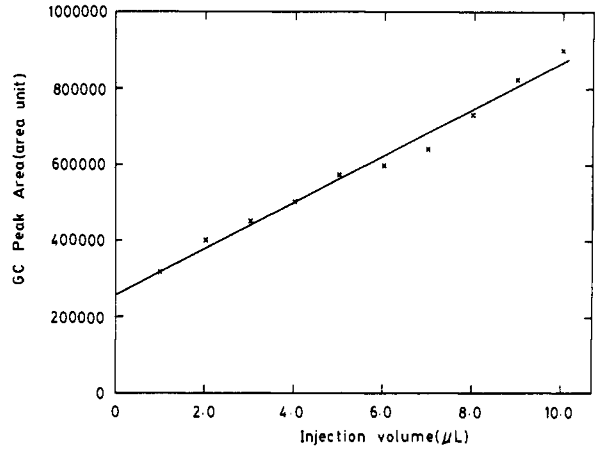

Figure 3. Same as in Figure 1 for toluene at 25 °C.

Table I. Comparison of Henry's Law Constants (*H*) with the Literature

compound	t/°C	H/(kPa·m^3·mol^{-1}) this study	H/(kPa·m^3·mol^{-1}) lit. (*8*)
benzene	29	0.649	0.661
carbon tetrachlorde	27.6	3.313	3.374
cyclohexane	27.9	16.617	19.961
toluene	28.5	0.722	0.768

Results and Discussion

Henry's law constants for 15 compounds which included 6 halogenated hydrocarbons, 5 alkanes, and 4 aromatic compounds, in dilute aqueous solution, were measured at three temperatures ranging from 25 to 46 °C. In order to test the validity of the EPICS procedure, four compounds, namely, benzene, toluene, cyclohexane, and carbon tetrachloride, for which the Henry's law constants are available in the literature (*8*) were used. Another reason for selecting these liquids is that they reflect a complete range of Henry's law constants to be determined. Since our experimental temperatures were somewhat different from those of Asworth et al. (*8*), the literature data given in Table I were corrected with the temperature regression equation. Good agreement is seen between the present data and those of Asworth et al. (*8*). The Henry's law constant of cyclohexane is high (16.617), while those of benzene and toluene are low (~0.65) and that of carbon tetrachloride is intermediate (3.313). The differences in the values of Henry's law constants result in a range of headspace concentration that must be measured accurately in order to calculate these data.

The results of Henry's law constants for the six halogenated compounds chosen in this study as given in Table II vary from 0.08 for 1,1,2-trichloroethane at 26.2 °C to 6.343 for carbon tetrachloride at 45 °C, the exception being that of hexachlorobenzene for which H varies from 26 to 29 kPa·m^3·mol^{-1}. It is found that, for the H values falling in this range for the compound mentioned above, equilibrium conditions are readily obtained and the EPICS method is quite satisfactory. Due to the low solubility of hexachlorobenzene (0.005 g/m^3) as compared to octane (0.66 g/m^3) and 1,1,1-trichloroethane (720 g/m^3), its headspace concentration is very low, thereby possibly introducing an error. This seems to be true when we compare our data with those of Mackay et al. (*2*).

The Henry's law constants of four aromatic hydrocarbons are in the range of 0.704–2.422 except 2-methylnaphthalene, which exhibits a range of H values from 20.265 to 26.243

Table II. Henry's Law Constants (*H*) and Coefficient of Variation

compound	$t/°\mathrm{C}$	$H/(\mathrm{kPa{\cdot}m^3{\cdot}mol^{-1}})$	CV^a (%)
Halogenated Compounds			
bromobenzene	30.0	0.256	2.76
	35.0	0.332	7.29
	44.8	0.579	4.97
carbon tetrachloride	27.6	3.313	0.52
	35.0	4.550	1.53
	45.0	6.343	3.01
trans-1,2-dichloroethylene	26.2	1.023	4.50
	35.0	1.591	2.57
	46.1	2.087	3.33
hexachlorobenzene	26.0	26.243	3.50
	46.0	29.587	10.00
1,1,1-trichloroethane	26.3	1.763	2.27
	35.0	2.412	3.86
	44.8	3.232	4.99
1,1,2-trichloroethane	26.2	0.082	5.29
	35.8	0.184	4.36
	44.8	0.259	4.08
Aromatic Compounds			
cumene	28.0	1.323	5.78
	35.0	1.547	11.37
	46.1	2.422	6.73
2-methylnaphthalene	26.0	20.265	6.54
	35.8	22.900	8.14
	46.0	26.243	6.28
p-xylene	27.0	0.856	9.06
	35.8	1.189	4.86
	46.0	1.576	4.57
1,2,4-trimethylbenzene	27.0	0.704	7.40
	35.0	1.135	4.29
	45.0	1.591	5.22
Alkanes			
cyclopentane	27.9	16.617	1.19
	35.8	24.318	2.96
	45.0	30.398	1.78
methylcyclohexane	27.3	12.666	2.13
	35.8	34.653	7.13
	45.0	72.447	7.80
2-methylhexane	26.9	51.878	5.43
	35.0	31.512	4.93
	45.0	25.939	5.43
n-heptane	26.0	91.294	7.31
	35.8	121.083	9.41
	45.0	193.024	7.17
n-octane	27.9	39.213	5.31
	35.0	93.827	4.82
	45.0	167.693	9.01

[a] Percent coefficient of variation = 100 (standard deviation/mean).

$\mathrm{kPa{\cdot}m^3{\cdot}mol^{-1}}$. For *p*-xylene, our measured value of *H* agrees well with the reported value of Ashworth et al. (*8*) which is 0.85 at 27 °C. The Henry's law constants of alkanes are in the range of 12.666–193.024 (kPa $\mathrm{m^3}$)/mol. These values are higher than those of both halogenated and aromatic compounds. It may be noted that the *H* of 2-methylhexane decreases as the temperature increases. To the best of our knowledge, there are no published data available to compare the present results. Table II also contains data of the percent coefficient of variation (CV) defined as the ratio of the standard deviation to the average value. The CV values vary generally in the range of maximum up to 5% and rarely, but in some cases, up to about 10%. Furthermore, chemicals exhibiting low values of *H* will have a tendency to accumulate in the aqueous phase, while those with high values will partition more into the gas phase. Notice that chemicals used in this study cover a wide volatility range and vary in chemical type and structure. This can be taken as an indication that the EPICS technique is broadly applicable. However, its accuracy may not be as high as that of obtaining H_c from vapor pressure and solubility measurements (*2–6*).

Table III. van't Hoff Parameters and Standard Errors of Equation 3

compound	A	B	$d \times 10^2$
bromobenzene	−5341 ± 346	16 ± 1.11	1.97
carbon tetrachloride	−3553 ± 230	13 ± 0.74	2.61
trans-1,2-dichloroethylene	−3396 ± 602	11 ± 1.96	9.38
1,1,1-trichloroethane	−3120 ± 93	11 ± 0.30	1.58
1,1,2-trichloroethane	−5901 ± 1158	17 ± 3.36	16.10
cumene	−3269 ± 564	11 ± 1.84	6.97
2-methylnaphthalene	−1234 ± 44	7 ± 0.14	0.70
p-xylene	−3072 ± 173	10 ± 0.56	2.29
1,2,4-trimethylbenzene	−4298 ± 686	14 ± 2.24	8.44
cyclopentane	−3351 ± 633	14 ± 2.03	7.63
methylcyclohexane	−9406 ± 1046	34 ± 3.39	11.76
2-methylhexane	3608 ± 1088	−8 ± 3.53	14.51
n-heptane	−3730 ± 686	17 ± 2.22	9.41
n-octane	−8014 ± 1617	30 ± 5.25	20.30

Table IV. Comparison of Values of Henry's Law Constants for Halogenated Compounds

		$H/(\mathrm{kPa{\cdot}m^3{\cdot}mol^{-1}})$	
compound	$t/°\mathrm{C}$	this study	lit. (*8*)
carbon tetrachloride	27.6	3.313	3.374
	35.0	4.550	4.651
	45.0	6.343	6.971
trans-1,2-dichloroethylene	26.2	1.023	1.064
	35.0	1.591	1.408
	46.1	2.087	1.966
1,1,1-trichloroethane	26.3	1.763	1.844
	35.0	2.412	2.553
	44.8	3.232	3.275
1,1,2-trichloroethane	26.2	0.082	0.107
	35.8	0.184	0.177
	44.8	0.259	0.295

It has been suggested (*10, 11*) that the temperature dependence of *H* follows the van't Hoff relationship:

$$\ln\{H/(\mathrm{kPa{\cdot}m^3{\cdot}mol^{-1}})\} = A/(T/K) + B \qquad (3)$$

The parameters *A* and *B* of eq 3 were obtained by a linear regression, and these are summarized in Table III along with the uncertainty values and standard errors. Table III, therefore, describes the data as a temperature regression equation coupled with a temperature-dependent error term based on 95% confidence limits. The error can be expressed as either the upper and lower limits in absolute terms (Henry's law constant units) or the upper and lower percentage limits. An examination of the standard deviations, σ, given in Table III reveals good correlation for most of the chemicals examined, but acceptable results have not been achieved for a few compounds.

As shown in Table IV, at 45 °C the results of Ashworth et al. (*8*) and Gossett (*12*) are higher than the present results; however, below 35 °C the values generally agree. It may be noted that the regression parameters of Ashworth and Gossett were obtained for the temperature interval of 10–30 °C. The discrepancies among the results around 45 °C may be attributed to differences in the experimental temperatures under which the regression parameters were determined. Since the linear relationship between *H* and temperature is only an assumption, extrapolation with the previous equation may not be valid. Therefore, the experimental results around 45 °C seem to be more accurate than those predicted from previous equations. The comparison of van't Hoff plots for *trans*-1,2-dichloroethylene and 1,1,1-trichloroethane is shown in Figures 4 and 5, respectively.

Conclusions

The Henry's law constants determined in this study are of acceptable accuracy as evidenced by comparison with the previously reported data and also by linear variation with

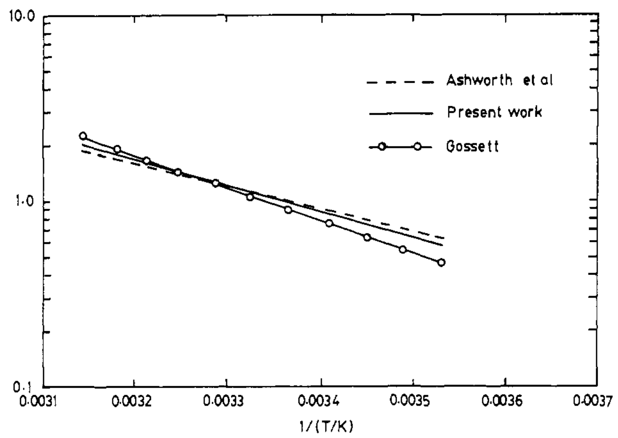

Figure 4. Temperature dependence of Henry's law constants (*H*) for *trans*-1,2-dichloroethylene.

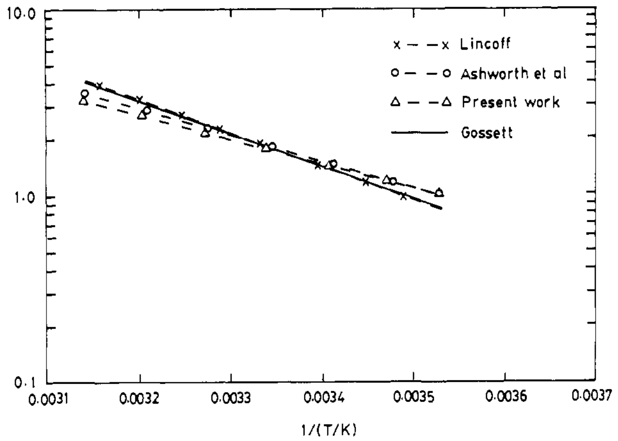

Figure 5. Temperature dependence of *H* for 1,1,1-trichloroethane.

increasing temperature. However, the value for hexachlorobenzene is questionable. This is attributed to a very low solubility of the compound which results in a very low headspace concentration. These concentrations cannot be measured reliably with a flame ionization detector. Probably, a more sensitive GC detector such as the electron capture detector would be an acceptable alternative for the chlorinated compounds which give extremely low headspace concentrations.

The EPICS procedure used here is a simple method for the determination of Henry's law constants of volatile organic compounds. The errors associated with the EPICS method vary with the values of the Henry's law constants. However, for halogenated and aromatic compounds, the values are small but acceptable. For alkanes, the values are high and associated errors are usually large. Thus, more care should be taken while using the resultant *H* values for alkanes.

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Appendix. Calculation of Henry's Law Constants

The Henry's law constant, *H*, is conveniently expressed as a ratio of the partial pressure, P_i, in the vapor (in various units such as Pa, atm, or Torr) to the concentration in the liquid, C_l (also in various units such as mole fraction and mass or mole concentration or ratio), so that

$$H = P_i/C_l \tag{4}$$

The most commonly used measures of concentration are the mole fraction, *x*, and amount of substance concentration (mol·m⁻³) which yields *H* (Pa·m³·mol⁻¹). In the environmental literature, Henry's law constant is also defined as the ratio of the gas-phase solute concentration, C_g (mol·m⁻³), to the liquid-phase solute concentration. Thus,

$$H_c = C_g/C_l \tag{5}$$

where H_c is Henry's law constant in dimensionless units. The Henry's law constants reported in this paper are expressed in kPa·m³·mol⁻¹, the units typically used by the Environmental Protection Agency.

In the present study, for each measurement three pairs of headspace concentrations were obtained. To convert the concentration values into H_c (dimensionless), eq 2 was used. The calculation procedure is shown as follows.

Let *C* represent the concentration values of the 20-mL EPICS samples

$$C = c_1, c_2, c_3 \tag{6}$$

and *M* those of the 200-mL samples

$$M = m_1, m_2, m_3 \tag{7}$$

The ratio of headspace concentrations was obtained by dividing the individual c_j values (i.e., c_1, c_2, c_3) successively by m_1, m_2, and m_3 values so that nine ratios represented by R_{ij} were obtained as

$$(c_1, c_2, c_3)/\begin{pmatrix} m_1 \\ m_2 \\ m_3 \end{pmatrix} = \begin{matrix} R_{11}, R_{12}, R_{13} \\ R_{21}, R_{22}, R_{23} \\ R_{31}, R_{32}, R_{33} \end{matrix} = R \tag{8}$$

where

$$R_{ij} = c_j/m_i \quad i = 1\text{–}3, \; j = 1\text{–}3$$

Substituting *R* for C_{g1}/C_{g2} in eq 2, nine values of H_c were obtained as

$$H_c = \begin{matrix} H_{c_{11}}, H_{c_{12}}, H_{c_{13}} \\ H_{c_{21}}, H_{c_{22}}, H_{c_{23}} \\ H_{c_{31}}, H_{c_{32}}, H_{c_{33}} \end{matrix} \tag{9}$$

The final result was obtained by averaging the nine values of H_c as

$$\bar{H}_c = \frac{1}{3 \times 3} \sum_{i=j=1}^{3} H_{c_{ij}} \quad i = 1\text{–}3, \; j = 1\text{–}3 \tag{10}$$

To convert $\bar{H}_c$ into *H* in units of kPa·m³·mol⁻¹, the factor *RT* was used to multiply H_c, in which *R* is the gas constant (8.3145 Pa·m³·mol⁻¹·K⁻¹) and *T* is the experimental temperature (K).

An example is presented below for *trans*-1,2-dichloroethylene at 35 °C wherein the averages of the GC peak areas are 344 838, 348 468, and 345 652 for the 20-mL EPICS samples and 244 212.7, 243 620.7, and 245 933.3 for the 200-mL EPICS samples. Therefore, the six average values can be paired in all possible permutations of the ratios of *C* to *M* to calculate nine estimates of H_c as

$$C = 344\,838, 348\,468, 345\,652$$

$$M = 244\,212.7, 243\,620.7, 245\,933.3$$

Thus,

$$R = C/M = \begin{matrix} 1.412, 1.427, 1.415 \\ 1.415, 1.430, 1.419 \\ 1.402, 1.417, 1.405 \end{matrix}$$

Then R is processed by eq 2, and H_c is obtained by

$$H_c = \begin{matrix} 0.6234, 0.6146, 0.6214 \\ 0.6214, 0.6125, 0.6194 \\ 0.6294, 0.6205, 0.6274 \end{matrix}$$

$$\bar{H}_c = 0.6211$$

From the $\bar{H}_c$ data, the dimensionless Henry's law constant is calculated as

$$H = 0.6211 \times 8.3145 \times 318.15 \times 10^{-3}$$
$$= 1.643\ \mathrm{kPa{\cdot}m^3{\cdot}mol^{-1}}$$

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