

PREFACE

The three gases, propane, butane and 2-methylpropane are rather unusual gases and possess rather unusual solubility characteristics. First of all, at ambient conditions these gases are well below their critical temperatures and, in fact, are closer in temperature to their normal boiling points than they are to their critical temperatures. The normal boiling points, and critical temperatures are respectively: for propane 231, 370 K, for 2-methylpropane 261, 408 K, and for butane 273, 425 K. Secondly, their solubilities are extremely high in non-polar solvents but, in contrast, they are relatively low in highly polar solvents such as water. The term "high solubility" has usually been reserved for solubilities in which the quantity of dissolved gas at a gas partial pressure of 101.325 kPa exceeds about 5 mole percent. In fact, particularly for butane and 2-methylpropane at low temperatures, solubilities in excess of 50 mole percent and even 80 mole percent solute in the saturated solution have been observed. In these cases the solvent becomes the minor component in the saturated solution, and the Ostwald coefficient expressing the solubility may be in the order of 500 volumes of gas to one volume of solvent¹.

The solubilities of propane, butane and 2-methylpropane increase dramatically as the temperatures are reduced toward the respective boiling points of the liquefied gases. As a result, the temperature-solubility relation is more complex and is more difficult to represent mathematically than for most other gases. Further, as for vapor-liquid equilibria, the composition corresponding to pure gas is an extension of the solubility relation¹. That is, if solubility experiments are performed at a constant total pressure of 101.325 kPa, then as the temperature is reduced toward the normal boiling point, the compositions of both the gas and liquid phases approach that of the pure gas. Thus the normal boiling point, corresponding to the composition of the pure liquefied gas can be considered as one point on the solubility curve for that particular gas in all solvents, provided that the solvents still exist as miscible liquids at the temperatures concerned. It is apparent that gas solubilities at 101.325 kPa cannot be measured for those solvents whose freezing point temperatures are higher than the normal boiling points of the liquefied gases.

For the treatment of solubility data corresponding to a gas partial pressure of 101.325 kPa, true gas molar volumes are required. Particularly for butane and 2-methylpropane, the deviation from ideality is as high as 5 percent. To aid in the work of reviewing solubility data, the second virial coefficients for the three gases as obtained from Dymond and Smith² were fitted by simple exponential functions and found to describe that data well. In the truncated form, the virial equation of state is:

$$PV / (RT) = 1 + B/V \quad (1)$$

The equation which may be used to successfully correlate virial coefficient data for many gases and vapors has the following form:

$$B = a T^b \quad (2)$$

When Equation (1) is used in estimating the gas molar volume, a quadratic equation for molar volume results:

$$V = C/2 + 0.5 (C^2 + 4BC)^{0.5} \quad (3)$$

$$C = RT/P \quad (4)$$

The resulting constants for the three cases for use in Equation (2), the percentage deviations in B and V, as well as the temperature ranges for which the equations apply, are shown in Table 1. Whereas the maximum deviation in B is 2.9 percent, the maximum deviation of the molar volume is 0.11 percent. It is noted that the correlation for the virial coefficients breaks down near the Boyle temperature and is useful only in the temperature range in which the second virial coefficients are negative. There are two advantages in using the above correlation for the second virial coefficients: interpolation to any arbitrary temperature is simplified, and the equation for the second virial coefficients can be easily incorporated in a computational sequence whereas tabulated information cannot.

A consistency check of the solubility data for high pressures was devised. It involves plotting the mole fraction solubility versus the partial pressure of solute on log scales. On such a graph the solubility - partial pressure relation is often nearly linear; a slope of unity is obtained if Henry's law is obeyed. Solubilities obtained at high pressures can be extrapolated to atmospheric pressure so that a comparison with solubilities actually measured at atmospheric pressure can be readily made. Equally useful is an extrapolation of solubility data obtained at one temperature to the higher pressure corresponding to the vapor pressure of pure liquefied solute gas. Interpolation between solubility isotherms

Table 1: Calculation of Second Virial
Coefficients and Gas Molar Volumes

For Propane: $B = -1.246 (10^8) T^{-2.224} \text{ cm}^3/\text{mole}$

/K	B(ref.2)	B(calc.)	B, % Diff.	V(ref.2)	V(calc.)	V, % Diff.
240	-640	-634	1.0	19032	19039	0.04
300	-382	-386	1.0	24230	24226	0.02
350	-276	-274	0.8	28442	28444	0.01
400	-208	-203	2.2	32615	32619	0.01
500	-124	-123	0.1	40906	40906	-
550	- 97	-100	3.3	45036	45033	0.01

For Butane: $B = -7.985 (10^8) T^{-2.436} \text{ cm}^3/\text{mole}$

250	-1170	-1151	1.7	19269	19269	0.11
300	-722	-738	2.2	23874	23857	0.07
360	-472	-473	0.3	29062	29061	-
400	-370	-366	1.0	32450	32454	0.1
500	-219	-213	2.9	40810	40816	0.02
560	-164	-161	1.6	45789	45792	0.01

For 2-Methylpropane: $B = -1.403 (10^9) T^{-2.542} \text{ cm}^3/\text{mole}$

273.2	-900	-899	0.1	21475	21476	-
303.2	-687	-690	0.4	24170	24167	0.01
360.9	-441	-443	0.4	29170	29168	-
406.9	-326	-326	-	33058	33058	-
477.6	-218	-217	0.4	38973	38973	-
510.9	-184	-183	0.5	41740	41741	-

Gas molar volume, V , in cm^3/mole .

Gas constant taken as: $R = 82.06 \text{ cm}^3 \text{ atm}/(\text{mole K})$

also appears possible with reasonable accuracy. Refer to the section "Alkane solvents at high pressure" for an example of the solubility-pressure diagram based on data reported by Reamer and Sage³ for the solubility of propane in decane.

When solubility data at 101.325 kPa pressure were available over a temperature range, the solubility was usually expressed as a function of temperature using an equation having one of the following forms:

$$\ln x_1 = a + b / (T/K) \quad (5)$$

$$\ln x_1 = a + b \ln (T/K) \quad (6)$$

$$\ln x_1 = a + b / (T/K) + c \ln (T/K) \quad (7)$$

The constants for the equations were determined by means of a regression analysis; then one of the equations was chosen on the basis of its being the best representation of the particular data. Smoothed values for mole fraction solubility as shown in some of the compiled sheets were obtained by means of the regression equation and may not be accurately extrapolated beyond the temperature range of the data on which the equation is based.

It is readily apparent from an examination of the pages of this volume, that in only a very few instances are data available indicating within narrow limits the solubility of any of the gases in a particular solvent. In many instances there is a wide discrepancy between data from two or more sources. In many other instances data are simply not available to draw any general conclusions. Perhaps a useful function of this compilation is to draw attention to the real shortage of accurate solubility data for propane, butane and 2-methylpropane in most solvents.

To permit maximum use of data as they become available, it is recommended that authors include an analysis of both the gas and liquid phases in future publications for solubilities of highly soluble gases. The vapor pressure of a volatile solvent containing a significant quantity of dissolved gas cannot usually be accurately determined by simple calculation. Nor can the true molar volume of gas saturated with solvent vapor be accurately calculated without auxiliary information. Finally, Henry's law cannot generally be expected to apply with good accuracy for gas solubilities as high as those for propane, butane and 2-methylpropane. If for any reason it is not possible to measure phase compositions, the raw data, at the actual conditions of measurement, should be included to permit useful comparisons by other workers who may be able to correct the

data for phase non-idealities at a later date. When only the results, extrapolated to a gas partial pressure of 101.325 kPa, are reported, it becomes impossible to make any subsequent corrections to the data. The gas molar volumes and solvent vapor pressures and densities that were used in the calculations would also be most helpful.

As may also be apparent, there is a considerable delay between the time that data from the technical literature are initially compiled and subsequently evaluated, and the time the volume is published in its final form. Hence, some data appearing in the very recent literature have not been included in this volume. Included in this volume are data appearing in the technical literature to the end of 1983. It has not been possible to process data from some few papers which contain solubilities of propane, butane or 2-methylpropane gases appearing in 1984.

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