CHROM. 15,762

Note

Effect of gas-phase non-ideality on the concentration of standard gaseous mixtures prepared by the saturation method

MICHAL ROTH*, JIŘÍ VEJROSTA and JOSEF NOVÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 61142 Brno (Czechoslovakia)

(Received February 9th, 1983)

In the development of analytical methods it is often necessary to prepare gaseous mixtures with known concentrations of standard substances. Usually the mixtures comprise a carrier gas (N_2, air, Ar, He) and the vapours of organic substances that are liquids and/or solids at ambient temperature. For this purpose, the saturation method has proved to be very advantageous, as it yields a continuous stream of a standard mixture, while enabling a reliable calculation and setting of the concentration of the reference substance in the mixture from its saturation vapour pressure and the ratio in which the saturated stream is diluted by a stream of pure carrier gas. In the saturator, the reference substance is present in its normal bulk form, or as a coating on the surface of an inert support.

The saturation of a stream of gas with vapours of volatile substances has been applied to various purposes, in addition to the preparation of standard gaseous mixtures[1–3], *e.g.*, the measurement of second cross-virial coefficients[4,5], saturation vapour pressures[6–8] and enthalpies of vaporization[9] of substances of low volatility.

Until now, applications of the saturation principle to the preparation of gaseous standard mixtures and to the measurement of saturation vapour pressures have usually disregarded the effects due to the non-ideality of the gaseous phase in the saturator. However, in the measurement of enthalpies of vaporization[9], both gas-phase non-ideality and the effect of pressure on the fugacity of the liquid phase were taken into account, assuming the solubility of the carrier gas in the liquid phase to be negligible. As the substances studied showed very low volatilities at the operating temperatures, relationships were derived only for the case of infinite dilution of the substances in the saturated (equilibrium) gaseous mixture. However, in the preparation of standard gaseous mixtures, *e.g.*, for calibration purposes, we usually work with substances having considerably high vapour pressures, so that it is necessary to consider also the concentration of the vapour of the reference substance in the gaseous mixture as a variable in order to estimate the effect of the non-ideal behaviour of the saturated gaseous mixture on its composition.

THEORETICAL

Calculation of the equilibrium composition of the gaseous mixture
 Let us consider a carrier gas (2) passing through a layer of bulk reference

substance (1) or of an inert support coated with the reference substance, which is gradually saturated with the vapour of the substance. At very low gas flow-rates through the saturator, expedient in terms of analytical applications, the composition of the saturator effluent corresponds to the equilibrium distribution of components 1 and 2 between the liquid and gaseous phases of the system. Hence, the fugacities of the reference substance in both phases are equal

$$f_{1G} = f_{1L} \tag{1}$$

and:

$$y_1 \Phi_1 P = (1 - x_2) \, \gamma_1 P_1^0 \, \Phi_1^0 \exp \left[\int_{P_1^0}^{P} (V_{1L}^0/RT) dP \right] \tag{2}$$

The meaning of the symbols is explained at the end of this article.

The pressure, P, at the saturator outlet is only slightly (a fraction of kPa) higher than the atmospheric pressure. At such pressures and usual temperatures, the solubility of carrier gases in organic liquids is generally very low, and it can be supposed that:

$$(1 - x_2) \, \gamma_1 = 1 \tag{3}$$

Liquids are practically incompressible at atmospheric pressures, so that the integral in eqn. 2 (Poynting's correction) can easily be evaluated. Under these assumptions, eqn. 2 may be simplified:

$$y_1 = (P_1^0/P) \, (\Phi_1^0/\Phi_1) \exp [V_{1L}^0 (P - P_1^0)/RT] \tag{4}$$

The dependence of the fugacity coefficients, Φ_1 and Φ_1^0, on the state variables is given by the relationships (see p. 30 of ref. 10):

$$\Phi_1 = \exp \left[(1/RT) \int_0^P (\bar{V}_{1G} - RT/P) \, dP \right] \tag{5}$$

$$\Phi_1^0 = \exp \left[(1/RT) \int_0^{P_1^0} (V_{1G}^0 - RT/P) \, dP \right] \tag{6}$$

At low pressures the behaviour of gases and gaseous mixtures can be described by the first two terms of the virial expansion with pressure as an independent variable (see Appendix A in ref. 10):

$$Z_M = 1 + B_M P / RT \tag{7}$$

The second virial coefficient of a binary gaseous mixture is given by the exact relationship:

$$B_M = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22} \tag{8}$$

Hence, in the context of the description of the behaviour of gaseous mixtures by eqn. 7, the partial molar volume of reference substance 1 in a mixture with carrier gas 2 is given by:

$$\bar{V}_{1G} = RT/P + (1 - y_2^2) B_{11} + 2 y_2^2 B_{12} - y_2^2 B_{22} \tag{9}$$

The molar volume of pure gaseous reference substance 1 is:

$$V_{1G}^0 = RT/P + B_{11} \tag{10}$$

On combining eqns. 4–6, 9 and 10, we obtain for the equilibrium mole fraction of reference substance 1 in the gaseous mixture leaving the saturator the equation:

$$a \exp [b - c(1 - y_1)^2] - y_1 = 0 \tag{11}$$

where

$$a = P_1^0 / P$$

$$b = (B_{11} - V_{1L}^0)(P_1^0 - P)/RT$$

$$c = (2 B_{12} - B_{11} - B_{22}) P / RT$$

Eqn. 11 can most easily be solved by the Newton–Raphson iteration method, the initial approximation being the mole fraction of reference substance in an ideal gaseous mixture:

$$y_1^{id} = P_1^0 / P = a \tag{12}$$

Thus, if the values of P_1^0, V_{1L}^0, B_{11}, B_{22} and B_{12} at the temperature, T, of the saturator are known, by solving eqn. 11 it is possible to estimate how the equilibrium composition of the gaseous mixture leaving the saturator differs from the ideal composition.

Example
        The procedure outlined will now be applied to several compounds of different

TABLE I

LIQUID MOLAR VOLUMES, SATURATION VAPOUR PRESSURES, SECOND VIRIAL COEF-
FICIENTS OF PURE REFERENCE SUBSTANCES AND SECOND CROSS-VIRIAL COEFFI-
CIENTS OF REFERENCE SUBSTANCE NITROGEN BINARY MIXTURES AT 303.15 °K

Reference substance	V_{1L}^0 [a] (cm^3/mol)	P_1^0 [b] (kPa)	B_{11} [c] (cm^3/mol)	B_{12} (cm^3/mol)
n-Pentane	117	82.003	−1169	− 93[d]
n-Hexane	132	24.963	−1838	−108[e]
n-Heptane	148	7.805	−2875	−121[d]
n-Octane	164	2.458	−4310	−147[d]
Benzene	82	15.916	−1582	−107[f]
Acetone	74	38.001	−1840	− 63[g]
Acetonitrile	52	14.796	−5607	−103[h]
Methanol	39	21.886	−1878	− 79[i]
Water	18	4.243[j]	−1100[k]	− 33[e]

[a] From a modified Rackett equation for the temperature dependence of molar volumes of liquids[12,13].
[b] From the Antoine equation[14].
[c] From the Tsonopoulos correlation[15].
[d] From an experimental value[16] at 40°C, using the Tsonopoulos correlation[15].
[e] Experimental value[17].
[f] Experimental value[18].
[g] From the square-well potential parameters for an acetone–nitrogen binary mixture[4].
[h] Estimated using the Tsonopoulos correlation[15] (k_{ij} set to 0.10).
[i] Interpolated from experimental data[5,19] at other temperatures.
[j] Tabulated value[21].
[k] Interpolated from experimental data quoted in ref. 20.

volatilities and polarities (dipole moments). It will be supposed that the temperature
of the saturator and the saturator outlet pressure are 303.15°K (30°C) and 98.925
kPa, respectively, and that nitrogen is used as the carrier gas. The values of
V_{1L}^0, P_1^0, B_{11} and B_{12} of the compounds studied are summarized in Table 1. The
critical data and Pitzer's acentric factors, necessary to calculate the virial coefficients
B_{11} and B_{12} by Tsonopoulos' correlation[15], were taken from Appendix A in ref. 11.
The value of the second virial coefficient of nitrogen ($B_{22} = -4$ cm^3/mol) was also
calculated by Tsonopoulos' correlation.

CONCLUSIONS

    In Table II, the mole fractions of the tested compounds in the gaseous mixture
leaving the saturator, calculated under the assumption of ideal behaviour of the
gaseous phase, y_1^{id}, are compared with the corresponding values, y_1, calculated by
eqn. 11. It is seen that, under the given conditions, the intermolecular interactions in
the gaseous phase result in an increase in the mole fraction of the reference substance
in the gaseous phase. Hence, the values of y_1^{id} suffer from a systematic negative error;
estimations of this error for the individual compounds tested are quoted in the last
column of Table II. However, when applying the saturation method to prepare cal-
ibration mixtures for trace analysis, where the gaseous mixture leaving the saturator
is diluted by a much higher concentration of pure carrier gas, the above errors may
be commensurate with those of setting the dilution ratios.

TABLE II

COMPARISON OF THE EQUILIBRIUM GAS-PHASE MOLE FRACTIONS OF REFERENCE
SUBSTANCES, CALCULATED FROM EQNS. 12 (y_1^{id}) AND 11 (y_1)

$\Delta = 100(y_1^{id} - y_1)/y_1 \quad$ (%).

Reference substance	y_1^{id}	y_1	Δ (%)
n-Pentane	0.8289	0.8353	−0.8
n-Hexane	0.2523	0.2581	−2.2
n-Heptane	0.0789	0.0806	−2.2
n-Octane	0.0248	0.0254	−2.1
Benzene	0.1609	0.1637	−1.7
Acetone	0.3841	0.3924	−2.1
Acetonitrile	0.1496	0.1553	−3.7
Methanol	0.2212	0.2253	−1.8
Water	0.0429	0.0431	−0.5

SYMBOLS

a, b, c Constants in eqn. 11
B_{11} Second virial coefficient (cm³/mol) of the pure reference substance
B_{22} Second virial coefficient (cm³/mol) of the pure carrier gas
B_{12} Second cross-virial coefficient (cm³/mol) of reference substance–carrier gas binary
B_M Second virial coefficient (cm³/mol) of a binary gas mixture
f_{1G} Gas-phase fugacity (kPa) of the reference substance
f_{1L} Liquid-phase fugacity (kPa) of the reference substance
P Pressure (kPa) at the saturator outlet
P_1^0 Saturation vapour pressure (kPa) of the reference substance
R Gas constant (8314.41 kPa cm³/mol · °K)
T Temperature (°K) of the saturator
V_{1L}^0 Molar volume (cm³/mol) of the pure liquid reference substance
V_{1G}^0 Molar volume (cm³/mol) of the pure gaseous reference substance
$\bar{V}_{1G}$ Partial molar volume (cm³/mol) of the reference substance in a mixture with the carrier gas
x_2 Liquid-phase mole fraction of the carrier gas
y_1 Gas-phase mole fraction of the reference substance
y_2 Gas-phase mole fraction of the carrier gas
Z_M Compressibility factor of a binary gas mixture
γ_1 Raoult's law activity coefficient of the reference substance
Φ_1 Fugacity coefficient of the reference substance in a mixture with the carrier gas
Φ_1^0 Fugacity coefficient of the vapour of the pure reference substance

REFERENCES

1 J. Novák, V. Vašák and J. Janák, *Anal. Chem.*, 37 (1965) 660.

2 M. Krzymien and L. Elias, *J. Phys. E*, 9 (1976) 584.

3 J. Vejrosta and J. Novák, *J. Chromatogr.*, 175 (1979) 261.

4 P. J. Hicks, Jr. and J. M. Prausnitz, *J. Chem. Eng. Data*, 26 (1981) 74.

5 H. Lazalde-Crabtree, G. J. F. Breedveld and J. M. Prausnitz, *AIChE J.*, 26 (1980) 462.

6 H. V. Regnault, *Anal. Chim.*, 15 (1845) 129.

7 S. J. Hawkes and J. C. Giddings, *Anal. Chem.*, 36 (1964) 2229.

8 J. Å. Jönsson, L. Mathiasson and A.-M. Olsson, *Acta Chem. Scand., Ser. A*, 34 (1980) 147.

9 N. Nováková and J. Novák, *J. Chromatogr.*, 135 (1977) 13.

10 J. M. Prausnitz, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 1969.

11 R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 2nd ed., 1966.

12 C. F. Spencer and R. P. Danner, *J. Chem. Eng. Data*, 17 (1972) 236.

13 C. F. Spencer and S. B. Adler, *J. Chem. Eng. Data*, 23 (1978) 82.

14 J. Dykyj and M. Repáš, *Tlak nasýtenej pary organických zlúčenín* (Saturation Vapour Pressures of Organic Compounds), Veda, Bratislava, 1979.

15 C. Tsonopoulos, *AIChE J.*, 20 (1974) 263.

16 B. W. Gainey and R. L. Pecsok, *J. Phys. Chem.*, 74 (1970) 2548.

17 C. P. Hicks and C. L. Young, *Trans. Faraday Soc.*, 64 (1968) 2675.

18 B. W. Gainey and C. L. Young, *Trans. Faraday Soc.*, 64 (1968) 349.

19 B. Hemmaplardh and A. D. King, *J. Phys. Chem.*, 76 (1972) 2170.

20 M. Rigby and J. M. Prausnitz, *J. Phys. Chem.*, 72 (1968) 330.

21 V. Sýkora, *Chemickoanalytické tabulky (Tables for Chemical Analysis)*, SNTL, Prague, 1976.