

MODIFIED APPARATUS FOR MEASURING V-L EQUILIBRIA BY STATIC METHOD

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A modified static apparatus for measuring the vapour-liquid equilibrium data is described. It is a modification of the apparatus originally proposed by Surovy and Dojcansky (1974). The construction alterations applied to the apparatus improve and simplify its functioning. It is checked on measuring three binary systems: benzene-n-heptane, cyclohexane-cyclohexanone and benzene-2-propanol. The agreement of the experimental and tabulated data proves the suitability of the apparatus for obtaining the V-L equilibrium data.

The crucial problem in measuring the saturated vapour pressures by the static method is the complete degassing of the liquid measured. Aim¹ showed that it was not possible to reach a satisfactory degassing of liquids in a real time interval on using the commonly used procedures. The recently published methods for rapid liquid degassing (Van Ness and Abbott², Aim¹, Weclawski and Bylicky³) have ensured practically thorough degassing; the disadvantage of these methods consists in their complexity.

In the apparatus described here, the degassing of the liquid sample under study as well as the measurement of saturated vapour pressure is carried out in the same part – in the equilibrium apparatus (see Experimental). The liquid degassing is performed in two-stage cycles: freezing and pumping at a high vacuum; thawing and desorption. The number of the degassing cycles required is studied on using the model system water-air.

THEORETICAL

The degassing cycles, and/or the changing state of the system in single stages, are illustrated in Fig. 1. We assume that the gas phase behaves like an ideal gas; in the first stage, it contains only incondensable gases; during evacuating, the liquid evaporation does not take place ($n_s^L = \text{const}$); after gas exhausting, in every cycle there is an identical residual pressure P_r ; cooling is rapid, without mixing, and therefore the gas reabsorption does not take place on cooling ($x_{ak} = x_{b(k+1)}$); in the low concentration region (i.e., our case), the Henry law

$$P_0 = H_0 x_0, \quad \text{at } T_0 \quad (1)$$

$$P_{bk} = H_b x_{bk}, \quad \text{at } T_b \quad (2a)$$

holds. Equation (2a) can be rewritten as follows

$$P_{bk} = H_b \frac{n_{bk}^L}{n_{bk}^L + n_s^L} \quad (2b)$$

From the balance of gas in stage "a" and "b", the relation

$$(n_{bk}^L)^2 + (n_{bk}^L) \left(\frac{H_b V^G}{RT_b} - n_{ak} + n_s^L \right) - n_s^L n_{ak} = 0 \quad (3)$$

was derived on the basis of the above-mentioned assumptions for calculating the gas amount of substance in liquid n_{bk}^L in the k -th cycle. For n_{ak} , i.e., the total amount of substance of gas in the "a" stage and the k -th cycle,

$$n_{ak} = n_{b(k-1)}^L + \frac{P_r V^G}{RT_a} \quad (4)$$

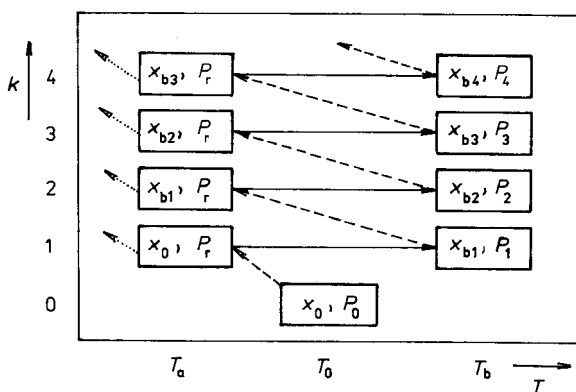


FIG. 1

State of system at the single stages of degassing cycles: solution heating (—), cooling (---), evacuating (····); P_r residual pressure, P_k partial pressure of gas in k -th cycle, T_a , T_b system temperature at stage a and b, respectively, T_0 initial temperature, x_{bk} mole fraction in k -th cycle

holds, or in the 1st cycle, we have

$$n_{a1} = \frac{1}{H_0/P_0 - 1} n_s^L + \frac{P_r V^G}{RT_a} \quad (5)$$

The analysis was applied to the model water-air system. We stemmed from the real conditions, i.e. the volumes of the liquid and vapour phases: $V^L = 1 \cdot 10^{-5} \text{ m}^3$, $V^G = 1 \cdot 10^{-5} \text{ m}^3$; the initial state of the system: $T_0 = 293 \text{ K}$, $P_0 = 100 \text{ kPa}$; temperature in the "a" stage of degassing cycle $T_a = 200 \text{ K}$. Two values of residual pressure, viz. $P_r = 10 \text{ Pa}$ and 1 Pa , temperature of desorption $T_b = 293 \text{ K}$ were chosen in the calculation.

The calculated pressures in single stages of degassing are given in Table I where the values of residual pressure and the minimum pressure are given as well. The lowest air partial pressure which can be reached in the system at temperature T_b on the assumption of a negligible solubility in liquid is calculated from the equation of state:

$$P_{\min} = P_r \frac{T_b}{T_a} \quad (6)$$

From the results of calculations (Table I) it is evident that four degassing cycles are sufficient to reach the minimum partial pressure of air in water, not only at the residual partial pressure of 10 Pa but also at 1 Pa^* .

TABLE I

Comparison of the partial pressures of gas at the temperature of desorption $T_b = 293 \text{ K}$ ($H_b = 6.72 \cdot 10^9 \text{ Pa}$) in the k -th degassing cycle with minimum partial pressures of gas P_{\min} in the model system water-air

k	$P_r = 10 \text{ Pa}$		$P_r = 1 \text{ Pa}$	
	$P_{\text{bk}}, \text{ Pa}$	$P_{\min}, \text{ Pa}$	$P_{\text{bk}}, \text{ Pa}$	$P_{\min}, \text{ Pa}$
1	2 004	14.65	1 991	1.47
2	54.2	–	41.0	–
3	15.43	–	2.25	–
4	14.65	–	1.48	–

* The number of degassing cycles needed for deaeration was calculated according to the simplified scheme. However, as the measurements showed, for the pressure drop to approximately the residual pressure of the vacuum pump, at most 1 or 2 more degassing cycles were needed in all the cases compared to the calculated 4 cycles for the water-air system.

EXPERIMENTAL

Description of Apparatus

The described modified static apparatus is made of glass. It works isothermally and/or isobarically on the same principle as the original apparatus designed by Surovy and Dojcansky⁴. It bears some design alterations which improve and simplify the apparatus functioning. The equilibrium apparatus E (Fig. 2a) is equipped with ground joint D for feeding or taking the liquid sample. The closure of the joint may be made, with respect to the system examined, of glass or Teflon. Special attention has to be paid to the tightness of the ground joint. Above the level of equilibrium vessel A, a platinum basket B is placed in which are molecular sieves (pore size 0.3 nm) for the adsorption of moisture remainders. The use of molecular sieves is needed above all with hydrophobic systems when the presence even small amounts of water may bring about, owing to its high partial pressure, an increase in pressure by several hundred Pascals.

Part of the equilibrium apparatus is placed in the fixed tempering jacket G, the equilibrium vessel A and ground joint D are equipped with fitting-on tempering jackets H1 and H2. The temperature in jacket H1 is the accurate equilibrium temperature, in jackets G and H2, the temperature 0.5 to 2 K higher is maintained to prevent the partial condensation of vapours in the upper part of apparatus. The mercury reservoir M (Fig. 2b) is located under the level of apparatus (analogy with Marsh⁵) and connected to it with a capillary. The mercury height in U-tube C is controlled by means of a system of PTFE valves F1 to F3. The thorough mixing of the liquid sample is ensured by magnetic stirrer S.

The overall assembly of the apparatus for measuring the saturated vapour pressures of solutions is depicted schematically in Fig. 3. The equilibrium apparatus proper E on the right-hand side of the diagram is connected to a precise manometer PM via valve V1 and a safety vessel. In our case, it is a mercury manometer making it possible to measure the pressure within the range of $100 - 1.5 \cdot 10^5$ Pa with an accuracy of ± 0.03 mm of the mercury column height, i.e., with the accuracy of about ± 4 Pa.

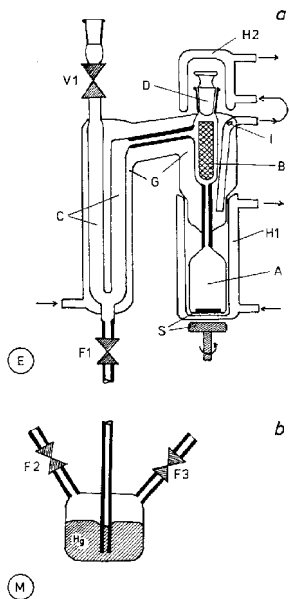


FIG. 2

Static apparatus for measuring the vapour pressure of solutions. *a* Equilibrium apparatus E, *b* mercury reservoir M. A Equilibrium vessel, B platinum basket, C U-tube, D glass ground joint, V1, F1 - F3 PTFE valves, G fixed heating jacket, H1, H2 fitting-on heating jackets, S magnetic stirrer, I vent hole

The apparatus may be connected through valves V6 and V3 with two vacuum systems. On the left-hand side of the diagram, there is the system with a higher vacuum which consists of: two-stage vacuum pump HV (or, if need be, even diffusion pump), Pirani vacuum gauge P and freezing trap S2. The second system, separated by valve V3, ensures the setting of the reference pressure and consists of oil vacuum pump LV, levelling vessel R of volume about 40 l, checking manometer CM and two valves V4 and V5.

Sample Degassing

The apparatus, excepting the equilibrium vessel, can be evacuated to a required residual pressure, as a rule 1 – 20 Pa (valves F1, F3 and V1 are closed). Approximately 10 cm³ liquid sample of a known composition is inserted into the equilibrium vessel through the filling opening with ground joint D. The apparatus is closed and the flask is immersed into the cooling mixture (solid CO₂ and acetone, or liquid nitrogen). After cooling down, the platinum gauze basket B filled with molecular sieves is inserted through opening D, and the apparatus is closed again. Valve F2 is closed and valve V1 and then valves F1 and F3 are opened. In this way the vapour space is partially degassed and simultaneously closed with the mercury sucked from vessel M. After reaching the required mercury level in U-tube C, valves F1 and F3 are closed, valve F2 is opened. The degassing is continued by heating the flask and intense mixing with magnetic stirrer S. After several minutes, the stirring is stopped and the content of flask is quickly cooled down in the cooling mixture. A portion of mercury from U-tube is let to flow to mercury reservoir M after opening valve F1, and the released air is exhausted from the vapour space. After several seconds, valve F2 is closed, and valves F1 and F3 are opened. After reaching the level in U-tube, valves F1 and F3 are closed and F2 is opened. Flask A is heated again. The degassing is repeated unless a constant difference of mercury levels in arms of internal U-manometer C is reached.

Vapour Pressure Measurement

After degassing, the measurement itself is started. The system is switched to the levelling pressure vessel R which was evacuated down to the pressure of 1 – 2 kPa. Temperatures of heating media in

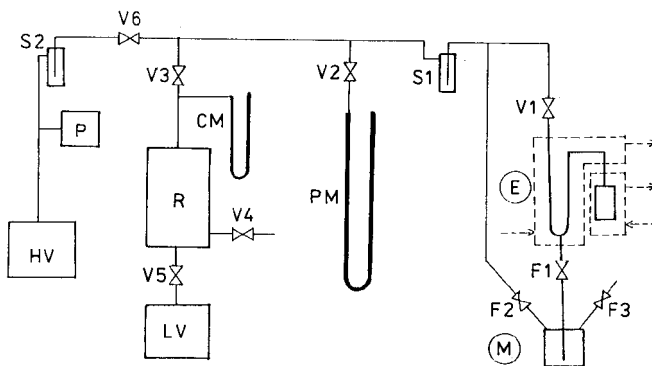


FIG. 3

Diagram of the assembly of static apparatus. E Equilibrium apparatus, M mercury reservoir, V1 to V6, F1 to F3 valves, PM precise manometer, P Pirani vacuum gauge, R vacuum tank, LV vacuum pump, CM checking manometer, HV two-stage oil vacuum pump, S1 safety vessel, S2 freezing trap

tempering mantels G, H1 and H2 are gradually increased, the liquid sample being intensively mixed. The pressure difference between the vapour space and pressure vessel R is equalized with respect to the difference of mercury levels in U-tube C, by letting in nitrogen or air to the pressure vessel R through valve V4. After tempering the solution to the required temperature, the equality of mercury levels in U-tube is checked by means of a cathetometer and as may be required, the levels are equalized via valves V4 and V5 (accuracy of level setting ± 0.03 mm). The pressure read on manometer PM is then equal to the solution vapour pressure. With respect to a small vapour space and low losses during degassing, it is possible to assume that the composition of liquid solution in the equilibrium state is practically identical with the composition of the weighed solution*.

RESULTS AND DISCUSSION

The modified static apparatus was tested by measuring the V-L equilibrium data of binary solutions with different relative volatility: benzene-n-heptane, $t = 60$ °C; cyclohexane-cyclohexanone, $t = 50$ °C and the azeotropic system benzene-2-propanol, $t = 45$ °C. The experimental data were fitted to the Wilson equation⁶. The parameters of the Wilson equation were calculated by minimizing the objective function

$$F = \sum_{m=1}^M [(P - P^C)_m]^2 \quad (7)$$

by the Gauss-Newton method. (It was assumed that the composition of the liquid phase is determined accurately). The solution vapour pressure P^C is calculated for the real liquid and ideal vapour phase, i.e.,

$$P^C = \gamma_1 x_1 P_1^* + \gamma_2 x_2 P_2^* \quad (8)$$

The calculated values of parameters of the Wilson equation and the values of mean and standard deviations in pressures corresponding to the parameters are given in Table II. The values of mean deviations of pressures are within 0.080 to 0.105 kPa, of standard deviations of pressures within 0.110 to 0.160 kPa.

For the above-mentioned binary systems, the sets of the P - x - y equilibrium data were calculated on the basis of the evaluated parameters of the Wilson equation and com-

* It has been assumed in the description of the apparatus function that the solution vapour pressure is lower than the atmospheric pressure. As a matter of fact, the apparatus is suitable even for the measuring at a mild overpressure. When the vapour pressure is higher than the atmospheric pressure, the measuring procedure is the same, only a source of overpressure is connected in front of valve V4.

pared with the published data (Gmehling et al.⁷⁻⁹). The results of the comparison are given in Tables III and IV. In Table III, the published experimental data are compared to our calculated data and to the calculated data by Gmehling et al.⁷⁻⁹. In Table IV, the mutual comparison of the data calculated by Gmehling and by us is presented. As it can be seen, the calculated set of Wilson coefficients gives in both the cases nearly comparable results, which should prove the suitability of the given method of measuring the vapour pressures for the chemical-engineering calculations.

The results of degassing are sufficient for obtaining the equilibrium data utilizable in chemical-engineering calculations. Furthermore, the static apparatus is simple and compact, the sample degassing and the measurement of vapour pressure is not too time-consuming (3 to 5 h for one measurement).

TABLE II

Values of parameters of the Wilson equation and the mean and standard deviations of calculated vapour pressures

Binary systems	Λ_{ij}	Λ_{ji}	d_p , kPa	σ_p , kPa
Benzene-2-propanol, $t = 45$ °C	0.5998	0.1838	0.126	0.160
Benzene-n-heptane, $t = 60$ °C	1.3330	0.3829	0.105	0.132
Cyclohexane-cyclohexanone, $t = 50$ °C	0.7636	0.3282	0.080	0.112

TABLE III

Comparison of the experimental equilibrium data from literature (Gmehling et al.⁷⁻⁹) with the data calculated: I on using the parameters of the Wilson equation from this work, II on using the parameters of the Wilson equation published by Gmehling et al.⁷⁻⁹

Deviation	Benzene-2-propanol $t = 45$ °C		Benzene-n-heptane $t = 60$ °C		Cyclohexane-cyclohexanone $t = 50$ °C	
	I	II	I	II	I	II
$\sum y_1^C - y_1 /M$	0.0073	0.0076	0.0076	0.0073	0.0059	0.0060
$(y_1^C - y_1)_{\max}$	+0.0121	-0.0133	+0.0151	-0.0122	-0.0265	+0.0231
$\sum (P^C - P) /M$, kPa	0.547	0.173	0.098	0.079	0.277	0.323
$(P^C - P)_{\max}$, kPa	-0.754	+0.356	+0.167	+0.183	-0.402	+0.580

TABLE IV

Comparison of the data calculated on using: I the parameters of the Wilson equation from this work and II from the monograph by Gmehling et al.⁷⁻⁹

Deviation	Benzene-2-propanol $t = 45\text{ }^{\circ}\text{C}$	Benzene-n-heptane $t = 60\text{ }^{\circ}\text{C}$	Cyclohexane-cyclohexanone $t = 50\text{ }^{\circ}\text{C}$
$\sum (y_I^{\text{CI}} - y_I^{\text{CII}}) /M$	0.0040	0.0020	0.0012
$(y_I^{\text{CI}} - y_I^{\text{CII}})_{\text{max}}$	-0.0096	+0.0040	-0.0061
$\sum (P^{\text{CI}} - P^{\text{CII}}) /M, \text{ kPa}$	0.318	0.198	0.124
$(P^{\text{CI}} - P^{\text{CII}})_{\text{max}}, \text{ kPa}$	-0.530	+0.308	+0.205

SYMBOLS

d	mean deviation
F	objective function
H	Henry's constant
M	total number of experimental points
n	amount of substance
P	pressure
R	gas constant
t	temperature
T	thermodynamic temperature
V	molar volume
x	mole fraction in the liquid phase
y	mole fraction in the gas phase
γ	activity coefficient
Λ	coefficient of Wilson equation
σ	standard deviation
Superscripts	
C	calculated value
I,II	calculated on using parameters of Wilson equation from this work or monograph by Gmehling et al. ⁷⁻⁹ , respectively
G	gas phase
L	liquid phase
*	pure component
Subscripts	
i, j	components
a, b	stages of degassing cycle
m	number of measurement
r	residual value
s	solution
k	designation of degassing cycle
p	pressure function
0	initial value

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