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Separation of Antimony from Copper in Vacuum Distillation

Yuhu Chen^{1, 2}, Hongwei Yang^{1, 2, *}

¹National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, 650093, China

²Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, 650093, China

*Corresponding author e-mail: hongweiy@aliyun.com

Abstract. Experiment of vapor-liquid equilibrium (VLE) for Cu-Sb alloy in the range of 1150 to 1550 K at 10 Pa was investigated. The experimental data are compared with those calculated using Wilson equation, and a good agreement between the experimental and calculated values is obtained. A thermodynamic consistency of experimental VLE data and calculated values were tested by Herington test and Van Ness test, respectively. It can be seen that Cu₃Sb is the main phase of the alloy from XRD pattern. The VLE diagram can be employed for designing the process and phase separation in vacuum distillation.

1. Introduction

Cu-Sb alloy is a good material for manufacturing wear-resistant parts due to its good mechanical properties and wear-resistance [1]. However, a large number of waste Cu-Sb alloys have been produced with the large-scale production and application of Cu-Sb alloy. Waste alloys not only cause a large amount of solid waste pollution, but also are not conducive to recycling of resources. How to recycle and reuse waste alloys is of great significance in the context of increasingly strict environmental requirements and lack of resources and energy. Vacuum distillation, which has such advantages as of high metal recovery rate, low resource consumption, simple process flow and environmental friendliness protection, was widely used for purifying and separating crude metals [2, 3].

Over past decades, researchers have done a lot of work on the separation and purification of alloy by vacuum distillation [4-6]. Vapor-liquid equilibrium (VLE) diagram is widely applied to predict and direct the operation of the distillation in chemical process. In our previous work, a method was proposed to guide the vacuum distillation operation of alloys based on VLE theory [7, 8]. The calculation and application of VLE theory in vacuum distillation are proposed. In this work, vapor-liquid equilibria of Cu-Sb alloy conditions were measured at 10 Pa. The experimental data were correlated with Wilson equation. The thermodynamic consistency of the experimental VLE data was tested using Van Ness and Herington methods.

2. Experimental section

2.1. Materials

The materials for the experiment from Hebei Guantai Metal Materials Co., Ltd. All samples were prepared from copper and antimony shots of 99.99% purity. The molar ratio of the samples composition



is Cu: Sb equal to 7:3. The samples, having masses approximately 70 g, were prepared in a resistance furnace under high purity argon.

2.2. Apparatus and experimental procedure

The schematic diagram of the experiment is shown in Fig. 1. The experimental vacuum furnace is shown in Fig. 2 which made by Kunming Diboo Technology Co., Ltd. The crucible was positioned the center of a water-cooled vacuum chamber (ID× height× thickness=0.22 m× 0.20 m× 0.05 m). The upper surface of the crucible is 0.01 meters away from the condensation plate. The temperature is regulated by the control system. The maximum furnace temperature can be heated to 1773 K. The pressure is regulated by controlling the rotary pump of the vacuum pump. The temperature of the experiment was measured with Pt-100 probes which error is ± 0.2 K and was controlled by a digital temperature meter (ANTHONE LU-900M). The pressure was measured by a stand McLeod Gauge (Shanghai Shuangyu Electronics Co., Ltd., PM-4) with error range less than ± 0.1 Pa.

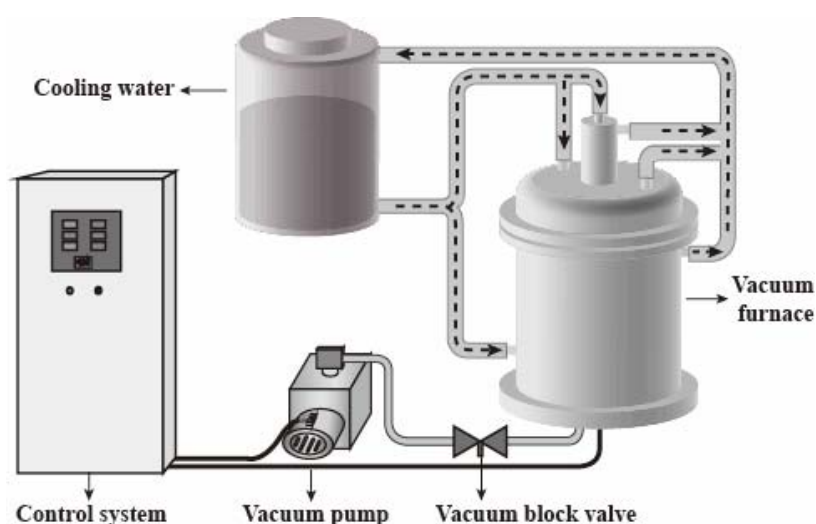


Figure 1. Schematic of apparatus used for vacuum distillation equilibrium experiments.

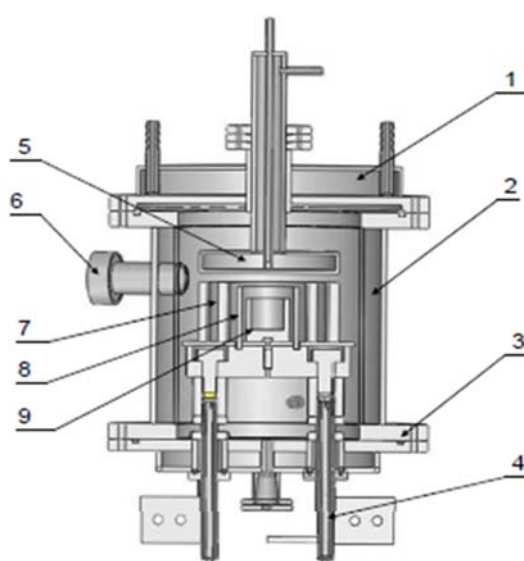


Figure 2. Schematic diagram of the internal structure of the vertical vacuum furnace: 1 furnace lid; 2 furnace body; 3 furnace bottom; 4 electrode; 5 condensation plate; 6 observation hole; 7 heat preservation cover; 8 heating unit; 9 graphite evaporator.

During the experiment, the prepared sample was first placed into a high purity graphite crucible ($ID \times height \times thickness = 0.04 \text{ m} \times 0.04 \text{ m} \times 0.01 \text{ m}$). The crucible with the sample was loaded into the vertical vacuum furnace. Secondly, the pressure was maintained at 10 Pa by controlling the rotary pump of the vacuum pump. Thirdly, the vertical vacuum furnace was heated to a specified temperature as fast as possible and was hold the temperature by adjusting the input current. Sufficient time is required during the distillation process to ensure a balanced state. In the process of distillation, element evaporates from the surface of melt and condenses rapidly on the condenser. The samples in vapor phase and liquid samples could be collected from the condensation plate and crucible, respectively.

Measurement of VLE data were carried out in a closed container. The components of distillation product approach to a stable level with the extension of time. This state at this time was regarded as the vapor-liquid equilibrium state. The time gradually decreases with increasing distillation temperature. Finally, the distillation time was set from 360 min at 1150 K to 120 min at 1550 K. In this equilibrium process, both the vapor and the liquid phases were continuously circulated to ensure that equilibrium could be established. Since vapor and liquid phase composition cannot be obtained at high temperature, the components of volatiles and residues are measured when the system is cooled to room temperature. The volatile is regarded as vapor phase and the residuum is regarded as liquid phase.

Flame atomic absorption spectroscopy (WFX-320 Atomic Absorption Spectrophotometer, supplied by Beijing Rayleigh Analytical Instrument Co., Ltd.) and potentiometric titration (848 Titrino plus, supplied by Metrohm) methods were used to analyze the contents of copper and antimony in liquid phase. The former will be adopted in the content of the determining element is below 2%. Finally, the uncertainty of mole fraction was ± 0.0001 .

3. Method

3.1. Theory of VLE

For a binary system, the equilibrium relationship between the vapor and liquid phase [9] is expressed by the following Eq. (1):

$$y_i \phi_i^v P = x_i \gamma_i \phi_i^s P_i^* \quad (1)$$

where x_i and y_i represent the mole fraction of element i in the liquid phase and vapor phase, respectively; γ_i is the liquid phase activity coefficient; ϕ_i^v is the fugacity coefficient of component i ; ϕ_i^s is the fugacity coefficient of component i at system temperature and corresponding vapor pressure of component i ; P is the pressure of system; P_i^* is the saturation vapor pressure of pure component i which is inquired from the literature [10]. Usually, the vapor phase can be considered as an ideal gas. ϕ_i^v and ϕ_i^s are all close to 1, as a result:

$$x_i \gamma_i P_i^* = y_i P \quad (2)$$

For a binary alloy system, the relationship between x_i and y_i can be expressed as

$$x_i = \frac{P - \gamma_j P_j^*}{\gamma_i P_i^* - \gamma_j P_j^*} \quad y_i = \frac{x_i \gamma_i P_i^*}{P} \quad (3)$$

3.2. Wilson equation

Wilson equation is an activity coefficient model which is used as the correlation to describe the VLE relationship [11]. For a binary mixture system, it presents

$$\ln \gamma_i = -\ln(x_i + x_j A_{ij}) + x_j \left(\frac{A_{ij}}{x_i + x_j A_{ij}} - \frac{A_{ji}}{x_j + x_i A_{ji}} \right) \quad (4)$$

$$\ln \gamma_j = -\ln(x_j + x_i A_{ji}) - x_i \left(\frac{A_{ij}}{x_i + x_j A_{ij}} - \frac{A_{ji}}{x_j + x_i A_{ji}} \right) \quad (5)$$

Where x_i and x_j are the mole fraction of components i and j , A_{ij} and A_{ji} are binary interaction parameters. A_{ij} and A_{ji} are expressed by:

$$A_{ij} = \frac{v_j}{v_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \quad A_{ji} = \frac{v_i}{v_j} \exp[-(\lambda_{ji} - \lambda_{jj})/RT] \quad (6)$$

Where v_i and v_j are the molar volumes of components i and j show in Table. 1; R is gas constant; λ_{ii} , λ_{jj} and λ_{ij} ($\lambda_{ij} = \lambda_{ji}$) are the atomic pair interaction energy of the $i-i$, $j-j$, and $i-j$, respectively. For Wilson Equation, $(\lambda_{ji} - \lambda_{ii})$ and $(\lambda_{ij} - \lambda_{jj})$ are considered independent of temperature. Then, values of A_{ji}' and A_{ij}' at other temperature T' can be calculated as follows:

$$A_{ji}' = \frac{v_j'}{v_i'} \left(\frac{A_{ji}}{v_j / v_i} \right)^{\frac{T}{T'}} \quad A_{ij}' = \frac{v_i'}{v_j'} \left(\frac{A_{ij}}{v_i / v_j} \right)^{\frac{T}{T'}} \quad (7)$$

Substituting the parameters A_{ji}' and A_{ij}' at different temperatures into Eqs. (4) and (5), the activity coefficients γ_i and γ_j can be calculated. The parameters of the Wilson equation for the Cu-Sb system were obtained by fitting experimental activities of components taken from literature [12]. The results are shown in Table 2.

Table 1. The related parameters of copper and antimony.

i	Vapor pressure equation (Pa)	v_{mi} (cm^3 / mol)
Cu	$\lg(P^*) = -17520T^{-1} - 1.21\lg T + 13.21$ ($T=1358\sim 3200$ K)	$7.94[1 + 1.00 \times 10^{-4}(T - 1356)]$
Sb	$\lg(P^*) = -6500T^{-1} + 4.25$ ($T=904\sim 1860$ K)	$17.0[1 + 0.87 \times 10^{-4}(T - 505)]$

Table 2. Calculated parameters of the Wilson equation for Cu-Sb system.

$i-j$	T/K	A_{ij}	A_{ji}
Cu-Sb	1375	0.3465	8.2472

3.3. Thermodynamic consistency test

The thermodynamic consistency test of VLE data is a method to verify whether the VLE data is reliable or may have significant errors. The consistency of the thermodynamic results was checked by the Herington semi-empirical method [13]. The Herington test is presented as follows:

$$\Delta S = 100 \times \left| \frac{S_A - S_B}{S_A + S_B} \right| = 100 \times \left| \frac{\int_0^1 \ln \gamma_2 / \gamma_1 d_{x_1}}{\int_0^1 \ln |\gamma_2 / \gamma_1| d_{x_1}} \right| \quad (8)$$

Where S_A is the area of figure $\ln \gamma_1 / \gamma_2$ vs. x_1 above the X-axis, S_B is the area of figure $\ln \gamma_1 / \gamma_2$ vs. x_1 below the X-axis. Under normal conditions, the calculated activities are considered consistent if the value of ΔS is less than 3.

Additionally, the thermodynamic consistency for all the experimental data was checked with the Van Ness test [14]. The Van Ness test is shown below:

$$y_{(MAD)} = \frac{1}{n} \sum_{i=1}^n 100 |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (9)$$

Where n is the number of the experimental data; y_i^{exp} stands for the experimental mole fraction of component i in the vapor phase; y_i^{cal} means predicted values by the Wilson Equation. If $y_{(MAD)}$ is less than 1, the measured VLE data can be considered as thermodynamic consistency.

4. Results and conclusion

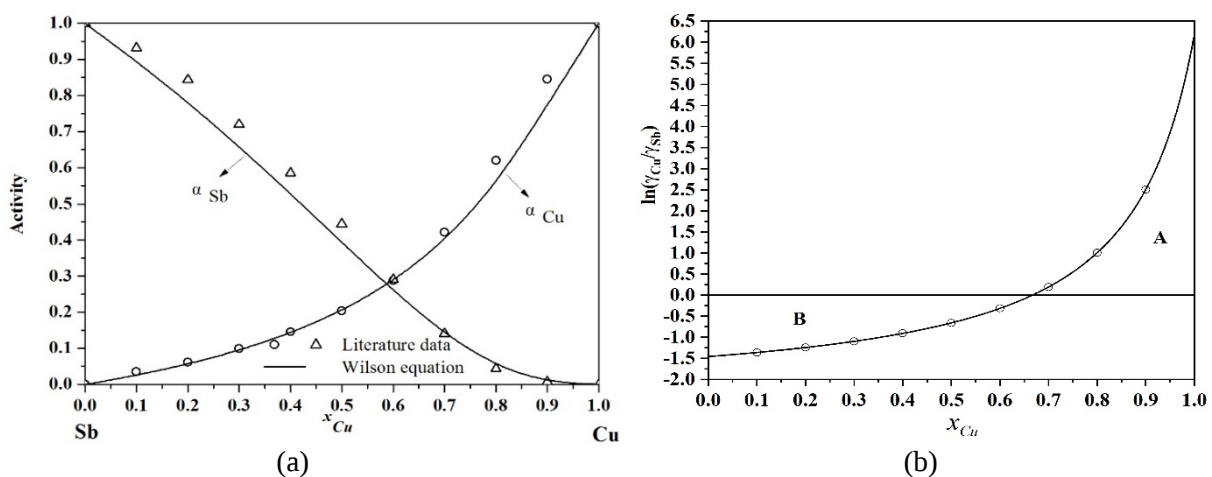


Figure 3. (a) Comparison of the predicted activities of the Wilson equation (lines) with experimental data (symbols) for the Cu-Sb system at 1375 K; (b) Testing the consistency of the activity coefficient calculated by Wilson Equation for Cu-Sb binary system at 1375 K

Comparison of the predicted activities using Wilson equation with experimental data for the Cu-Sb system at 1375 K are shown in Fig. 3 (a). The average standard deviation and average relative deviation of copper and antimony are ± 0.0342 , ± 0.0418 , $\pm 7.68\%$ and $\pm 7.46\%$, respectively. The reliability of the calculated activity coefficients of Cu-Sb binary system was checked by Herington test. All experimental

data were checked by Van Ness test and the results are show in Table 3 and Fig. 3 (b). It indicates that calculated activities data are satisfied with the thermodynamic consistency and the calculated activity data can be correlated with Wilson equation.

Table 3. Thermodynamic consistency checking results for the binary system of Cu-Sb

system	Herington (ΔS)	Van Ness ($Y_{(MAD)}$)
Cu-Sb	1.45	0.89

The vapor-liquid equilibria of Cu-Sb system were measured at 10 Pa. Experimental values of VLE between 1150 K and 1550 K for the Cu-Sb system are presented in Table 4. The content of antimony in the residue is higher than the calculation result. The experimental results showed that the content of copper in the liquid phase reached above 0.8362 mole fraction at the residual vapor pressure of 10 Pa and the distillation temperature of 1550 k. It is far below the calculated value of 0.9993 mole fraction.

Table 4. Experimental VLE data for the Cu-Sb binary alloy system at 10 Pa.

T / K	Time/min	$x_{Cu,exp}^a$	$x_{Cu,cal}^a$	$y_{Cu,exp}^a$	$y_{Cu,cal}^a$	δy^b
1150	390	0.5605	0.9594	0.0000	0.0000	0.0000
1200	330	0.6066	0.9767	0.0001	0.0001	0.0001
1250	270	0.6213	0.9861	0.0002	0.0004	0.0002
1300	210	0.6525	0.9915	0.0004	0.0012	0.0008
1350	180	0.6671	0.9947	0.0044	0.0037	0.0007
1400	150	0.7436	0.9967	0.0281	0.0104	0.0177
1450	120	0.7931	0.9979	0.0512	0.0269	0.0243
1500	120	0.8133	0.9987	0.0715	0.0647	0.0068
1550	120	0.8362	0.9993	0.1214	0.1512	0.0298

$$^a \delta y = |y_{exp} - y_{cal}|.$$

All experimental data were checked by Van Ness test, and the results are show in Table 3. Calculation based on the Wilson equation and experimental vapor-liquid equilibria for Cu-Sb system are compared in Fig. 4. It can be seen that the trend of the experimental point and the liquid phase diagram is not consistent with the change of temperature. The strong interaction of copper with antimony was found in smaller volatilities of antimony than the calculation. The X-ray diffraction (XRD) pattern of high temperature vacuum distillation residue can also prove this conclusion from Fig.5. It can be seen that the main phase of the alloy is Cu_3Sb . Copper and antimony in the alloy are all in the form of Cu_3Sb . It is obvious that the bonding force between copper and antimony is strong. Antimony cannot be completely separated from the alloy since there are strong forces between the elements.

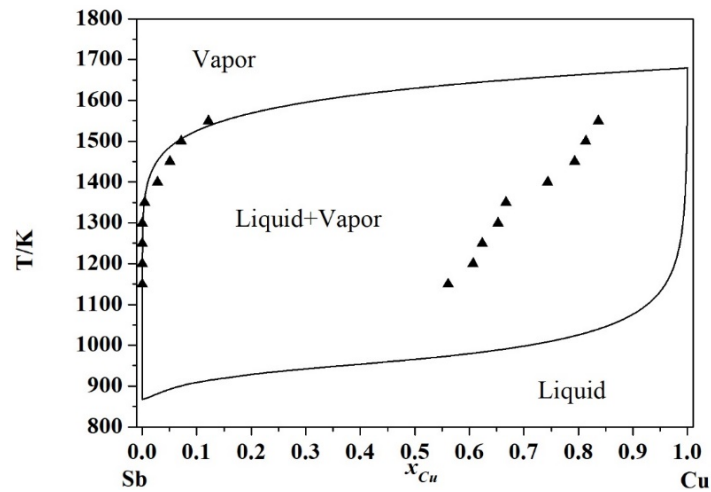


Figure 4. Comparison of the predicted vapor phase of Wilson with experimental data of Cu-Sb alloy at 10 Pa.

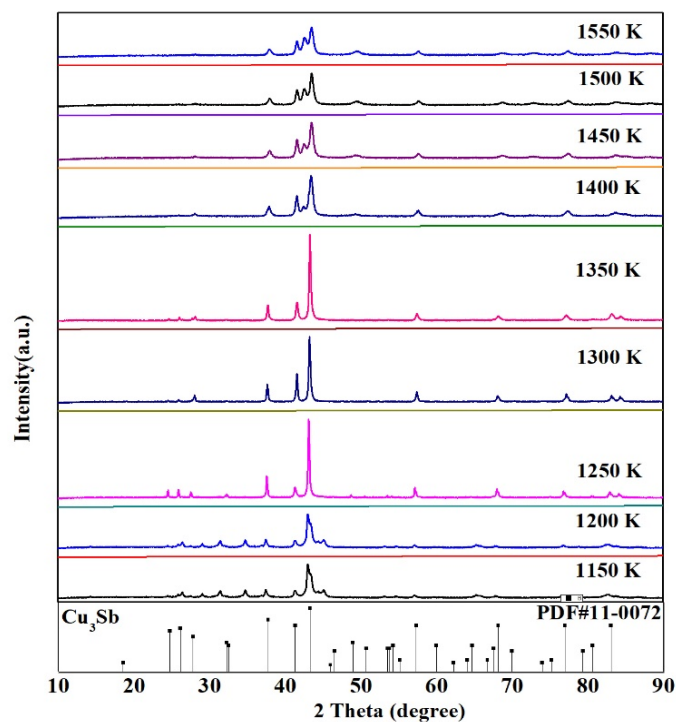


Figure 5. X-ray diffraction pattern for Cu-Sb at different temperatures.

5. Conclusion

The vapor-liquid equilibria of Cu-Sb system were measured at 10 Pa. The thermodynamic consistency of VLE experimental data was tested of using the Herington and Van Ness methods. The Wilson equation and theory of VLE have been used to predict the VLE phase diagram of the Cu-Sb system at pressure of 10 Pa. The calculated activities of components for Cu-Sb system are in good agreement with experimental data. The calculations of vapor phase diagram agree well with the experimental data. The VLE phase diagrams of binary system Cu-Sb in vacuum distillation were modeled based on the Wilson equation. It is reasonable to assume that VLE phase diagram can be applied to the process of vacuum distillation of alloys.

Acknowledgments

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References

- [1] H. L. De Villiers Lovelock, Powder/processing/structure relationships in WC-Co thermal spray coatings: A review of the published literature, *J. Therm. Spray Technol.* 7 (3) (1998) 357 - 373.
- [2] Y.N. Dai, *Vacuum Metallurgy of Nonferrous Metals*, Metallurgical Industry Press, Beijing, 2009.
- [3] O. Winkler, R. Bakish, *Vacuum metallurgy*, Elsevier London, UK, 1971.
- [4] X.M. Chen, B.Q. Xu, B. Yang, D.C. Liu, H.W. Yang, Prediction of vapor-liquid equilibria for Pb-Pd and Pb-Pt alloys using ab initio Methods in vacuum distillation, *J. Solution Chem.* 46 (7) (2017) 1514 - 1521.
- [5] B. Yang, L.X. Kong, B.Q. Xu, D.C. Liu, Y.N. Dai, Recycling of metals from waste Sn-based alloys by vacuum separation, *Transactions of Nonferrous Metals Society of China* 25 (2015) 1315 - 1324.
- [6] X.F. Kong, B. Yang, H. Xiong, L.X. Kong, D.C. Liu, B.Q. Xu, *Transactions of Nonferrous Metals Society of China* 6 (2014) 1946 - 1950.
- [7] H.W. Yang, C. Zhang, B. Yang, B.Q. Xu, D.C. Liu, Vapor-liquid phase diagrams of Pb-Sn and Pb-Ag alloys in vacuum distillation, *Vacuum* 119 (2015) 179 - 184.
- [8] C. Zhang, W. L. Jiang, B. Yang, D.C. Liu, B.Q. Xu, H.W. Yang, Experimental investigation and calculation of vapor-liquid equilibria for Cu-Pb binary alloy in vacuum distillation, *Fluid Phase Equilibria* 405 (2015) 68 - 72.
- [9] C.D. Maranas, C.M. Mcdonald, S.T. Harding, C.A. Floudas, Locating all azeotropes in homogeneous azeotropic systems, *Comput. Chem. Eng.* 20 (1996) S413 - S418.
- [10] T. Iida, R.I.L. Guthrie, *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, 1988.
- [11] G.M. Wilson, A new expression for the excess free energy of mixing, *J. Am. Chem. Soc.* 86 (1964) 127 - 130.
- [12] H. Landolt, R. Börnstein, Berlin: Springer-Verlag; 1993.
- [13] Wisniak, Jaime, The Herington test for thermodynamic consistency, *Ind. Eng. Chem. Res.* 3 (1994) 177 - 180.
- [14] P.L. Jackson, R.A. Wilsak, Thermodynamic consistency tests based on the Gibbs-Duhem equation applied to isothermal, binary vapor-liquid equilibrium data: data evaluation and model testing, *Fluid Phase Equilibria* 103 (2) (1995) 155 - 197.