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A New Gas-Gas Equilibria Prediction Method

RICHARD KAPLAN

Yale University, New Haven, Connecticut

The phenomenon of gas-gas equilibrium—limited mutual solubility of gases at temperatures above the critical point of the least volatile component—was predicted by van der Waals (*1*) in 1894 on the basis of fold theory, but was not observed experimentally until 1940, when Krichevski (*2*) determined that homogeneous ammonia-nitrogen mixtures decompose into two gas phases at elevated pressures. At present, seventeen binary and two ternary systems are known to exhibit the phenomenon.

Two types of gas-gas equilibria are possible, designated as type I or type II, depending on whether the $P(T)$ critical curve, starting from the critical point of the least volatile component, has a positive or negative slope, respectively. More detailed discussions of gas-gas equilibria are given in references *3* and *4*.

Kreglewski (*5*) showed that the greater the differences in the D^2 values of the components of a binary system ($D^2 = 3\ RT_c/2\ V_c$), the greater is the probability that gas-gas equilibrium will occur. The D^2 parameter equation was obtained when Hildebrand's (*6*) equation, $D^2 = -\ E/V$, was combined with van Dranen's (*7*) hypothesis that $E = -3\ RT_c/2$,[*] which results from his assumption that the potential energy equals the negative of the kinetic energy at the critical point.

Arranging systems in order of increasing D^2 difference and thereby predicting that all systems with a D^2 difference greater than that of the first system—the one with the least D^2 difference that does exhibit gas-gas equilibria—show the phenomenon (and conversely, that all systems with a D^2 difference less than that of the last system—the one with the largest D^2 difference that does not exhibit the equilibria—will not show the phenomenon) is not an acceptable way to predict systems; because, although no system with a D^2 parameter difference of less than 159 atm. has shown the phenomenon, there are systems with larger D^2 differences that fail to exhibit this behavior (for example, hydrogen-carbon dioxide with a 333-atm. difference and hydrogen-benzene with a 203-atm. difference).

If, however, the components are arranged in a table in order of increasing D^2 values toward the right and toward the bottom, the systems formed by the intersecting horizontal rows and vertical columns can be predicted to exhibit the phenomenon or not on the basis of experimental findings, and the rule that in a series of systems containing one compound or element in common, the greater the D^2 differences between the components, the greater is the probability that gas-gas equilibrium will occur. This slight alteration of the Kreglewski concept is a logical one, since it helps to eliminate any large molecular interaction differences between the components of the two systems whose D^2 differences are being compared.

The following are examples of the method: since nitrogen-sulfur dioxide (D^2 difference = 263 atm.) shows gas-gas equilibria, nitrogen-methanol (D^2 difference = 362 atm.) is predicted to exhibit the behavior. But, since hydrogen-hexane (D^2 difference = 107 atm.) does not show this type equilibrium, hydrogen-octane (D^2 difference = 80 atm.) is predicted not to exhibit this type of behavior.

Four tables have been formulated. The first includes only those systems that have been studied experimentally and attests to the validity of the method by the fact that no system violates the D^2 difference trend. The second contains those systems from the previous table and predictions made on the basis of the first table. The third contains those systems from the previous tables and predictions made on the basis of the second table (predictions based on the first predictions, and therefore, perhaps, are not as reliable as the first predictions). The fourth lists the predictions made for as yet unstudied systems. Due to space limitations, only Tables 3 and 4 are presented here.[†]

These tables are limited to only those elements and compounds that have been experimented upon in gas-gas equilibria studies, plus oxygen and octane, which are included because they are components of systems that have been predicted to show the phenomenon by other methods. Among the systems formed by these components, twenty-seven new binaries are predicted to exhibit the behavior and seventy new binaries are predicted not to exhibit this type of equilibrium (see Table 4).

The Temkin (*8*) criteria for gas-gas equilibrium correctly predict only a few of the systems that exhibit this phenomenon and all such systems also are predicted by the D^2 method. However, whereas the Temkin criteria have forecast no gas-gas equilibria incorrectly in numerous cases (that is, helium-propane, helium-benzene, helium-

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[*] This approximate relation may be derived by using a corrected van der Waals approach in the following manner: with the van der Waals equation

$$P = \left(\frac{RT}{V-b}\right) - \frac{a}{V^2}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Therefore

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \left(\frac{RT}{V-b}\right) - \left(\frac{RT}{V-b}\right) + \frac{a}{V^2} = \frac{a}{V^2}$$

or

$$E = -\frac{a}{V}$$

By the familiar van der Waals relation

$$a = \frac{27\ R^2T_c^2}{64\ P_c}$$

Thus

$$E = -\frac{27\ R^2T_c^2}{64\ P_cV_c} = -\frac{27\ RT_c}{64\ Z_c}$$

Since Z_c for a real gas is approximately 0.27, $E \cong 100/64\ RT_c \cong 3/2\ RT_c$.

[†] Tables 1 and 2 have been deposited as document 9167 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

Table 3. D^2 Prediction Method: Experimentally Studied Systems (*10* to *16*) and Predictions Made from Tables 1 and 2

Element or compound (D^2 value)	He (11.3)	H_2 (63.2)	C_8H_{18} (143)	C_6H_{14} (170)	N_2 (173)	C_4H_{10} (205)	C_3H_8 (228)	CH_4 (237)	A (244)	O_2 (259)	C_6H_6 (266)	C_2H_4 (280)	Xe (314)	CO_2 (396)	SO_2 (436)	CH_3OH (535)	NH_3 (688)	H_2O (1420)
He				Y^E	Y	Y^E	Y^E	Y	Y	Y	Y^E	Y^E	Y^E	Y^E	Y^E	Y^E	Y^E	Y
H_2			N	N^E	N	N	N	N	N	N	N^E	N	N	$\underline{N}^E$	Y	Y	Y	Y
C_8H_{18}		N		N	N	N	N	N	N	N	N	N	N	N	Y	Y	Y	Y
C_6H_{14}	Y^E	N^E	N		N^E	N	N	N	N	N	N	N	N	N	Y	Y	Y	Y
N_2	Y	N	N	N^E		N	N	N	N	N	N	N^E	N	$\underline{N}^E$	Y^E	Y	Y^E	Y^E
C_4H_{10}	Y^E	N	N	N	N		N	N	N	N	N	N	N	N			Y	Y^E
C_3H_8	Y^E	N	N	N	N	N		N	N	N	N	N	N	N			Y	Y
CH_4	Y	N	N	N	N	N	N		N	N	N	N	N	$\underline{N}^E$			Y^E	Y
A	Y	N	N	N	N	N	N	N		N	N	N	N	N			Y^E	Y
O_2	Y	N	N	N	N	N	N	N	N		N	N	N	N				Y
C_6H_6	Y^E	N^E	N	N	N	N	N	N	N	N		N	N	N				Y
C_2H_4	Y^E	N	N	N	N^E	N	N	N	N	N	N		N	N^E				Y
Xe	Y^E	N	N	N	N	N	N	N	N	N	N	N		N				Y
CO_2	Y^E	$\underline{N}^E$	N	N	$\underline{N}^E$	N	N	$\underline{N}^E$	N	N	N	N^E	N					Y^E
SO_2	Y^E	Y	Y	Y	Y^E													
CH_3OH	Y^E	Y	Y	Y	Y													
NH_3	Y^E	Y	Y	Y	Y^E	Y	Y	Y^E	Y^E									
H_2O	Y	Y	Y	Y	Y^E	Y^E	Y	Y	Y	Y	Y	Y	Y	Y^E				

Y^E signifies that gas-gas equilibrium was observed experimentally.
N^E signifies that no gas-gas equilibrium was observed experimentally.
Y signifies that gas-gas equilibrium is predicted to occur.
N signifies that gas-gas equilibrium is predicted not to occur.
$\underline{N}^E$ signifies that gas-gas equilibrium was not observed experimentally but may have been obscured by the formation of a solid phase.

TABLE 4. PREDICTIONS OF THE SOLUBILITY PARAMETER METHOD

1. Systems predicted to exhibit gas-gas equilibrium on the basis of Table 1

He-N_2
He-CH_4
He-A
He-H_2O
He-O_2
SO_2-H_2
SO_2-C_6H_{14}
SO_2-C_8H_{18}
CH_3OH-H_2
CH_3OH-C_6H_{14}
CH_3OH-N_2
NH_3-H_2
NH_3-C_6H_{14}
NH_3-C_4H_{10}
NH_3-C_3H_8
NH_3-C_8H_{18}
H_2O-Xe
H_2O-C_2H_4
H_2O-C_6H_6
H_2O-A
H_2O-CH_4
H_2O-C_3H_8
H_2O-C_6H_{14}
H_2O-H_2
H_2O-O_2
H_2O-C_8H_{18}

2. System predicted to exhibit gas-gas equilibrium on the basis of Table 2

CH_3OH-C_8H_{18}

3. Systems predicted not to exhibit gas-gas equilibrium on the basis of Table 1

H_2-N_2
H_2-C_4H_{10}
H_2-C_3H_8
H_2-CH_4
H_2-A
H_2-C_2H_4
H_2-Xe
N_2-C_4H_{10}
N_2-C_3H_8
N_2-CH_4
N_2-A
N_2-C_6H_6
N_2-Xe
C_6H_6-C_6H_{14}
C_6H_6-C_4H_{10}
C_6H_6-C_3H_8
C_6H_6-CH_4
C_6H_6-A
C_2H_4-C_4H_{10}
C_2H_4-C_3H_8
C_2H_4-CH_4
C_2H_4-A
C_2H_4-C_6H_6
C_2H_4-Xe
CO_2-C_6H_{14}
CO_2-C_4H_{10}
CO_2-C_3H_8
CO_2-C_6H_6
CO_2-A
CO_2-Xe
CH_4-A
CH_4-Xe
O_2-H_2
O_2-N_2
O_2-CH_4
O_2-C_6H_6
O_2-C_2H_4
O_2-CO_2
C_8H_{18}-H_2
C_8H_{18}-C_6H_{14}
C_8H_{18}-C_6H_6
C_8H_{18}-CO_2

4. Systems predicted not to exhibit gas-gas equilibrium on the basis of Table 2

C_6H_{14}-C_4H_{10}
C_6H_{14}-C_3H_8
C_6H_{14}-CH_4
C_6H_{14}-A
C_6H_{14}-C_2H_4
C_6H_{14}-Xe
C_4H_{10}-C_3H_8
C_4H_{10}-CH_4
C_4H_{10}-A
C_4H_{10}-Xe
C_3H_8-CH_4
C_3H_8-A
C_3H_8-Xe
A-Xe
C_6H_6-Xe
C_8H_{18}-Xe
C_8H_{18}-C_2H_4
C_8H_{18}-O_2
C_8H_{18}-A
C_8H_{18}-CH_4
C_8H_{18}-C_3H_8
C_8H_{18}-C_4H_{10}
C_8H_{18}-N_2
O_2-C_6H_{14}
O_2-C_4H_{10}
O_2-C_3H_8
O_2-A
O_2-Xe

ethylene), thus far the D^2 technique has proved correct in each of its tested predictions.

Rott's (9) method, which only predicts whether or not type I gas-gas equilibrium will occur, is in agreement with the D^2 method, both predicting the phenomenon for the systems water-hexane, water-octane, and water-butane (that is, water-butane was predicted by the D^2 method on the basis of the water-carbon dioxide findings, prior to experimental confirmation).

The one shortcoming of the D^2 method is that it does not predict what type of gas-gas equilibrium will occur. Usually sufficient data are available for determining the D^2 parameter, however, and the method is very easy to use, being limited only by lack of experimental gas-gas equilibria data (Of the one hundred and fifty-three systems formed by the components chosen to comprise the tables, no prediction can be made on thirty-one systems, due to lack of experimental data; however, ninety-seven new systems can be predicted on the basis of only twenty-five pieces of experimental information.) Some of the predictions made are subject to possible errors, due to the uncertainty in the results of some of the experimental work [carbon dioxide-hydrogen, carbon dioxide-nitrogen and carbon dioxide-methane (*10*)].

The D^2 method is the only wide-range gas-gas equilibrium prediction method that has been found to be correct in every instance, probably because it, unlike other prediction methods, uses experimental findings of gas-gas equilibria studies as its starting point.

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NOTATION

a, b = van der Waals constants
D = solubility parameter
E = energy of vaporization
P = pressure
P_c = critical pressure
R = universal gas constant
T = temperature
T_c = critical temperature
V = molar volume
V_c = critical molar volume
Z_c = critical compressibility

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