TABLE VI

| Temp., °C. | $k_{MeEtCO}$ × $10^3$ sec.$^{-1}$ | $k_{acetone}$ × $10^3$ sec.$^{-1}$ | $k_{MeEtCO}/k_{Acetone}$ |
|---|---|---|---|
| 550 | 1.73 | 0.709 | 2.44 |
| 580 | 7.25 | 3.01 | 2.40 |
| 600 | 17.5 | 7.50 | 2.33 |
| 630 | 28.5 | 65.5 | 2.30 |

$\ln k_{MeEtCO} = 34.73 - 67{,}200/RT$ $\quad$ $\ln k_{Acetone} = 34.33 - 68{,}000/RT$

In view of the close agreement of the terms in the rate equations, one is tempted to conclude that the same mechanism of decomposition, namely, rearrangement, is the predominant one for both reactions. Such an assumption is not altogether unwarranted when one compares other similarities. Nitric oxide inhibits both reactions to the same order of magnitude—which is not very large. Further, the values of the activation energies are higher than one normally expects for decompositions which proceed mainly by a chain mechanism. Although free radicals are undoubtedly produced in both reactions, kinetic and analytical evidence favor a rearrangement as being the predominant process.

## Summary

The kinetics of the thermal decomposition of gaseous methyl ethyl ketone has been investigated between 547 and 630°. The reaction was found to be homogeneous and of the first order down to 50 mm. initial pressure. Below 50 mm. the rate falls off and the order approaches that of second.

A new method of calculating the specific velocity constants for the initial process is presented. From these rate constants at seven different temperatures the activation energy was determined and the Arrhenius equation may be given as $\ln k = 34.73 - 67{,}200/RT$.

It was found that the methyl ethyl ketone decomposition proceeded through the formation of an intermediate ketene product. Analyses were made for the ketenes and calculations revealed that the intermediate ketenes decomposed eight times as fast as the ketone. Analyses of the gaseous reaction products were made throughout the course of the decomposition.

Nitric oxide was found to produce some inhibition in the early stages of the decomposition but after the inhibition reached a maximum, further addition of nitric oxide caused marked catalysis.

The kinetic and product analysis evidence indicated that methyl ethyl ketone decomposed predominantly through a rearrangement rather than a free radical mechanism, and a decomposition mechanism is proposed that is in keeping with the experimental facts.

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[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY OF THE TECHNICAL UNIVERSITY, DELFT, HOLLAND]

# On Critical Phenomena of Saturated Solutions in Binary Systems

BY G. A. M. DIEPEN AND F. E. C. SCHEFFER

## Introduction

The purpose of this investigation was to find out some binary systems which might be adapted for exact measurement of the solubility of solids in supercritical gases.

The fact that slightly volatile solids can be dissolved in supercritical gases has been ascertained by several workers. The examination of Smits,[1] supplemented later by Smits and Treub[2] concerning the system ether–anthraquinone explained this phenomenon by means of the phase rule.

When we consider the most simple systems formed by a volatile substance, A, and a slightly volatile substance, B, having its melting point above the critical temperature of A, *i. e.*, those systems in which no chemical compounds nor mixed crystals are formed and in which no immiscibility in the liquid phase occurs, we conclude that they can be divided into two main groups:

1. Systems in which the three-phase line $S_B$-L-G ($S_B$ = solid B, L = liquid, G = gas) runs without interruption from low temperatures to the triple-point of B. The critical line runs without interruption from the critical point of A to the critical point of B.[3] In such a system saturated solutions cannot show critical phenomena; only unsaturated solutions have a critical point, L = G.

If at a temperature lying above the critical temperature of A, one starts with a sufficient quantity of solid B, and compresses gas upon it, he finds that a homogeneous gas phase can only be reached after the system has passed through a liquid state. For, at the three-phase pressure, a saturated solution is formed along with solid B and gas. With further decrease in the volume, the pressure remains constant until all solid B has disappeared; at that instant the system enters the area of unsaturated solution plus gas phase.

With further increase of pressure the critical point of the unsaturated solution is finally attained, provided at least that the volume and the

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[1] Smits, *Verslag Akad. Wetenschappen Amsterdam*, **12**, 335 (1905); *Z. physik. Chem.*, **51**, 193 (1905); *ibid.*, **52**, 587 (1905).

[2] Smits and Treub, *Verslag Akad. Wetenschappen Amsterdam*, **20**, 142 (1911); *ibid.*, **20**, 148 (1911).

[3] For the *p–t* projection of such a system see Bakhuis–Roozeboom, "Die heterogene Gleichgewichte," Vol. II, 1, p. 372.

concentration of the mixture are regulated in such a way that the critical phenomenon is possible.

In such a system a solid dissolves in a high-pressure gas in considerable quantity only after meanwhile having passed through a liquid state.

2. Systems in which the solubility of B in liquid A is so small that the three-phase line $S_B$–L–G cuts the critical line.[4] At the two points of intersection of the critical line with the three-phase line the vapor–pressure of the saturated solution becomes identical with the critical pressure so that saturation temperature and critical temperature coincide.

In consequence, we find here critical points for saturated solutions and at the same time an area is formed between the temperatures of these points of intersection where critical phenomena, at least in the stable state, are impossible. In this area one can, therefore, raise the pressure unrestrictedly without any separation of a liquid state.

The fact that in this area peculiar phenomena will arise is easily noticed from $p$–$x$ and $t$–$x$ sections.[5]

The solubility of B in the fluid phase does not depend on the vapor pressure of B but rather is determined by the solubility of B in the liquid phase (at lower temperatures). So in this area the solubility of solid B in the fluid phase can be increased considerably over the ideal value expected on the basis of the vapor pressure of the solid at the specified temperature and pressure.

When the temperature is raised at constant pressure, the solubility at first diminishes and then increases again. Consequently the solubilities are to a high degree dependent on pressure and temperature.

The system ether–anthraquinone, examined by Smits, is an example of a system of this type.

Büchner[6] drew attention to the fact that still another kind of system showing the same phenomena is possible, *viz.*, systems with metastable immiscibility in the liquid phase.

Here, too, we find two critical end-points, L = G, along with the solid phase, and a temperature range in which no stable critical phenomena are possible. The only difference between these two last types is that the second critical end-point of systems with metastable immiscibility will in general lie at considerably higher pressures than those of the ether–anthraquinone type, since the critical line has two points of inflexion in the metastable region.

Büchner ascertained the $p$–$t$ projection of the system diphenylamine–carbon dioxide, which showed clearly behavior of the metastable immiscibility type.

Consequently both types of systems are suitable for the exact determination of solubilities of the solid in a supercritical gas-phase. The two conditions to be satisfied in order to find a similar system are: (1) The melting point of the less volatile substance has to lie above the critical temperature of the volatile substance; (2) the solubility of the solid in the liquid phase of the volatile substance must not be too great.

Since we wish to find a system suitable for exact determinations of concentration without too many experimental difficulties it is self-evident that the fluid component has to be chosen in such a way that the critical temperature is situated at about room temperature and the critical pressure is not too high. Therefore we have chosen ethylene as the volatile component.

For second components we have taken some halogen substitution products of benzene, some aliphatic hydrocarbons, naphthalene, biphenyl, benzophenone and menthol.

## Experimental Results

All of the measurements in this study were carried out in glass Cailletet tubes. Pressures were determined with adjusted Schaeffer and Budenberg pressure-gages designed for precision measurements. Temperatures were determined with Anschütz thermometers.

The data for the system ethylene–$p$-dichlorobenzene (m. p. 52.8°) are shown in Table I and a graphical representation of the $p$–$t$ projection of this system is presented in Fig. 1.

TABLE I

THE SYSTEM ETHYLENE–$p$-DICHLOROBENZENE

| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
|---|---|---|---|---|---|
| L–G Ethylene | | $L_1 = L_2$ | | S–L–G | |
| $9.5 = t_K$ | $49.95 = p_K$ | 44.4 | 95.10 | 45.0 | 20.15 |
| 5.0 | 45.40 | 41.4 | 90.55 | 40.0 | 32.05 |
| 0.0 | 40.45 | 39.7 | 87.70 | 35.0 | 41.70 |
| − 5.0 | 35.90 | 38.6 | 85.90 | 30.0 | 49.65 |
| −10.0 | 32.05 | 37.0 | 83.35 | 25.0 | 55.75 |
| −15.0 | 28.20 | 35.4 | 80.55 | 22.4 | 57.20 |
| L = G | | 33.1 | 76.70 | 21.4 | 57.45 |
| | | 32.2 | 75.55 | 21.0 | 57.55 |
| 26.5 | 65.40 | 31.4 | 73.85 | 20.8 | 57.45 |
| 24.2 | 62.50 | 29.8 | 71.15 | 20.4 | 57.25 |
| 20.8 | 59.00 | 26.0 | 64.75 | 20.0 | 57.10 |
| 17.8 | 56.25 | $L_1$–$L_2$–G | | 15.0 | 52.45 |
| 11.0 | 50.95 | | | 10.0 | 47.80 |
| 9.5 | 49.95 | $26.5 = t_K$ | $65.40 = p_K$ | 5.0 | 43.35 |
| | | 26.4 | 65.20 | 0.0 | 39.00 |
| | | 26.2 | 64.95 | − 5.0 | 34.95 |
| | | $26.0 = t_K$ | $64.75 = p_K$ | −10.0 | 31.35 |

Table II gives the experimental data for the system ethylene–1,3,5-trichlorobenzene (m. p. 63.0°) and Fig. 2 shows these data plotted to give the $p$–$t$ projection of this system. Similarly Tables III, IV, V, VI, VII, VIII, IX and X summarize the data for binary systems of ethylene with $p$-chlorobromobenzene (m. p. 64.4°), $p$-chloroiodobenzene (m. p. 53.3°), $p$-dibromobenzene (m. p. 86.8°), octacosane ($C_{28}H_{58}$, m. p. 61.0°), hexatriacontane ($C_{36}H_{74}$, m. p. 76.0°), naphthalene (m. p. 80°), diphenyl (m. p. 68.5°),

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[4] For the $p$–$t$ projection of such a system see Bakhuis-Roozeboom, Vol. II, 1, p. 389.

[5] For the $p$–$x$ sections see Bakhuis–Roozeboom, Vol. II, 1, p. 386; for the $t$–$x$ sections see P. Niggli, "Das Magma und seine Produkte," p. 238.

[6] Büchner, *Z. physik. Chem.*, **56**, 257 (1906).

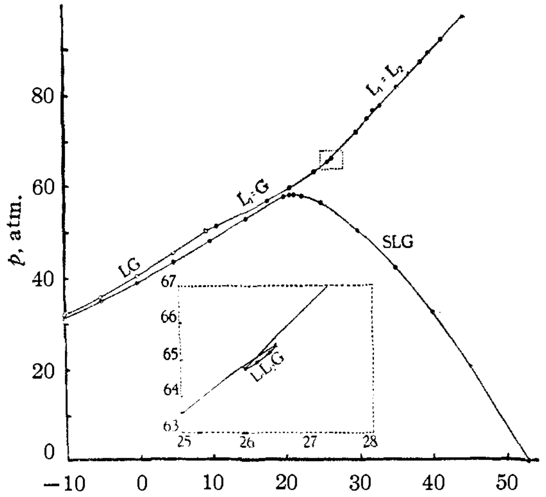

Fig. 1.—Pressure–temperature projection of the system ethylene–$p$-dichlorobenzene.

and benzophenone (m. p. 47.8°), respectively. Graphs for these systems are not given since the $p$–$t$ projections show the same picture as that of the ethylene–1,3,5-trichlorobenzene system depicted in Fig. 2.

TABLE II

THE SYSTEM ETHYLENE–1,3,5-TRICHLOROBENZENE

| S–L$_1$–G |  | S–L$_2$–G |  |
|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 13.1 = $t_K$ | 52.70 = $p_K$ | 49.9 | 39.00 |
| 9.9 | 49.25 | 48.2 | 43.75 |
| 4.9 | 44.50 | 46.3 | 48.85 |
| − 0.1 | 39.75 | 44.4 | 53.60 |
| − 5.1 | 35.40 | 42.5 | 58.90 |
| −10.1 | 31.60 | 40.8 | 63.15 |
|  |  | 39.4 | 67.20 |

TABLE III

THE SYSTEM ETHYLENE–$p$-CHLOROBROMOBENZENE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 13.4 = $t_K$ | 53.05 = $p_K$ | 53.7 | 33.80 | 44.7 | 60.40 |
| 9.9 | 49.25 | 52.1 | 38.65 | 43.8 | 62.80 |
| 4.9 | 44.20 | 50.4 | 43.55 | 43.6 | 63.25 |
| − 0.1 | 39.80 | 48.8 | 48.30 | 41.7 | 67.75 |
| − 5.1 | 35.45 | 48.7 | 48.45 | 40.2 | 72.50 |
| −10.1 | 31.60 | 47.1 | 53.15 | 39.1 | 77.30 |
|  |  | 46.3 | 55.55 | 38.4 | 82.10 |
|  |  | 45.5 | 57.95 |  |  |

TABLE IV

THE SYSTEM ETHYLENE–$p$-CHLOROIODOBENZENE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 12.0 = $t_K$ | 51.85 = $p_K$ | 46.4 | 24.15 | 35.8 | 57.95 |
| 9.9 | 49.55 | 44.9 | 28.95 | 34.4 | 63.05 |
| 4.9 | 44.85 | 43.4 | 33.85 | 33.0 | 68.05 |
| − 0.1 | 40.05 | 41.8 | 38.65 | 32.4 | 72.50 |
| − 5.1 | 35.65 | 40.1 | 43.50 | 32.1 | 77.75 |
| −10.1 | 31.65 | 38.6 | 48.30 | 31.7 | 82.55 |
|  |  | 37.1 | 53.15 |  |  |

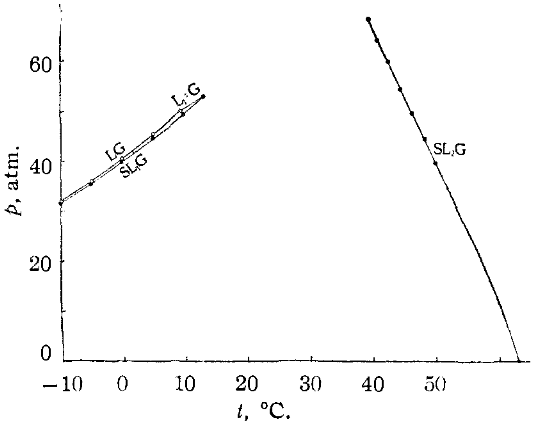

Fig. 2.—Pressure–temperature projection of the system ethylene–1,3,5-trichlorobenzene.

TABLE V

THE SYSTEM ETHYLENE–$p$-DIBROMOBENZENE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 10.6 = $t_K$ | 50.70 = $p_K$ | 80.2 | 28.95 | 74.2 | 57.95 |
| 4.9 | 45.05 | 79.2 | 33.80 | 73.3 | 62.80 |
| − 0.1 | 40.20 | 78.1 | 38.65 | 72.2 | 67.65 |
| − 5.1 | 35.80 | 77.0 | 43.45 | 71.2 | 72.45 |
| −10.1 | 31.85 | 76.0 | 48.30 | 70.3 | 77.40 |
|  |  | 75.2 | 53.40 | 69.6 | 82.40 |

TABLE VI

THE SYSTEM ETHYLENE–OCTACOSANE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 9.5 = $t_K$ | 49.85 = $p_K$ | 54.2 | 28.75 | 48.0 | 62.85 |
| 4.9 | 45.35 | 53.0 | 33.80 | 47.2 | 67.70 |
| − 0.1 | 40.80 | 52.2 | 38.60 | 46.4 | 72.85 |
| − 5.1 | 36.15 | 51.3 | 43.50 | 46.0 | 77.10 |
| −13.1 | 29.95 | 50.5 | 48.40 | 45.6 | 82.00 |
|  |  | 49.6 | 53.15 | 45.2 | 86.95 |
|  |  | 48.8 | 57.95 |  |  |

TABLE VII

THE SYSTEM ETHYLENE–HEXATRIACONTANE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 9.6 = $t_K$ | 49.90 = $p_K$ | 69.7 | 34.65 | 65.9 | 62.40 |
| 8.5 | 48.75 | 69.1 | 38.85 | 65.2 | 67.65 |
| 4.9 | 45.30 | 68.4 | 43.90 | 64.5 | 72.45 |
| − 0.1 | 40.45 | 67.7 | 48.40 | 64.0 | 77.25 |
| − 5.1 | 35.85 | 67.1 | 53.20 | 63.6 | 82.25 |
| −10.1 | 31.90 | 66.5 | 57.70 | 63.1 | 88.40 |

TABLE VIII

THE SYSTEM ETHYLENE–NAPHTHALENE

| S–L$_1$–G |  | S–L$_2$–G |  | S–L$_2$–G |  |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 11.0 = $t_K$ | 51.20 = $p_K$ | 77.2 | 10.85 | 68.7 | 43.65 |
| 9.0 | 48.90 | 76.1 | 14.65 | 67.4 | 48.50 |
| 7.0 | 47.00 | 74.7 | 19.50 | 66.2 | 53.45 |
| 5.0 | 45.10 | 73.5 | 24.30 | 64.5 | 59.80 |
| 0.0 | 40.30 | 72.2 | 29.15 | 63.8 | 63.20 |
| − 5.0 | 35.90 | 71.0 | 33.70 | 62.6 | 68.65 |
| −10.0 | 32.05 | 70.8 | 34.65 | 61.3 | 75.10 |
| −15.0 | 28.25 | 70.0 | 38.65 |  |  |

TABLE IX

THE SYSTEM ETHYLENE–BIPHENYL

| S–L₁–G | | S–L₂–G | | S–L₂–G | |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 11.2 = $t_K$ | 50.95 = $p_K$ | 55.5 | 43.35 | 49.0 | 67.55 |
| 5.0 | 45.40 | 54.0 | 48.60 | 47.8 | 72.35 |
| | | 53.0 | 53.00 | 46.2 | 80.60 |
| | | 51.6 | 57.85 | 45.6 | 84.75 |
| | | 50.3 | 62.75 | | |

TABLE X

THE SYSTEM ETHYLENE–BENZOPHENONE

| S–L₁–G | | S–L₂–G | | S–L₂–G | |
|---|---|---|---|---|---|
| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
| 9.9 = $t_K$ | 50.20 = $p_K$ | 37.2 | 29.80 | 29.6 | 62.75 |
| 5.0 | 45.60 | 36.3 | 33.60 | 28.8 | 67.55 |
| 0.0 | 40.45 | 35.1 | 38.60 | 28.3 | 72.80 |
| − 5.0 | 35.85 | 33.9 | 43.35 | 28.2 | 77.55 |
| −10.0 | 31.80 | 32.6 | 48.15 | 28.1 | 82.15 |
| | | 31.3 | 53.05 | 27.7 | 87.05 |
| | | 30.4 | 57.90 | | |

The system ethylene–menthol (m. p. 40.6°) exhibits different behavior. Data for the system are collected in Table XI and the $p$–$t$ projection is shown in Fig. 3.

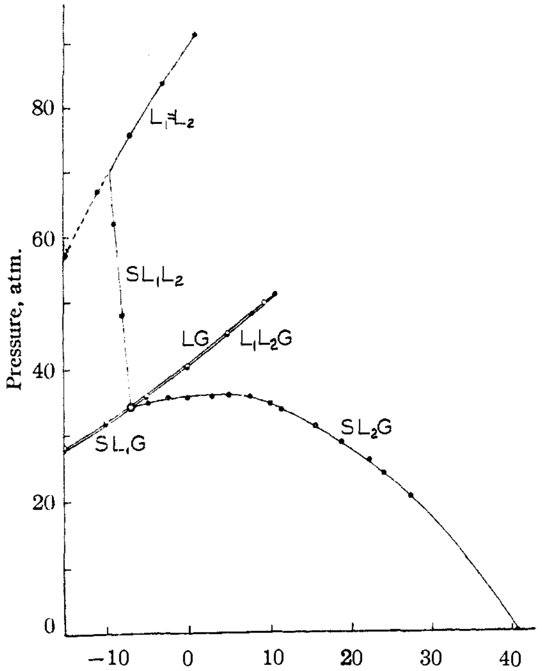

Fig. 3.—Pressure–temperature projection of the system ethylene–menthol.

## Discussion of Results

Reviewing the above-mentioned measurements, we conclude that in the system ethylene–$p$-dichlorobenzene there is no intersection of the three-phase line S-L₁-G and the critical line $L_1 = G$, but that there is a small area where immiscibility in the liquid occurs.

TABLE XI

THE SYSTEM ETHYLENE–MENTHOL

| $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. | $t$, °C. | $p$, atm. |
|---|---|---|---|---|---|
| L₁–L₂–G | | S–L₁–L₂ | | 0.0 | 35.60 |
| 10.9 = $t_K$ | 51.15 = $p_K$ | −8.0 | 48.00 | − 2.4 | 35.55 |
| 8.0 | 48.15 | −9.0 | 62.10 | − 4.9 | 34.80 |
| 5.0 | 45.25 | S–L₂–G | | S–L₁–L₂–G | |
| 0.0 | 40.25 | 27.5 | 20.75 | − 7.0 | 34.20 |
| − 5.0 | 35.55 | 24.2 | 24.05 | L₁ = L₂ | |
| −10.0 | 31.70[a] | 22.4 | 26.15 | 1.0 | 91.55 |
| −15.0 | 27.85[a] | 18.9 | 28.85 | − 3.0 | 83.90 |
| S–L₁–G | | 15.7 | 31.25 | − 7.0 | 75.80 |
| −10.0 | 31.70 | 11.5 | 33.65 | −11.0 | 66.90[a] |
| −15.0 | 27.85 | 10.1 | 34.65 | −15.0 | 57.25[a] |
| | | 7.7 | 35.65 | | |
| | | 5.0 | 36.00 | | |
| | | 3.0 | 35.75 | | |

[a] Metastable points.

The system ethylene–menthol shows a quadruple-point S-L₁-L₂-G, an intersection of the three-phase line L₁-L₂-G with the critical line $L_1 = G$ and an intersection of the three-phase line S-L₁-L₂ with the critical line $L_1 = L_2$. All the remaining nine systems show an intersection of the three-phase line S-L₁-G with the critical line $L_1 = G$.

It is highly probable that these are all systems with metastable immiscibility in the liquid phase, considering the form of the three-phase line S-L₂-G and the fact that at higher pressures none of the L₂ liquids show any tendency to exhibit critical phenomena.

Consequently, above the critical temperature of the saturated solution, these nine systems achieve an equilibrium between the solid and fluid phases. Therefore all these nine systems are essentially suitable for the determination of solubilities of solid in the fluid phase. In making a choice among these systems we have been led by the following considerations:

We want to have a system with which we may expect a noticeable solubility of the solid in the fluid phase. An indication of this solubility can be found in the difference between the vapor-pressure of pure ethylene and that of the saturated solution, at temperatures below the critical temperature of ethylene. However these differences are small and are of the order of the errors of the pressure measurements. A better indication is to be found in the difference between the critical temperature of pure ethylene and the critical temperatures of the saturated solutions.

These differences of critical temperature are distinctly measurable in the systems of ethylene with 1,3,5-trichlorobenzene, $p$-chlorobromobenzene, $p$-dibromobenzene, $p$-chloroiodobenzene, naphthalene and biphenyl.

As naphthalene is readily obtained in large quantities and in a pure condition, and since a simple method is known for the determination of small quantities of naphthalene with sufficient accuracy, we have chosen the system ethylene–naphthalene for our detailed examination.

The determinations of solubility in this system will be treated in another paper.

## Summary

1. Phase-rule studies in the neighborhood of the critical point for ethylene have been carried out for several binary systems composed of ethylene and organic materials with low vapor pressures and melting points well above the critical temperature of ethylene. The types of phase equilibria observed have been discussed and classified.

2. Data for a number of the systems studied indicate a substantial solubility of the solid component in fluid ethylene above its critical temperature. Of these the system ethylene–naphthalene has been selected for a more extensive study of the supercritical solubility phenomenon.

LABORATORY OF INORGANIC CHEMISTRY
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DELFT, HOLLAND
RECEIVED MARCH 1, 1948

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[CONTRIBUTION FROM THE LABORATORY FOR INORGANIC CHEMISTRY AT THE TECHNICAL UNIVERSITY, DELFT, HOLLAND]

# The Solubility of Naphthalene in Supercritical Ethylene

BY G. A. M. DIEPEN AND F. E. C. SCHEFFER

In a previous paper[1] we have shown that, for a binary system with two components differing greatly in volatility, in which the three-phase line S–L–G cuts the critical line, the solubility of the solid in the supercritical gas phase will in general be increased over the ideal value expected on the basis of the vapor pressure of the solid.

It is our present purpose to establish a $p$–$x$ section through the $p$–$T$–$x$ diagram of the system ethylene–naphthalene for some temperatures a little higher than the critical temperature of the naphthalene-saturated solution. Previously only Cailletet types of apparatus have been used for such determinations. However these are very ill-suited for this purpose since the solubilities are mostly slight and the attainment of mixtures of very one-sided composition is of considerable practical difficulty.

We have, therefore, looked for a method enabling us to fix with satisfying accuracy these relatively slight solubilities.

The problem comes to this, that a solid-saturated fluid phase has to be prepared at a constant pressure and temperature, and a part of this has to be separated at constant pressure and temperature, and then has to be analysed. So we have developed the apparatus shown in Fig. 1, with which we could achieve our end.

The steel autoclave, A, is filled with mercury from the valve C to the T-piece D. In the steel autoclave, B, is inserted a small linen bag containing the solid substance. This bag fits closely all over the inside wall of the autoclave.

Both autoclaves are in a thermostat. In order to start the determination the valve, E, is connected with a vacuum pump and the apparatus is evacuated with valves I, G and F open (C is closed). To remove the last trace of air E is now closed, some ethylene is admitted from the cylinder K and then the apparatus is reevacuated through E. After this valve E is again closed and ethylene is passed from the cylinder K into autoclave B, until the desired pressure is attained, which is read on the pressure-gage H. Now the naphthalene is going to dissolve, causing the pressure to decrease again. Additional gas is then admitted until the desired pressure is restored. This procedure is repeated until the pressure remains constant. The required time for this varies with the pressure (at low pressures there is less solubility, consequently quicker saturation). The pressure is maintained for half an hour. Comparison experiments have proved that it makes no difference to extend this time to one or two hours.

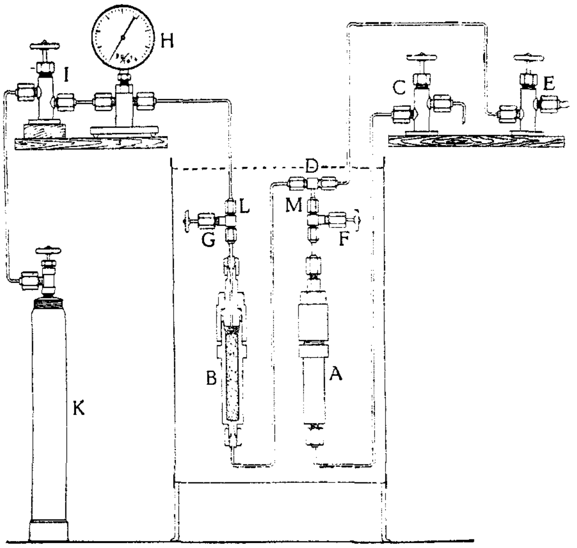

Fig. 1.—Apparatus for preparation of saturated fluid solutions.

We have now, therefore, a saturated solution in autoclave B, a part of which we must transfer into autoclave A.

The solutions in the pipe between the lower end of autoclave B and valve E are unsaturated, so that we have to displace these with saturated solution. To this end both valves E and I are somewhat opened at the same time, taking care that the pressure remains constant. The valve of cylinder

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[1] Diepen and Scheffer, THIS JOURNAL, **70**, 4081 (1948).