Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Selective Clathration during the Formation of Gas Hydrates

R. M. Barrer[a]; A. V. J. Edge[a]
[a] PHYSICAL CHEMISTRY LABORATORIES, CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE, LONDON, ENGLAND

To cite this Article Barrer, R. M. and Edge, A. V. J.(1967) 'Selective Clathration during the Formation of Gas Hydrates', Separation Science and Technology, 2: 2, 145 — 154

To link to this Article: DOI: 10.1080/01496396708049922

URL: http://dx.doi.org/10.1080/01496396708049922

SEPARATION SCIENCE, 2(2), 145–154 (1967)

Selective Clathration during the Formation of Gas Hydrates

R. M. BARRER and A. V. J. EDGE
PHYSICAL CHEMISTRY LABORATORIES,
CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE,
LONDON, ENGLAND

Summary

An account has been given of some new experiments in which mixtures of the heavier inert gases have been partially fractionated by selective clathration at low temperatures in gas hydrates of types I and II. Some previous measurements (8) have also served to give theoretical equilibrium fractionation factors for other binary gas mixtures, and, as with the new results, indicate good fractionations. The preference of the host lattice is for spherical molecules small enough to occupy the cavities and otherwise as condensable as possible.

The process of selective clathration has been very successful in separating molecular mixtures, according to differences in sizes and shapes, or to differences in boiling points, of the molecules. Urea by clathration effectively separates *n*-paraffins from C_7 upward from *i*-paraffins (*1*), and certain Werner complexes can fractionate aromatic hydrocarbons, such as *o*-, *m*-, and *p*-xylenes (*2–4*). In view of the interest in new methods of separation and the many researches on clathrate gas hydrates, the use of these hydrates for separating mixtures has been surprisingly little explored. Hydrate formation has recently been examined as a possible means of desalinating water (*5*). Also Hammerschmidt (*6*) in 1936 found that low-molecular-weight hydrocarbons (C_1, C_2, C_3, C_4, C_5) underwent some fractionation during hydrate formation, but he made no systematic study of binary hydrocarbon mixtures. Von Stackelberg (*7*) in 1949 reported that air released from its double hydrate with chloroform was enriched in oxygen ($O_2:N_2 \simeq 1:1$). A more systematic study was made by Barrer and Ruzicka (*8*), who measured an enrichment factor of 1.9 for oxygen in air in the same hydrate, and still larger enrichment factors for Kr + Ar and Xe + Kr. The hydrates were formed by circulating the gas mixtures through chloroform and then through aqueous salt solutions a little below 0°C. They also measured fractionation factors during double hydrate formation with the pairs CH_3I + $CHCl_3$, CCl_4 + $CHCl_3$, CH_2Cl_2 + $CHCl_3$, C_6H_6 + $CHCl_3$, and $C_6H_5CH_3$ + $CHCl_3$. In the mixtures containing benzene and toluene, the hydrate phases extracted only chloroform during their crystallization. Barrer and Ruzicka (9) also observed that reaction between ice crystals and guest molecules was promoted by agitation of the crystals, and Barrer and Edge (*10*) discovered quite rapid and almost complete reaction between ice and guest species, even at liquid air temperatures, when the ice crystals were rapidly shaken with small steel ball bearings. The relative ease of the reaction thus promoted, the ready availability of water, the high capacity of the host lattices of water for clathrating gases (equivalent to the best gas-sorbing carbons or zeolites), and the possibility of enhanced separation factors at the much lower temperatures now accessible for reaction (*10*) have led us to make some additional fractionations of inert-gas mixtures, this time during their reaction with ice.

From the present viewpoint two hydrate structures are important (*11,12*). Each is cubic, type I having a cell edge of ~ 12 Å and type II of ~ 17 Å. In the unit cell of type I there are 46 water molecules, enclosing two pentagonal dodecahedral cavities of free diameter ~ 5.2 Å and six tetradecahedral cavities of free diameter ~ 5.9 Å. Each cavity is capable of accommodating a guest molecule, although some cavities remain unoccupied.

In the unit cell of type II hydrates there are 136 water molecules enclosing 16 pentagonal dodecahedral cavities of free diameter 4.8 Å and 8 hexakaidecahedral cavities of free diameter 6.9 Å. Thus the limiting composition would be one guest molecule for 5.67 water molecules, if all cavities were occupied, or one guest per 17 water molecules, if, as is often the case for larger guest molecules such as chloroform, only the larger cavities are occupied.

EXPERIMENTAL

The gases used were pure argon, krypton with < 1% xenon, and xenon with < 1% krypton. The additional reactants were pure chloroform and distilled water, the former being used when type II double hydrates of chloroform, water, and inert gas were required. In the type II hydrates the chloroform fills nearly all the large cavities, leaving only the dodecahedral ones for the inert gas.

The apparatus employed in the experiments is shown in Fig. 1. It

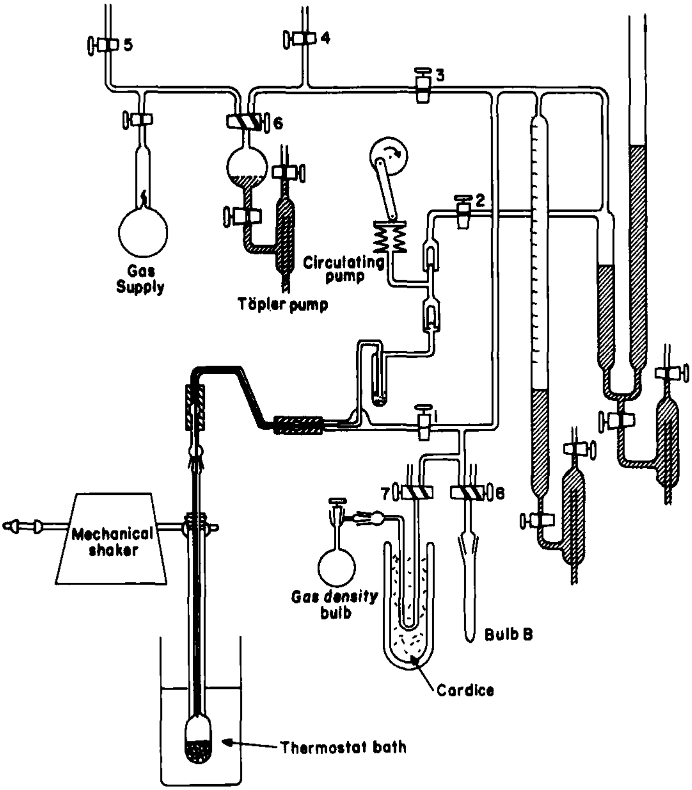

FIG. 1. The apparatus used in the fractionation of pairs of inert gases during gas hydrate formation.

incorporated means of circulating the inert-gas mixture through the reaction zone, which is in the bulb immersed in the thermostat bath. The bulb contained small steel ball bearings agitated by means of a mechanical shaker. The reaction vessel was connected by two short lengths of pressure tubing to the rest of the apparatus in the manner shown in the diagram, so that the necessary flexibility was achieved. The circulating pump was of bellows type and operated through valves to achieve the necessary driving of the gas mixture. This mixture was circulated through the reaction vessel by means of a fine nylon tube, coaxial with the glass tube leading from the reaction vessel, as shown in the figure. The mercury manometer on the right of the diagram served for pressure control and the gas buret next to it was used to measure uptake of gas at constant pressure. A means was provided for sampling the gas and determining the density, and hence its composition, using the gas density bulb. An MS 10 mass spectrometer was also used as a second method of analyzing the mixtures.

Measured samples of each gas were introduced into the circulation system by means of the Töpler pump, so that initial gas compositions were known. The ice and, when desired, chloroform had previously been introduced into the reaction vessel in the manner described elsewhere (*10*). About 0.1 g each of water and of chloroform (where required) were transferred from bulb B to the reaction vessel in each experiment.

The fractionation factor was calculated from the gas law and the known volumes and temperatures of the several parts of the apparatus. Initially the total amount, n_1, of the gas mixture in moles was

$$n_1 = P_0(V_0 + V_d)/RT_0 \qquad (1)$$

where T_0 is the room temperature, P_0 the total pressure, V_d the doser volume to the top graduation of the gas buret, and V_0 the volume of the rest of the gas buret occupied by the gas. After clathration, the amount of nonsorbed gas was

$$n_2 = \frac{(P_1 - P_{H_2O} - P_{CHCl_3})}{R}\left[\frac{(V_1 + V_d)}{T} + \phi_T\right] \qquad (2)$$

where P_1, P_{H_2O}, and P_{CHCl_3} are, respectively, the final total pressure and the vapor pressures of ice and of chloroform (liquid or solid) at the temperature of the reaction bulb. V_1 is the new occupied volume of the gas buret and T_1 the new value of the room temperature (T_1 and T_0 are not necessarily equal, because the experiments lasted some time). ϕ_T denotes the sum $\Sigma(\delta V/T)$ for all the elements of volume in the reaction system and connecting tube. It was determined by expanding gas from the doser volume into the evacuated reaction volume and connecting tube in the absence of ice crystals. Hence, in the absence of reaction, ϕ_T was constant for each bath temperature but varied with different bath temperatures. In this way proper account was taken of the temperature gradient along the connecting tube.

If the gas mixture comprises species A and B, the initial mole fractions, X, are $X_\mathrm{A} = P_\mathrm{A}/P_0$ and $X_\mathrm{B} = P_\mathrm{B}/P_0$, where P_A and P_B are the partial pressures of A and B. After reaction, the mole fraction Y_A of A in the clathrated gas is

$$Y_\mathrm{A} = \frac{[P_\mathrm{A}(V_0 + V_d)/T_0 - (P_1 - P_{\mathrm{H_2O}} - P_{\mathrm{CHCl_3}})[(V_1 + V_d/T_1) + \phi_T]X_\mathrm{A}}{[P_0(V_0 + V_d)/T_0] - (P_1 - P_{\mathrm{H_2O}} - P_{\mathrm{CHCl_3}})[(V_1 + V_d/T_1) + \phi_\mathrm{T}]} \tag{3}$$

Also $Y_\mathrm{B} = (1 - Y_\mathrm{A})$ and the fractionation factor is then

$$\eta = Y_\mathrm{A}(1 - X'_\mathrm{A})/(1 - Y_\mathrm{A})X'_\mathrm{A} \tag{4}$$

where X'_A is the mole fraction of A in the residual gas. To ensure equilibrium between clathrated gas and the gas phase the reaction was continued for at least 24 hr. From measurements of clathration isotherms of inert gases in inert gas–chloroform double hydrates this period was known to be adequate for adjustments of composition.

The density measurements of the residual gas, required to determine X'_A, were accurate to not more than ±2%. The mass-spectrometric analyses of this gas were thought to give its composition to better than ±1%.

RESULTS AND DISCUSSIONS

The separations obtained by selective clathration during formation of hydrates of types I and II are summarized in Table 1. Those gas mixtures in column 2 which are marked with an asterisk were analyzed mass spectrometrically. The fractionation factors recorded in the last column of the table are often very large, and they increase as the temperature of clathration decreases. The clathration of gas during hydrate formation is notably selective toward the heavier inert gas of the pair.

An interpretation of the separation factors, η, was made by Barrer and Stuart (*13*) using the solid-solution theory (*14*) of clathrate phases. If P^d_A and P^d_B are the dissociation pressures of the type I

TABLE 1

Measured Fractionation Factors for Binary Mixtures of Ar, Kr, and Xe

		Composition of residual gas, %			Composition of clathrated gas, %				
Hydrate	Mixture	Ar	Kr	Xe	Ar	Kr	Xe	T, °C	Fractionation factor
Type I	Kr/Ar	44.2_4	55.7_6	—	8.2_2	91.7_8	—	−100	9.0
	Xe/Kr°	—	90.3_5	9.6_5	—	23.2_8	76.7_2	−78	31
	Xe/Ar°	92.7_3	—	7.2_7	12.1_1	—	87.8_9	−78	93
Type II	Kr/Ar	78.8_8	21.1_2	—	43.9_3	56.0_7	—	−30	4.8
	Kr/Ar	79.9_3	20.0_7	—	35.1_6	64.8_4	—	−30	7.3
	Kr/Ar°	72.7_3	27.2_7	—	41.2_4	58.7_6	—	−30	3.8
	Kr/Ar°	92.3_2	7.6_8	—	54.5_3	45.4_7	—	−78	10.0
	Xe/Kr	—	84.3_8	15.6_2	—	57.9_3	42.0_7	−30	3.9
	Xe/Kr	—	63.8_7	36.1_3	—	24.7_6	75.2_4	−30	5.4
	Xe/Kr°	—	79.6_9	20.3_1	—	53.2_7	46.7_3	−30	3.4
	Xe/Ar	94.3_0	—	5.7_0	37.6_5	—	62.3_5	−30	27
	Xe/Ar	94.0_1	—	5.9_9	43.4_1	—	56.5_9	−30	21

° Compositions determined mass spectrometrically.

hydrates containing only A and only B, then, neglecting the vapor pressure of water over the clathrate phases,

$$\eta = P_A^d / P_B^d \tag{5}$$

Also, if as in the chloroform-inert gas double hydrates of type II, the sorption of the inert gas obeys the Langmuir isotherm equation (*10*), the enrichment factor is

$$\eta = K_B / K_A \tag{6}$$

where

$$K_A = \theta_A / P_A(1 - \theta_A) \qquad \text{and} \qquad K_B = \theta_B / P_B(1 - \theta_B)$$

for each of the gases when clathrated in absence of the other and θ denotes the fraction of the smaller cavities occupied by inert gas [the larger are virtually all filled by chloroform (see the introductory section)].

It is therefore of interest to compare the theoretical and the experimental values of η. Decomposition pressures of type I hydrates have recently been measured for xenon hydrate between 0 and −62°C, for krypton hydrate between −70 and −124°C, for argon hydrate between −124 and −183°C. The dissociation pressures are also known for krypton and argon at about 0°C. Linear plots of log P^d vs. $1/T$ were found, so P^d can be interpolated at any desired temperature and log P_A^d/P_B^d readily derived. The theoretical and ob-

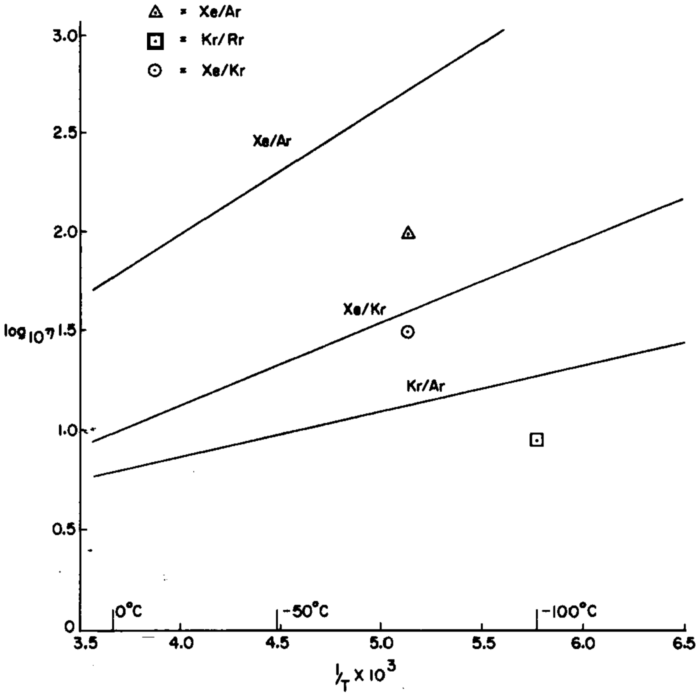

FIG. 2. Lines denote $\log_{10} \eta$ according to Eq. (5) plotted against $1/T$. The points refer to separation factors determined experimentally.

served separation factors are compared in Fig. 2. Experimental values of η are in all cases less than those derived from Eq. (5). This may indicate that complete mixing of the components of the gas mixture was not maintained by the circulation arrangements in the apparatus (Fig. 1), but also may represent limitations in the theory giving Eq. (5). Because in type I hydrates inert-gas molecules occupy some of both kinds of cavity, Langmuir's isotherm equation should not adequately describe the over-all sorption isotherm.

On the other hand, as noted earlier, for the type II chloroform hydrate the uptake of Xe, Kr, and Ar obeys Langmuir's isotherm equation, so that η should be described by Eq. (6). The equilibrium constants K_A and K_B have been determined for each gas at temperatures between 0 and −78°C (*10*), and curves of $\log K_B/K_A$ vs. $1/T$ are shown in Fig. 3, together with experimental values of $\log \eta$. Except for two of the results for Xe/Kr mixtures, η is again somewhat less than the predicted equilibrium separations. However, both theory

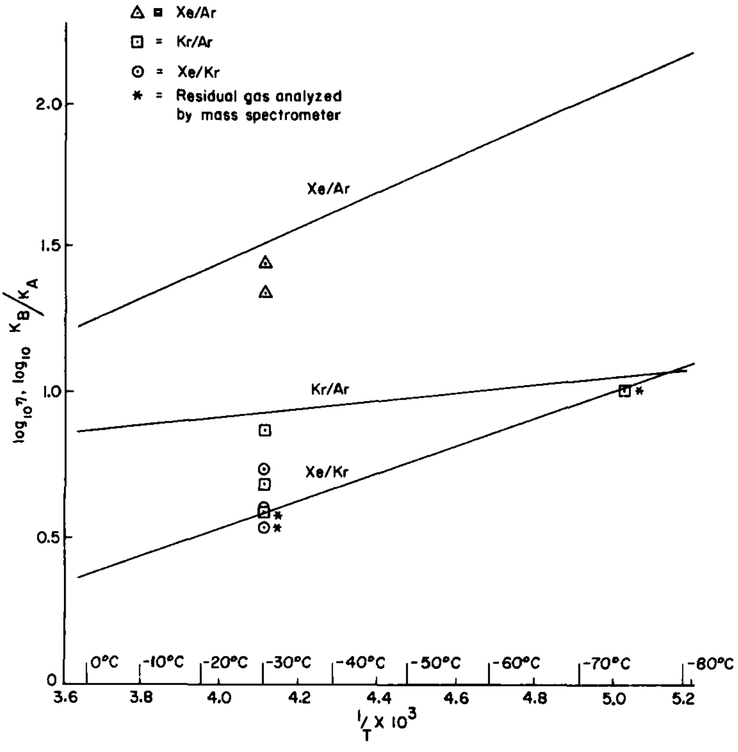

FIG. 3. Lines denote $\log_{10} K_B/K_A$ plotted against $1/T$. The points indicate experimental separation factors.

and experiment agree that very good fractionations of Xe, Kr, and Ar are possible. It may be also inferred that at low temperature Ar could be removed from Ne or He.

Barrer and Ruzicka (8) measured the uptakes of the inert gases and of H_2, O_2, N_2, CH_4, C_2H_4, C_2H_6, and CO_2 in the chloroform hydrate at 70 cm Hg and at ~0°C. When the uptakes were plotted against the boiling temperatures of the gases, the spherical molecules (inert gases and methane) lay on an upper curve and the dumbbell-shaped molecules on a lower one. Thus argon could be selectively removed from air, nitrogen, or oxygen by clathration, and krypton and xenon should be notably enriched. In accordance with Figs. 2 and 3, the equilibrium value of η should rise exponentially with falling temperatures. At ~0°C some ratios K_B/K_A for pairs of gases can be found from the uptakes (*8*) observed in the chloroform hydrate. These ratios, representing equilibrium values of η according to the theory of Barrer and Stuart (*13*), are given in Table 2. They are large even at 0°C and show some interesting

TABLE 2

K_B/K_A for Some Gas Pairs in Chloroform Hydrate at ~0°C

Gas pair[a]	K_B/K_A	Gas pair[a]	K_B/K_A
$Ne + H_2$	3.7	$Kr + Ar$	4.1(3.4[b])
$N_2 + H_2$	6.8	$Xe + Kr$	5.7(2.9[b])
$Ar + Ne$	4.1	$Xe + Ar$	23.4
$Ar + O_2$	1.67	$CH_4 + N_2$	4.6
$Ar + N_2$	2.26	$CH_4 + C_2H_4$	4.7
$O_2 + N_2$	1.35(1.9[b])	$CH_4 + C_2H_6$	5.7

[a] The first-mentioned component is that which should be enriched in the clathrated gas.

[b] The figures in parentheses are values of η measured experimentally (*8*).

trends. Thus methane should concentrate in the clathrate phase in strong preference to nitrogen (or air) and to ethylene or ethane, even though the latter two gases are considerably more condensable than methane. The preference for methane or rare gases as compared with dumbbell-shaped molecules has been ascribed to restricted rotation and hence to reduced rotational entropy of the dumbbell molecules in the cavities, as compared with their full rotational entropy in the gas phase (*8*).

CONCLUSION

Clathration during the formation of gas hydrates both of type I and type II has considerable promise as a means of fractionating mixtures. Guest molecules must first be sufficiently small to fit comfortably into the cavities in the host crystals. Preferential uptake as between pairs of molecules each small enough to occupy cavities is found for spherical molecules, such as rare gas atoms, which are most condensable in their liquids. Spherical molecules are much preferred to dumbbell-shaped molecules of comparable or greater condensability.

REFERENCES

1. M. Baron, in *Physical Methods of Chemical Analysis*. Vol. IV (W. G. Berl, ed.), Academic Press, New York, 1961, p. 248ff.

2. W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and C. G. Christian, *J. Am. Chem. Soc.*, **79**, 5870 (1957).

3. J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitsky, *Bull. Soc. Chim. Belges*, **74**, 381 (1965).

4. J. Hanotier, *Ind. Chim. Belge*, **31**, 19 (1966).

5. A. J. Barduhn, H. E. Towlson, and Y. C. Hu, *Am. Inst. Chem. Eng.*, **8**, 176 (1962).

6. E. G. Hammerschmidt, *Am. Gas Assoc. Monthly*, **18**, 273 (1936).

7. M. von Stackelberg, *Naturwiss.*, **36**, 327, 359 (1949).

8. R. M. Barrer and D. J. Ruzicka, *Trans. Faraday Soc.*, **58**, 2239 (1962).

9. R. M. Barrer and D. J. Ruzicka, *Trans. Faraday Soc.*, **58**, 2262 (1962).

10. R. M. Barrer and A. V. J. Edge, in preparation.

11. M. von Stackelberg and H. R. Müller, *Naturwiss.*, **38**, 456 (1951).

12. H. R. Müller and M. von Stackelberg, *Naturwiss.*, **39**, 20 (1952).

13. R. M. Barrer and W. I. Stuart, *Proc. Roy. Soc.*, (*London*), **A242**, 172 (1957).

14. J. H. van der Waals, *Trans. Faraday Soc.*, **52**, 184 (1956).

Received by editor December 27, 1966
Submitted for publication January 4, 1967