Reports

Phase Composition of Commercial "Ammonium Carbonate"

Abstract. *A unique crystalline phase was the sole constituent in newly opened containers of commercial reagent-grade "ammonium carbonate." The chemical composition, optical constants, x-ray powder diffraction pattern, infrared absorption spectrum, and density indicate a double salt, ammonium bicarbonate-carbamate ($NH_4HCO_3{\cdot}NH_4CO_2NH_2$), which is unstable in air at ambient temperature and decomposes rapidly to ammonium bicarbonate.*

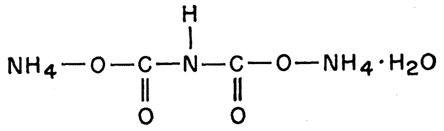
Despite widespread industrial and laboratory use of reagent-grade "ammonium carbonate," there is considerable uncertainty regarding its phase composition. Commercial reagent-grade "ammonium carbonate" is commonly reported to be a mixture of about equal parts of ammonium bicarbonate (NH_4HCO_3) and ammonium carbamate ($NH_4CO_2NH_2$) (*1*), but some reference works state that it is either a mixture of ammonium bicarbonate and ammonium carbamate or a double salt (ammonium bicarbonate-carbamate) with the formula ($NH_4HCO_3{\cdot}NH_4CO_2NH_2$) (*2*). Commercial "ammonium carbonate" transforms rapidly to ammonium bicarbonate on exposure to air with evolution of ammonia. The NH_3 assay of "ammonium carbonate," as given on the manufacturers' label on each container, ranges from 30 to 33 percent in accord with the specifications for reagent-grade ammonium carbonate of the American Chemical Society (1960) which require a minimum NH_3 assay of 30 percent.

Only three of the many solid phases which reportedly occur in the system NH_3-CO_2-H_2O appear to have been characterized by optical or x-ray crystallographic data or both, namely, ammonium bicarbonate (mineral teschemacherite) (*3–5*), ammonium carbamate (*6, 7*), and ammonium carbonate-hydrate [$(NH_4)_2CO_3{\cdot}H_2O$] (*6*).

Microscopic examination of several newly opened containers representing different lots of Mallinkrodt and of Baker lump "ammonium carbonate" revealed that all of the samples were composed solely of a unique colorless coarsely crystalline biaxial negative phase that is neither NH_4HCO_3 nor $NH_4CO_2NH_2$. Its refractive indices are $\alpha = 1.430$, $\beta = 1.578$, $\gamma = 1.588$, all $\pm$ 0.003; birefringence: $\gamma\text{-}\alpha = 0.158$; optic angle: $2V_x = 26.5°$ measured by Mallard's method, $2V_x = 27°$ calculated from the refractive indices. Noteworthy is its very strong birefringence and its superficial resemblance to ammonium bicarbonate from which it may be differentiated readily by its higher intermediate refractive index (β) and its smaller optic angle (NH_4HCO_3 has $\beta = 1.536$ and $2V_x = 42°$) (*8*). This phase is unstable in air at ambient temperature and changes rapidly to ammonium bicarbonate. The transformation may be monitored either microscopically or by x-ray powder-diffraction methods (Table 1).

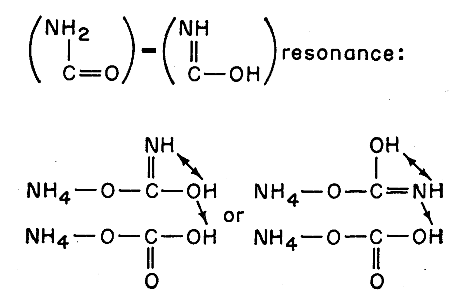
Infrared absorption spectra for the phase which constitutes "ammonium carbonate" and for ammonium bicarbonate are shown in Fig. 1. The spectra were obtained from Baker "ammonium carbonate" and Baker ammonium bicarbonate with a Perkin-Elmer "Infracord" recording spectrophotometer. The Nujol window technique was used to prevent transformation of the "carbonate" to the bicarbonate. The identity of the ammonium bicarbonate was verified by both optical examination and x-ray powder diffraction, and its infrared spectrum is in good agreement with previously published data (*9*). The infrared spectrum of the "carbonate" is similar to but nevertheless uniquely different from that of the bicarbonate (especially the 13 to 15 micron region).

Assays of NH_3 and CO_2 of the "ammonium carbonate" from both sources range from 29.5 to 33 percent and 54 to 56 percent, respectively, and are not compatible with the stoichiometry of either $(NH_4)_2CO_3$, $(NH_4)_2CO_3{\cdot}H_2O$, NH_4HCO_3, or $NH_4CO_2NH_2$ or a mixture of NH_4HCO_3 with either $(NH_4)_2CO_3$ or $(NH_4)_2CO_3{\cdot}H_2O$. Rather, the chemical composition of "ammonium carbonate" suggests that it is either a 1 : 1 molar mixture of ammonium bicarbonate and ammonium carbamate or a double salt ammonium bicarbonate–carbamate ($NH_4HCO_3{\cdot}NH_4CO_2NH_2$) which might be represented as either



$$NH_4{-}O{-}\underset{\underset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}\underset{\underset{O}{\|}}{C}{-}O{-}NH_4\cdot H_2O$$

or possibly a hydrogen-bridged double salt with



The optical, x-ray, and infrared data presented strongly support the double-salt hypothesis advocated, on chemical grounds, by E. Divers (*10*) nearly 100 years ago. He distilled solids with chemical compositions equivalent to $(NH_4)_2CO_3{\cdot}H_2O$, $2NH_4HCO_3{\cdot}NH_4CO_2NH_2{\cdot}2H_2O$, and NH_4HCO_3, and condensed products whose respective bulk chemical analyses matched that of the double salt. The slight departures from chemical stoichiometry of commercial "ammonium carbonate" probably reflect partial transformation to the bicarbonate. The double salt would decompose to ammonium bicarbonate in air according to the reaction ($NH_4HCO_3{\cdot}NH_4CO_2NH_2$) $\rightarrow$ $NH_4HCO_3 + 2NH_3 + CO_2$.

The density of ammonium bicarbonate calculated from x-ray data is 1.545 (*5*), but the measured density is reportedly 1.58 (*11*). The density of the "ammonium carbonate" phase is 1.475 $\pm$ 0.005 as measured pycnometrically in toluene. Jaffee (*12*) has shown that most inorganic compounds for which accurate density and refractive index data are known obey the rule of Gladstone and Dale, $K = [(n\text{-}1/d]$. The double salt is no exception and the calculated mean refractive index (n) based on the specific refractive energies of its elements (*13*) is 1.530 as compared with the experimentally determined mean refractive index $[(\alpha\beta\gamma)^{\frac{1}{3}}]$ of 1.530. Correspondingly, the calculated molar refraction $M(n^2-1)/d(n^2+2)$ of the double salt (M molecular weight) based on the sum of the atomic refractions of the components in the two structural configurations suggested above is 32.96 (*14*) and 32.79 (*15*) as compared with the experimentally determined molar refraction of 32.88. By using its x-ray density, ammonium bicarbonate gives $n_{\text{exptl.}} = 1.504$ and $n_{\text{calc.}} = 1.503$ for the Gladstone-Dale rule and an experimental molar refraction of 15.14 compared with a calculated molar refraction of 15.55 (*16*). The close agreement between these experimental and calculated refractive index-density data strongly supports the identification of the "ammonium carbonate" phase as the double salt ammonium bicarbonate-carbamate.

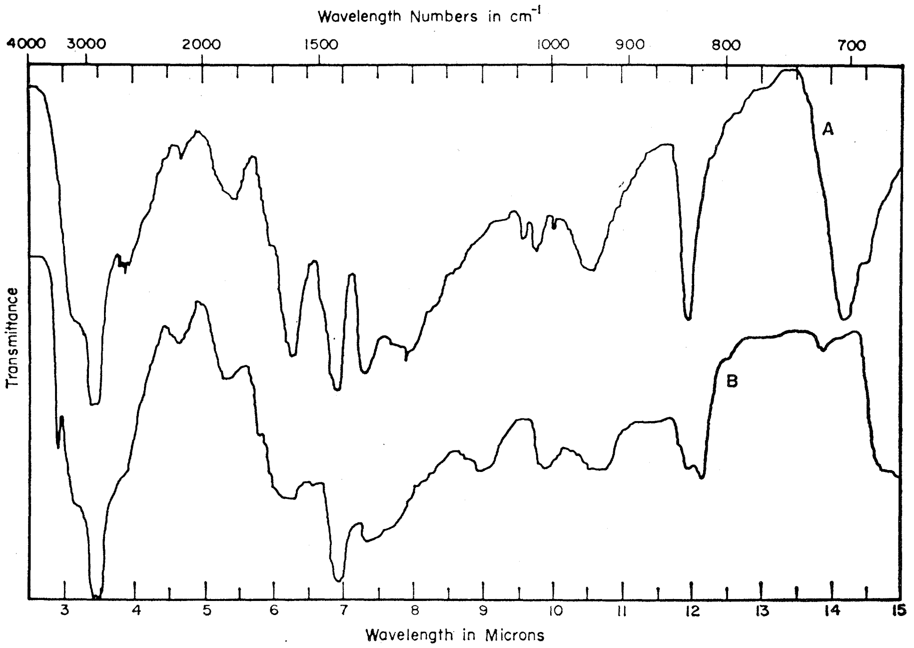


Fig. 1. Infrared absorption spectra of ammonium bicarbonate (*A*) and of "ammonium carbonate" or ammonium bicarbonate-carbamate (*B*). The Nujol window has absorption bands at 3.45, 6.92, and 7.35 microns.

Table 1. X-ray powder-diffraction data for ammonium bicarbonate–carbamate ($NH_4HCO_3 \cdot NH_4CO_2NH_2$), 57.3 mm camera, Mn-filtered FeKα_1 radiation, $\lambda = 1.93597$ Å. I, intensity; d, interplanar distance; B, broad band.

d, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
6.87	5	2.21	5	1.272	2
5.96	7	2.14	3	1.248	2
5.47	2	2.09	15	1.235	3
5.07 B*(1)	20	1.981	<1	1.223	1
4.58 B*(2)	10	1.927	2	1.205	4
4.09	3	1.861	12	1.197	2
3.78 3.66 B*(3)	80	1.799	5	1.161	1
		1.745	5	1.157	3
3.60	5	1.681	10	1.143	<1
3.44 3.36 B*(4)	40	1.671	10	1.136	2
		1.625	3	1.123	4
3.26	4	1.597	1	1.107	<1
3.17	5	1.536	3	1.096	1
3.03 2.97 B	100	1.474	5	1.068	1
		1.452	1	1.057	2
2.89	50	1.436	4	1.032	7
2.46 B*(5)	25	1.413	2	1.022	1
2.30 2.25 B*(6)	40	1.357	<1		
		1.292	3		

* Resolved into two or more lines with vanadium-filtered CrKα_1 radiation, $\lambda = 2.28962$, 57.3 mm camera:

	d,Å	*I*		*d*,Å	*I*		*d*,Å	*I*		*d*,Å	*I*		*d*,Å	*I*		*d*,Å	*I*
(1)	5.15	10	(2)	4.65	5	(3)	3.76	20	(4)	3.44	20	(5)	2.47	15	(6)	2.30	10
	5.03	20		4.54	10		3.68	65		3.37	20		2.45	15		2.28	20
																2.25	15

Galinos (*17*) showed that low temperatures (−20°C) are required to prepare $(NH_4)_2CO_3$ and stated that its infrared absorption spectrum is different from that of commercial "ammonium carbonate" which he considered to be a mixture of NH_4HCO_3, $NH_4CO_2NH_2$, and $(NH_4)_2CO_3$.

The x-ray powder data for $(NH_4)_2CO_3 \cdot H_2O$ reported by Hanawalt, *et al.* (*6*), which constitute ASTM Card 1-0858 (American Society of Testing Materials) compare rather closely with the x-ray data for the double salt given in Table 1. As stated by Hanawalt *et al.* most of their materials were shelf reagents which were not analyzed chemically. Their x-ray powder data for $(NH_4)_2CO_3 \cdot H_2O$ represent the double salt ammonium bicarbonate–carbamate contaminated with ammonium bicarbonate (*20*).

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14. Based on two carbonyl oxygen, two ester oxygen, two carbon, nine hydrogen, one water molecule, one nitrogen as secondary amide, and two ammonia nitrogen. The atomic refraction values are those given by Dreisbach (*18*) except for ammonia nitrogen which was based on the molar refraction for ammonia, calculated from $n = 1.3638$ and

$d = 0.682$ at $-34°C$ (*19*) minus the atomic refraction of three hydrogen atoms.
15. Based on two ammonia nitrogen, eleven hydrogen, two carbon, two ester oxygen, one carbonyl oxygen, one hydroxyl oxygen, average of one primary amide nitrogen and one secondary amide nitrogen (assuming resonance), and average of one hydroxyl oxygen and one carbonyl oxygen (assuming resonance); ammonia nitrogen value calculated from the molar refraction of ammonia.
16. Based on one carbonyl oxygen, one ester oxygen, one hydroxyl oxygen, one carbon, five hydrogen, and one ammonia nitrogen as calculated from the molar refraction of ammonia (double salt calculation).
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Geothermal Heat Flow in the Gulfs of California and Aden

Abstract. *Eighteen measurements in and near the gulfs of California and Aden indicate the geothermal flux is several times the world-wide mean of* 1.2×10^{-6} *cal/cm² sec in both regions. Both gulfs closely coincide with the intersection of oceanic rises with continents and have likely been formed under tensional forces, which suggests an association with mantle convection currents.*

The gulfs of California and Aden (Figs. 1 and 2) are two elongated indentations of the sea into the continents, located nearly halfway around the earth from each other. They are of similar dimensions, and Girdler (*1*) has given a recent interpretation of the geology and geophysical measurements in both gulfs. Both regions are seismically active (*2*), probably in association with the San Andreas fault system for the Gulf of California, and with the great African Rift system for the Gulf of Aden.

Measurements of the geothermal flux in Table 1, shown in Figs. 1 and 2, range from 0.62×10^{-6} cal/cm² sec [μ (*3*)] to 6.15 μ in the Gulf of California, and from 2.47 μ to 5.98 μ in the Gulf of Aden. The mean of the measurements for the two regions, respectively, is 3.12 μ and 3.68 μ; this compares with the mean of the oceanic values of 1.2 μ to 1.4 μ (*4, 5*). The measurements were made in the usual method with a cylindrical probe to measure the temperature gradient in the ocean-floor sediments (*6*) and a transient needle-probe method to measure the thermal conductivity of a cored sample of the sediments (*7*). The distance between temperature-sensing elements in the probes used for temperature-gradient measurements ranged from 1.4 to 2.6 m. Thermal conductivities were corrected for ambient conditions of the sea floor, following Ratcliffe (*8*). The thermal conductivity values enclosed by parentheses in Table 1 were taken as the mean of the measurements on cores at adjacent stations.

Many of the measurements in Table 1 were made at locations where sea depths are about one-half the average for deep-sea regions. Such relatively shallow depths may introduce some uncertainty concerning the temperature stability of the bottom water, on which the accuracy of the measurements depends. Nevertheless, to account for the whole of the observed temperature gradient corresponding to a heat flow of 3 μ requires an improbable temperature drop of several tenths of a degree (C) of the bottom water immediately before a measurement is made. Except for the deep parts of the basins in the Gulf of California beneath sill depths, the deep waters of the gulfs of California and Aden are open to the oceans; the water temperatures at 2000 m for the respective gulfs are about 2.3°C and 3.2°C. Meager hydrographic data in the Gulf of California indicate the bottom water temperature there has remained constant to within 0.1°C over the past 70 years. Therefore, systematic errors due to changes of bottom water temperature are not likely to be significant in either region.

Recent carbon-14 data give present rates of sedimentation up to 300 cm/1000 years for topographic basins in the Gulf of California (*9*). These values are consonant with the high sedimentation rates for other basins near the coast off California (*10*), and about two orders of magnitude greater than normal rates for the deep-sea floor (*11*). There are two possible effects on the surface heat flow of a high-sedimentation rate: (i) after some time a reduced heat flow may result, as part of the heat from the interior is used to raise the temperature of the rapidly depositing sediments; (ii) an increased heat flow could result from chemical or other reactions producing heat after sedimentation, such as oxidation of organic carbon. As a result of (i), calculations indicate the equilibrium heat flow in the Gulf of California may be significantly greater than that measured in areas where the high rates of sedimentation occur (*5*); this increase would not change the conclusions presented here. At station V-6, the only low value measured in both gulfs also may result from a local high sedimentation rate or irregular topography; there is no clear evidence, however, to demonstrate that these effects are especially important at this locality. As many of the sediment cores obtained in the Gulf of California show chemically reducing conditions, the oxidation of carbon is probably not an important source of the heat flow measured there. Little is known about the Gulf of Aden, but both effects seem likely to be less important than for the Gulf of California.

The high heat-flow values in the Gulf of California are comparable to those obtained farther south on the East Pacific Rise (*4, 5*), where the results have been interpreted as an association with convection in the earth's mantle. Hamilton (*12*) has presented evidence that Baja California has split away from the mainland of Mexico as a result of tensional stresses, leaving behind the Gulf of California. A similar interpretation seems reasonable for the Gulf of Aden

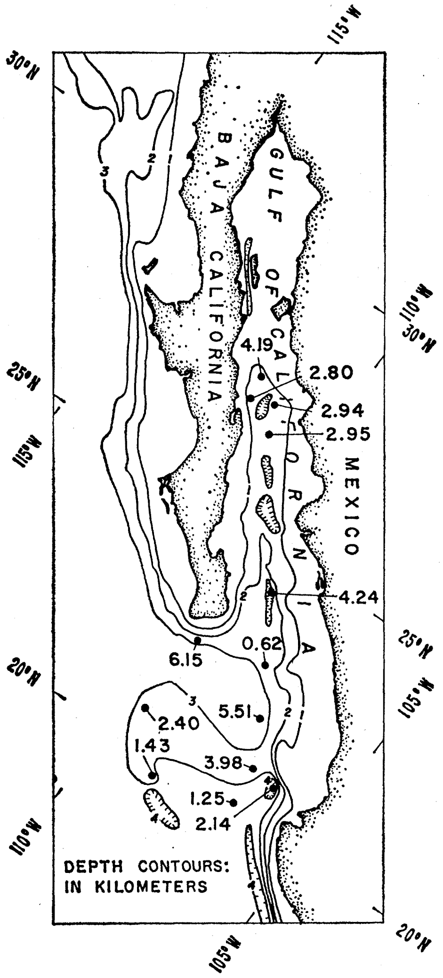

Fig. 1. Geothermal flux in the Gulf of California.