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Vapour deposition for the refinement, separation and production of high-purity ammonium thiocyanate and thiourea

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Based on the high volatility and difference in the vapour pressures of ammonium thiocyanate and thiocarbamide and the reaction of mutual isomerization, new methods were developed for refining, separating and producing the pure isomers from commercial ammonium thiocyanate.

Commercial or coke-chemical ammonium thiocyanate NH_4NCS is the product of recovery of prussic acid by ammonium polysulfides from a coke-oven gas.[1] The NH_4NCS content of commercial ammonium thiocyanate is 60–93%. Ammonium thiocyanate is a pseudohalide[2] with the melting point T_m = 150 °C and a unique property to change[3] into its organic isomer, thiourea $(NH_2)_2CS$, a molecular crystal with $T_m \approx 180$ °C. The mutual isomerization $NH_4NCS \leftrightarrow (NH_2)_2CS$ can be used for producing thiourea.[4–6] It is well known[6,7] that this reaction proceeds in a solid phase, a melt and a solution at 140–180 °C at a noticeable rate as a kinetically reversible first-order reaction. The forward and reverse reactions lead to the formation of an equilibrium eutectic fusion containing ~75% ammonium thiocyanate and ~25% thiourea (melting point of ~104 °C).

We have developed a 'dry' method for the separation and production of pure ammonium thiocyanate and thiourea from coke-chemical ammonium thiocyanate. The kinetics of interconversion and the purity of separated isomers were observed by measuring the conductivity of aqueous solutions.[8,9] An ammonium thiocyanate solution is an electrolyte, whereas thiourea solutions do not exhibit conductivity.

To measure the vapour pressures of isomers and to refine, separate and produce pure ammonium thiocyanate and thiourea, we used a set-up shown in Figure 1. The set-up is based on a glass double-neck round-bottom 1 l flask *1* with turning device *2* and desublimator cells *3–6*, pressure gauge *7* (vacuum, oil, membrane and thermal-conduction manometers), nitrogen trap *8*, backing pump *9*, and valves (⊗). Items *1–6* were joined *via* ground glass sections with Teflon gaskets (0.2 mm thick). The temperature of the inner walls of glass articles *1–6* was controlled by thermostats *10–14* with water (*10*, *11*; up to 100 °C) or silicon oil (*12–14*; up to 230°C) to within ~0.5 °C. Flask *1* was filled with an inert gas from cylinder *15*.

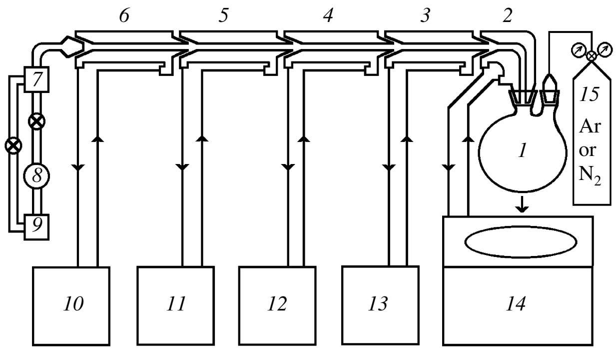

Figure 1 Schematic diagram of the set-up for measuring vapour pressures, refining, separating and preparing ammonium thiocyanate and thiocarbamide (see the text).

The vapour pressure of ammonium thiocyanate is 0.3–0.4 Pa (~2×10^{-3} torr) at 313.13 K (~40 °C).[10] To estimate the vapour pressures of ammonium thiocyanate and thiourea at high temperatures, we used the published method.[11] The accuracy of this method is ±0.5 torr. Owing to the isomerization $NH_4NCS \leftrightarrow (NH_2)_2CS$, the pressures of the isomers can be reliably measured only at the melting point of thiourea. The measurements were conducted on a simplified device without cells *3–6*. Flask *1* was filled with finely ground and pure ammonium thiocyanate or

Table 1 Refinement of commercial ammonium thiocyanate.

Impurities in commercial ammonium thiocyanate and the parameters of refinement	Purity of ammonium thiocyanate, NH_4CNS		Temperature of cells *1–2*/K (°C), yield of NH_4CNS (%) and impurity contents of sublimates *3–6*						Temperatures of cells *3–6*/K (°C) at a temperature of *14* equal to 180 °C and NH_4CNS purity (%)			
	Initial commercial ammonium thiocyanate from Donetsk (wt%)	Certified by All-Union State Standard 3768-64 for pure ammonium thiocyanate (wt%)	403 (130)	423 (150)	443 (170)	463 (190)	483 (210)	503 (230)	Cell *3* 363 (90)	Cell *4* 343 (70)	Cell *5* 323 (50)	Cell *6* 293 (20)
NH_4CNS, no less than	92.5	99	99.8	99.5	99.5	99	94	89	99.8	99.6	99.0	97–99
Nonvolatile substances, no more than	0.13	0.01	no	no	no	no	no	no	no	no	no	no
Water-insoluble substances, no more than	0.6	0.005	—	—	—	—	—	—	—	—	—	—
Sulfates, no more than	0.7	0.0025	no	no	no	no	no	no	no	no	no	no
Heavy metals, no more than	—	0.0003						10^{-5}%				
Chlorides, no more than	0.9	0.002						10^{-3}%				
Iron, no more than	0.9	0.001						10^{-5}%				
Substances oxidesed by iodine (in terms of sulfides), no more than	—	0.002						10^{-3}%				
Absorbance of alcohol solutions	—	0.05	—	—	—	—	—	—	—	—	—	—
Thiourea	—	—	no	no	no	traces	1%	3%	traces	no	no	no

Table 2 Separation of ammonium thiocyanate and thiourea by a gas-phase method.

Run no.	Temperature of cells *1–6*/°C					Yield of products by cells *3–6* (%)					Content of basic substance by cells *3–5* (%)			Melting point/°C (±1 °C)		Presure/torr
											Thiourea	Mixture thiourea–ammonium thiocyanate	Ammonium thiocyanate			
	1–2	*3*	*4*	*5*	*6*	*3*	*4*	*5*	*6*	Total	*3*	*4*	*5*	Thiourea	Ammonium cyanate	
1	150	145	100	70	20	19	19	50	6	94.0	99.1	17.2/82.4	98.4	180	148	5×10^{-3}
2	160	130	130	80	20	26	5	63	3	97.0	99.7	—	99.5	182	149	5×10^{-3}
3	170	140	90	70	20	20	30	45	2	97.0	99.5	16.8/83.0	99.5	181	149	5×10^{-2}
4	180	130	110	80	20	23	11	63	2	98.0	99.8	—	99.5	182	149	5×10^{-2}
5	180	130	110	80	20	26	7	63	2	98.0	99.7	—	99.5	182	149	5×10^{-3}
6	180	135	110	50	20	26	4	68	0.6	98.6	99.6	—	91.6	182	142	~5
7	180	150	110	80	20	5	22	68	2	97.0	—	18.7/80.7	99.5	172	149	5×10^{-3}
8	180	120	110	80	20	20	10	65	2	97.0	99.8	—	99.5	182	149	5×10^{-1}
9	190	130	130	80	20	26	4.3	66	0.3	96.6	99.7	—	99.5	182	149	5×10^{-1}
10	200	130	110	80	20	21	2	62	8	93.0	98.0	—	99.2	178	147	5×10^{-3}

thiourea. The system was pumped out and filled with argon to atmospheric pressure at room temperature. Flask *1* was placed in thermostat *14*. Synchronously with the termination of sample melting by a needle-like valve located between *7* and *8*, the rate of pumping was determined, which allowed us to measure vapour pressures, typically, within 1 min. The melting point was registered visually and using a thermocouple, and it was compared at that moment with the reading of gauge *7*. The averaged data for vapour pressures at 180 °C are 3–4 torr for thiourea and ~35 torr for ammonium thiocyanate.

The initial coke-chemical ammonium thiocyanate (mp 130°C; NH_4NCS content, ~90 wt%) was obtained from Kemerovo by-product coke plants. Table 1 lists its average technical characteristics compared with those of pure ammonium thiocyanate. The method for cleaning ammonium thiocyanate involves sublimation-desublimation process at specified sublimation temperatures (1–2: 130–230 °C, see columns 4–9 in Table 1) and the desublimation of substrates (3–6: 90–20 °C, columns 10–13) at reduced pressures (10^{-1}–10^{-3} torr). The resulting melt boils and transforms into a gas phase. The ammonium thiocyanate vapour desublimates on substrates 3–6. The end of the process is determined by the disappearance of boiling. Nonvolatile impurities remained in flask *1*.

A specific feature of this method is that, on heating the starting substance in a vacuum, only a portion of the substance melts and evaporates, which is in contact with the heated surface. Thus, in spite of rather high temperatures in unit *14*, their absolute value does not affect the quality of cleaned ammonium thiocyanate (*cf.* columns 3 and 10–12 in Table 1). The chosen range of temperatures in units *1* and *2* has an optimum at 150–180 °C.

The equilibrium isomers mixture was produced due to the known kinetics of isomerization.[5–9] Flask *1* was filled with cleaned ammonium thiocyanate under argon and kept for a given time in unit *14* heated to 150 °C. Then, the obtained fusion was poured from flask *1* into a vessel with liquid nitrogen. The resulting porous ingot was powdered. After analysing the composition of fusion powders, optimal temperatures (155–170 °C) for making a fusion and the corresponding holding times after the complete melting of ammonium thiocyanate have been determined (1–3 h). The colourless fusions contained 20–30% thiourea, 80–70% ammonium thiocyanate and less than 1% decomposition products.

To separate ammonium thiocyanate and thiourea, we placed the powdered fusion in flask *1*, evacuated the system and specified some parameters for the separation of isomers. In preliminary experiments, the optimal weight of the charge was found to be 1 g. This yielded the highest indices of purity of ammonium thiocyanate and thiourea. In the alternate evacuation and filling of the system with an inert gas, up to 20 g of a powder can be consumed (in Table 2, we spent only 5 g). Table 2 shows the results of 10 runs for separation of isomers. We can state that in this method on the substrate with a temperature higher than 120 °C no ammonium thiocyanate can be desublimated, and 150 °C is too high for producing pure thiourea owing to its isomerization into ammonium thiocyanate. The optimal conditions for desublimating thiourea are created at 120–140 °C, and for ammonium thiocyanate at < 100 °C.

Using optical analysis, we found that ammonium thiocyanate and thiourea crystals produced by known solution methods have plenty of faults including vacuoles filled with crystallization medium and gas. In ammonium thiocyanate (fine acicular shape, 98.4–99.5% purity) and thiourea (fine tabular, 98.0–99.8%) crystals produced by this method, no gas–liquid inclusions have been found. The refinement and separation of isomers is performed in one stage, it does not require other chemicals, and is an ecologically clean process with minor and easily trapped by-products.

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