

Table 1. Binding energies of ammonia in the calcium and barium chloride amines.

Salt	Density (ρ)	ΔH (kcal/mole)	U (kcal/mole)	E (kcal)	Transition
CaCl ₂	2.1741§		513.6*		
Ca(NH ₃)Cl ₂	1.8049	17.0	443.9†	86.7	Mono → anhydrous
Ca(NH ₃) ₂ Cl ₂	1.6060	15.0	413.5	45.4	Di → mono
Ca(NH ₃) ₄ Cl ₂	1.3816	10.1	370.4	53.1	Tetra → di
Ca(NH ₃) ₆ Cl ₂	1.1877	9.8	320.6	59.6	Octa → tetra
BaCl ₂	3.8888		408.5‡		
Ba(NH ₃) ₈ Cl ₂	1.5260	9.0 (6)	318.4†	99.1	Octa → anhydrous

* Assume a rutile lattice.

† Assume a fluorite lattice.

‡ Assume a layer lattice.

§ Density of solid at 25° relative to water at 4°C.

some preliminary results on the hexammines of the alkaline earth halides. The total binding energy of the ammonia ligands was calculated for these salts and was found to be of the order of magnitude of 145–180 kcal. The problem that presents itself is to see how the binding energy of ammonia to the metallic cation changes from the lower amines to the amines of greater magnitude.

If one knows the lattice energies for the anhydrous salt and the ammine complex and the energy for the transition between them, it is possible to calculate the energy with which the ammonia forming the difference between them is bound. From the crystal type, the lattice energy U can be calculated by use of the equation

$$U = 279.0(\rho/M)^{1/3}A_d \left(1 - \frac{0.345}{R}\right),$$

where A_d is the appropriate Madelung constant, ρ is the density of the solid, M is the formula weight of the substance, and R is the ion-distance parameter (in angstroms). For purposes of calculation,

$$R = 10^8 / (3 \times 6.023 \times 10^{23} \rho / M)^{1/3}.$$

The binding energy E is the energy necessary to dissociate the ammonia molecules from the gaseous ammoniated cation, the end products also being in the gaseous state. It can be expressed as

$$(b-a)E = (U_a - U_b) + (b-a)\Delta H,$$

where ΔH is the heat of formation of the ammine calculated from the Nernst equation (3, 4). The calculated binding energies for the amines of calcium and barium chlorides are shown in Table 1.

The results in this table show the same trends as the work on the pyridinates of cobalt (II) salts (2). In the calcium chloride amines, it can be seen that the ammonia in the transition from mono-ammine to anhydrous has a binding energy of twice the magnitude of the di-ammine to mono-ammine transition. Then as ammonia is added, the binding energy decreases considerably, falling off to 59.6 kcal for the transition, octa-ammine to tetra-ammine. Since barium chloride forms only an octa-ammine, only one transition, the octa-ammine to anhydrous, is possible, and it has a much smaller value than the similar transition in the calcium chloride system.

References

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Transparent Light Baffle for Electrophysiological Recording

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One difficulty encountered by investigators who are dependent on photographic records of electric phenomena is the reflection of light from the face of the cathode-ray tube. Shielding from direct and ambient light can become a cumbersome and expensive task.

This problem can be mitigated when Eastman Kodak Linagraph paper or film is used for recording from the face of a P7 cathode-ray tube (orange-blue fluorescing). Since Linagraph paper and film are both insensitive to red light, a light baffle constructed of transparent red Plexiglas may be used. A baffle of this type permits continuous observation of the cathode-ray tube while a photographic record is being obtained from the same tube. It is possible to focus the electron beam with the baffle in place. This item has proved satisfactory in shielding the light of a 75-w bulb reflected directly onto the tube face from a distance of 2 ft (Fig. 1).

A shield of this type has been constructed in our laboratory as follows: 1/8-in. transparent red Plexiglas sheet (catalog number 2444, Rohm & Haas or equivalent) was used to construct a box open at each end and a truncated pyramid open at each end (Fig. 2). The opening in the box was made large enough to receive the small shield around the face of the



Fig. 1. Demonstration of light shield: 75-w bulb at 2-ft distance, shining directly onto oscilloscope face, with (left) and without (right) red baffle in place. Without the baffle in place the image is obscured by the over-all exposure of the recording film, resulting in a completely black record.

cathode-ray tube, and yet not large enough to interfere with any of the controls on the front panel of the scope. The small opening of the pyramid was made just large enough to receive the lens of the camera. The base of the pyramid was made just large enough to telescope into the box. By telescoping in this manner the entire assembly may be removed or set in place with ease. During use the small aperture rests on the camera lens, and the large aperture rests on the shield encircling the tube face.

A horizontal rod may be used to support the baffle in place. Set screws may be used in place of the horizontal rod. We used one of the scrap triangles left over from cutting the sides of the pyramid fastened at right angles to the upper surface of the pyramid to prevent the baffle from telescoping after it had been set in place. Slots may be made for the insertion of data cards to be photographed from the face of the cathode-ray tube.

If a P11 (blue fluorescing) tube is used, the baffle should be made of blue Plexiglas, since the red filter will not transmit blue light and, therefore, does not permit continuous visual monitoring of the oscilloscope during the experiment.

Blue filters do not shield the effects of direct illumination of the screen as well as red plastic; however, the blue baffle has proved adequate to shield the film from the effects of indirect light.

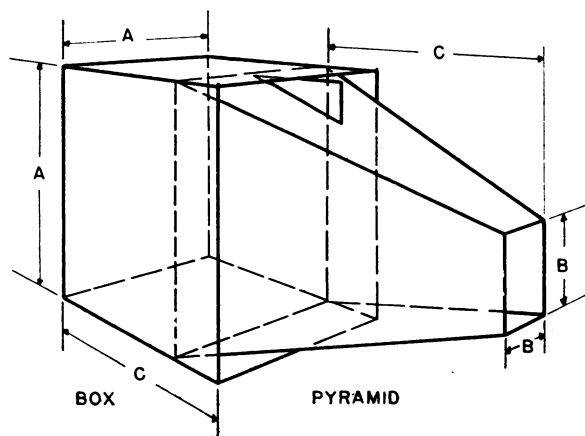


Fig. 2. Diagram of transparent light baffle. Dimensions: A, outside diameter of oscilloscope bezel; B, outside diameter of lens mount; C, approximately $\frac{5}{8}$ lens to oscilloscope distance.

In summary, a plastic light baffle is here described for use with an oscilloscope that permits continuous observation of the cathode-ray tube while a photographic record is being obtained from the face of the same cathode-ray tube. This baffle shields the tube face and film from both direct and ambient light.

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Conversion of 3-Hydroxykynurenine to 4,8-Dihydroxyquinoline by Mouse Liver Homogenate

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When incubated with mouse liver homogenate, 3-hydroxykynurenine was degraded in various ways. Paper chromatographic analysis of the reaction mixture revealed the presence of several diazo-positive substances, two of which were identified as xanthurenic acid and 4,8-dihydroxyquinoline, respectively.

Recently Makino and Takahashi (1), in this laboratory, detected 4,6-dihydroxyquinoline and 4,6-dihydroxyquinoline-2-carboxylic acid in the incubation mixture of 5-hydroxykynurenine with liver homogenate of mice. The present finding (2) may be considered to be analogous to that of Makino and Takahashi.

3-Hydroxykynurenine, synthesized by the method of Sakan (3) *et al.* with a slight modification was incubated with mouse liver homogenate in Krebs-Ringer-phosphate buffer of pH 7.4 at 37°C. After 3 hr the reaction mixture formed a dark red pigment, which on a paper chromatogram moved very little from the starting line. The substances that were produced from 3-hydroxykynurenine by the incubation with liver homogenate were investigated by paper chromatography (solvent: butanol, acetic acid, water, 4:1:5). After 3 hr of incubation there appeared, under ultraviolet irradiation, four fluorescent substances at Rf values of 0.61, 0.48, 0.41, 0.32, respectively, and three spots (Rf = 0.45, 0.32, 0.12) detectable with diazo-reagent. A dark green fluorescent spot showing Rf 0.32 and positive diazoreaction was the residual 3-hydroxykynurenine. Other fluorescent spots and a diazo-positive spot having Rf 0.12 are now under investigation.

After 4 hr of incubation, 3-hydroxykynurenine and the fluorescent spot at Rf 0.41 disappeared, but on testing with the diazo-reagent, two other faster moving spots (Rf = 0.79, 0.64) were found. The spot at Rf 0.64 gave a brown-red color with diazo-reagent, while the one at Rf 0.79, which gave with ultraviolet light a greenish-blue fluorescence when present in sufficient amount, showed an orange-red color with the diazo-reagent. The behavior of the latter was the same as that of 4,8-dihydroxyquinoline. The diazo-positive spot at Rf 0.45 turned spontaneously green in color