average, to 0.2 cc. The results obtained by this method have been satisfactory as the following table will indicate.

Substance	% N without cartridge	% N with cartridge	Calcd.
Sparteine mercuric chloride	2.01	4.83	4.86
Alkaloid A from *Lupinus caudatus*	5.90 6.17 9.62 9.73	10.03 10.13	10.02
Alkaloid from *Lupinus cruckshanksii*	6.97 9.60	10.34 10.23	
Alkaloid from *Lupinus palmeri*	9.54 9.31	9.97 10.07	
Alkaloid from *Lupinus andersoni*	6.61 6.51	10.47	

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CONCERNING THE EXISTENCE OF THE SO-CALLED HEATS OF TRANSFER (Q^* VALUES) IN PELTIER HEATS

Sir:

To explain the Ludwig-Soret effect, Eastman [THIS JOURNAL, **48,** 1482 (1926)] introduced the concept of the heat of transfer (Q^*) [the heat of transfer of a mole of component A is designated as $\overline{Q}_A$ by Eastman], a latent heat which appears at some point in a homogeneous solution when a mole of dissolved component is transferred from this point to another place in the solution. The same quantity occurs in a discussion of electrolytic thermal forces. Wagner [*Ann. Physik,* (5) **3,** 629 (1929)] and later Lange and co-workers [Lange and Mischtschenko, *Z. physik. Chem.*, **A149,** 1 (1930)] extended these considerations to the electrolytic Peltier heats. According to them

$$ {}_{\text{metal/solution}}\pi_i = T({}_{\text{metal}}\overline{S}_i - {}_{\text{solution}}\overline{S}_i) - z_iQ^*_\theta - n_CQ^*_C + n_AQ^*_A \qquad (1) $$

(π_i is the Peltier heat given up at the anode by a mole of the potential determining ion i of valence z_i, n_C and n_A are transference numbers and Q^*_C and Q^*_A are molar heats of transfer of cation and anion).

To date the following evidence for the existence of these novel heat effects (Q^*) could be advanced: (1) Eastman [THIS JOURNAL, **50,** 292 (1928)] found a certain agreement between the Q^* values determined from Ludwig-Soret coefficients and estimated from suitable thermo-electric measurements.

(2) Thermo-electric forces between differently oriented single crystals of the same metal can only be explained by Q^* values depending on direction [Wagner, *loc. cit.*] if one does not wish to postulate a directional dependence of $\overline{S}$.

(3) Measurements of the Ludwig-Soret effect and of thermoelectric forces on solid salts and mixed crystals have been explained by use of heats of transfer [Reinhold, *Z. physik. Chem.*, **B11,** 321 (1931)].

All these proofs rest on measurements made on non-isothermal systems, which, because of unavoidable irreversible heat conductivity, can only be treated thermodynamically under limited conditions [*cf.* Boltzmann, *Sitzungsber. Akad. Wiss. Wien, Math. Naturw. Klasse*, **96,** 1285 (1887)].

It therefore seemed desirable to test the assumption of heats of transfer by means of electrolytic Peltier heats which can be measured *isothermally* [Lange and Monheim, *Z. physik. Chem.*, **A150,** 186 (1930)].

Peltier heats, measured with a sensitive differential calorimeter [Lange and Robinson, *Chem. Rev.*, **9,** 89 (1931)] of the system $Ag/AgNO_3$ confirmed more exactly than previously the validity of the Thomson relationship between Peltier heat (π) and thermo-electric force (ϵ)

$$\pi/T = \epsilon$$

for electrolyte systems, so that objections raised against the non-isothermal foundations mentioned above have been weakened [Lange and Hesse, *Z. Elektrochem.*, **38,** 428 (1932)].

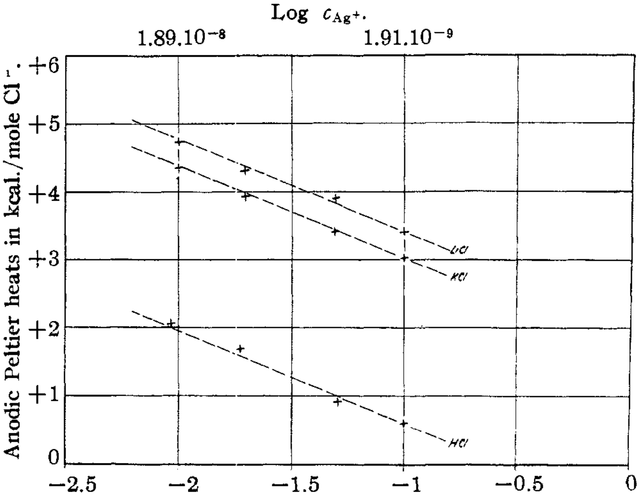

Fig. 1.—Electrolytic Peltier heats of the system Ag/AgCl/HCl (KCl, LiCl).

Peltier heats were also measured at 25° for the system $Ag/AgCl/Cl^-$ in the presence of different cations (K^+, H^+, Li^+).

According to equation (1) it follows for equal Cl^- concentration that

$$\begin{aligned}{}_{\mathrm{AgCl/KCl}}\pi_{\mathrm{Cl^-}} - {}_{\mathrm{AgCl/HCl}}\pi_{\mathrm{Cl^-}} &= T({}_{\mathrm{HCl}}\bar{S}_{\mathrm{Cl^-}} - {}_{\mathrm{KCl}}\bar{S}_{\mathrm{Cl^-}}) \\ &+ ({}_{\mathrm{HCl}}n_{\mathrm{H^+}}Q^*_{\mathrm{H^+}} - {}_{\mathrm{KCl}}n_{\mathrm{K^+}}Q^*_{\mathrm{K^+}} + {}_{\mathrm{KCl}}n_{\mathrm{Cl^-}}Q^*_{\mathrm{Cl^-}} - {}_{\mathrm{HCl}}n_{\mathrm{Cl^-}}Q^*_{\mathrm{Cl^-}})\end{aligned}$$

A more exact discussion shows that the first term on the right is practically zero for the small concentrations of the investigation. Therefore without consideration of the Q^* terms the electrolytic Peltier heats should be equal within the limits of experimental error for the different electrolytes.

As a matter of fact there are appreciable differences (almost 3 kcal.) even in 0.01 *M* solutions as the figure shows.

The existence of and therewith the necessity for considering these Q^* terms which Eastman introduced is thus established. It is also evident that the differences of partial molar entropies can not be determined by employing Peltier heats and thermo-electric forces alone [*cf.*, on the contrary, Bruzs, *Z. physik. Chem.*, **A161,** 83 (1932)].

A more detailed presentation of this material will be published shortly in a German journal.

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THE THERMAL INTERCONVERSION OF MIXED BENZOINS

Sir:

Julian and Passler [THIS JOURNAL, **54,** 4756 (1932)] record another case of the transformation of the mixed benzoin not formed by the cyanide condensation (anisbenzoin) into the isomer formed by the cyanide method (benzanisoin). The reverse transformation, which is the object of our work, has not hitherto been recorded. The present writers have found that pure benzanisoin (cyanide condensation), after heating for three hours at 125–130° and fractionation from cold dilute alcohol, gives appreciable amounts of anisbenzoin, m. p. 89°, identical with Asahina and Terasaka's compound. Evidently, above the melting point, an equilibrium lying far over to the side of benzanisoin exists. The amount of pure anisbenzoin isolated, after heating, from 20 g. of benzanisoin was 0.10 g. but considerably more was present.

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THE NEUTRON, THE ATOMIC NUCLEUS AND MASS DEFECTS

Sir:

Two general theories of the constitution of atomic nuclei have been proposed: (1) that the nucleus is built up largely from α-particles (Harkins and Wilson[1]) and (2) that the Harkins–Masson[2] nuclear formula $(p_2e)_z(pe)_I$ (a), $(np)_z n_I$ (b) or $(\alpha/2)_z n_I$ (c), represents the constitution of any nucleus

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(1) (a) Harkins and Wilson, *Proc. Nat. Acad. Sci.*, **1,** 276 (1915); (b) THIS JOURNAL, **37,** 1368, 1383 (1915).

(2) (a) Harkins, THIS JOURNAL, **42,** 1956 (1920); *Phil. Mag.*, **42,** 305 (1921). See also Ref. 1(b) and Durrant, THIS JOURNAL, **39,** 621–7 (1917). (b) Masson, *Phil. Mag.*