Table VI. Thermodynamic Properties at 25° C.

Reaction	$-\Delta H_c$, Kcal. Mole^{-1}	$-\Delta H_T$, Kcal. Mole^{-1}	$-\Delta G$, Kcal. Mole^{-1}	ΔS^a, Cal. Deg.$^{-1}$ Mole^{-1}
		Metal β-Alaninates		
$Co^{2+} + A^-$	3.32 ± 0.22	3.60	5.74 ± 0.02	8.1 ± 0.8
$Ni^{2+} + A^-$	3.81 ± 0.14	3.46	6.84 ± 0.01	10.2 ± 0.5
		Metal Glycinates		
$Co^{2+} + G^-$	2.48 ± 0.05	2.82(*3*)	6.29 ± 0.01	12.8 ± 0.3
$Ni^{2+} + G^-$	4.14 ± 0.10	4.09(*3*)	8.43 ± 0.01	14.4 ± 0.4
$Cu^{2+} + G^-$	6.76 ± 0.04		11.71 ± 0.01	16.6 ± 0.3
$Zn^{2+} + G^-$	3.39 ± 0.17		7.50 ± 0.02	13.8 ± 0.7
$CoG^+ + G^-$	2.55 ± 0.02	3.55	5.42 ± 0.02	9.6 ± 0.2
$CuG^+ + G^-$	6.89 ± 0.09		9.47 ± 0.02	8.7 ± 0.3

^{a} Calculated ΔS values are based upon the calorimetric ΔH_c.

glycine. This probably reflects the greater loss of librational entropy of the substituted ligand when it chelates with the metal ion.

For the corresponding five- and six-membered ring oxalate and malonate complexes, the heats of formation are endothermic (*12*) which is consistent with the essentially electrostatic forces involved. Their stabilities are wholly dependent on the large favorable entropy changes accompanying the reactions which offset the unfavorable enthalpy effects. In contrast, the inclusion of a nitrogen atom in the chelate ring gives rise to a greater covalency, owing to the increased electron-donor capability of the nitrogen atom, and this is reflected by the exothermic heats of complex formation. In Table V the calorimetric heats of formation follow the order predicted from a consideration of ligand field stabilization, increasing in exothermicity from Co^{2+} to Cu^{2+}.

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Ethanol–Acetic Acid Esterification Equilibrium with Acid Ion-Exchange Resin as Catalyst

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Equilibrium coefficients, $Q = (X_{EtA})(X_{H_2O})/(X_{HA})(X_{EtOH})$, in terms of mole fractions, X, were determined in various mixtures of the four substances in contact with sulfonic acid resin at 15°, 25°, 35°, and 50° C. At 25° C., Q varied from 1.91 to 4.58 over the composition range studied. The effect of temperature on Q was small. The times required for equilibration were about the same as those with strong acid homogeneous catalysts which, however, give higher Q values.

SINCE the work of Berthelot and St. Gilles in 1862, the ethyl acetate equilibrium has been studied extensively with strong acid homogeneous catalysts or at high temperatures to accelerate the slow reactions. Published equilibrium coefficient values, Q, at room temperatures range from about 3 to 15. (Q is dimensionless and numerically the same whether concentrations are expressed in molality, molarity, or mole fraction.) Q is used in place of a true equilibrium constant because activity coefficients are not available and they may vary as much as 100-fold in these concentrated, nonideal solutions. Studies employing HCl (*1*) and $HClO_4$ (*5*) as homogeneous catalysts yield results different from each other. An ebullioscopic study (*4*) and experiments in which dioxane was used as an inert solvent (*3*), among many others, also give divergent results. Data obtained before 1950 are reviewed in (*2*).

Preliminary work by the present authors showed that HCl, $HClO_4$, HNO_3, and H_2SO_4, as homogeneous catalysts, each affect Q differently in otherwise similar esterification mixtures. A general trend—Q increasing with catalyst concentration—was confirmed in agreement with (*1*) and (*5*). However, Q also varies with the proportions of the four reactants. This study with the ion-exchange heterogeneous catalyst was made to determine equilibrium coefficients in media lacking the complication of high concentrations of ionized acid catalysts.

EXPERIMENTAL

One batch of Fisher Scientific Co. Rexyn AG 50(H)(Lot No. 712143), 40- to 100-mesh, a strongly acidic sulfonated polystyrene copolymer of medium porosity, was used throughout. It was washed with alternating portions of 3*M* HCl, water, and ethanol, followed by at least three washings with the stock esterification mixture to be used, allowing several minutes of standing between each.

Fisher reagent grade acetic acid was used. Its purity was determined to be 99.83% by its freezing point. The remaining 0.17% was added to the weight of water.

Absolute ethanol, Commercial Solvents Corp., was stored over $CaSO_4$ (Drierite) before use.

Ethyl acetate, reagent grade, was subjected to azeotropic fractional distillation (*6*) to remove water and ethanol. It was stored over $CaSO_4$.

Stock mixtures of reactants were prepared by weighing each component to five or more significant figures. Equilibrium was approached from both sides. After washing the resin with stock, about 40 ml. of stock and 5 ml. of resin were placed in glass bottles having polyethylene-lined screw caps. Tests showed negligible evaporation loss from these. The nearly full bottles were stored in constant temperature baths (±0.1° C.) and agitated one to five times daily. After several days (weeks at 15° C.), at least four samples were withdrawn, weighed to four or five significant figures, immediately diluted with water, and titrated with 0.1*M* NaOH to the phenolphthalein end point. The base was prepared from low carbonate 50% NaOH, standardized against constant boiling HCl, and stored in a CO_2-free atmosphere.

The titration was tested with known mixtures of acetic acid and ethyl acetate. The 0.1*M* NaOH gave results within one part per thousand of the acid weight taken, while 0.5*M* NaOH gave high results presumably because of ester reaction during titration. For each of the first five mixtures and the $HClO_4$ tests mentioned below, another set of samples from the same bottles was taken after periods from several days to several weeks and titrated to check for any change indicating lack of equilibrium. Except for two 50° C. cases noted later, no significant change was found after 11 days (the shortest initial period used) at 25° C. and above, in checks up to 6 weeks after mixing. One mixture at 15° C. changed slightly between the 16th and 49th days. Since any changes were slight or nil, the average of successive titrations was used in calculations.

After experiments 1 through 5, experiments 6 through 13 were performed with mixtures to provide widely different compositions. These were done with the same resin and kept at 50° C. for 4 days to accelerate reaction, and at 25° C. for 4 days to reach equilibrium at that temperature. Two samples from each of these mixtures were taken for titration.

In experiments 4 and 5 at 50° C., a slight increase in acidity was noted from the first to the second week perhaps indicating some resin decomposition since equilibrium was surely achieved rapidly at 50° C. Duplicates of these were made which showed less increase in titer, not over 0.5%. Estimated best average values were used for Q calculation in these two cases.

To test possible effect of the resin on Q, a mixture was allowed to equilibrate in the presence of 0.01197 mole fraction of $HClO_4$ both with and without resin in the bottles. The Q values at four temperatures were:

Temperature, ° C.	15	25	35	50
No resin	5.06 ± 0.01	4.83 ± 0.03	4.72 ± 0.03	4.50 ± 0.01
Resin added	5.05 ± 0.05	4.85 ± 0.04	4.70 ± 0.01	4.48 ± 0.02

Table I. Experimental *Q* Values

Expt. No	X_{HA}[a]	X_{EtOH}[a]	X_{EtA}[a]	X_{H_2O}[a]	*Q*, 15° C.[b]	*Q*, 25° C.[b]	*Q*, 35° C.[b]	*Q*, 50° C.[b]
1	0.2394	0.2353	0.1402	0.3851	4.36 ± 0.02	4.18 ± 0.02	4.09 ± 0.01	3.96 ± 0.02
	0.1589	0.1547	0.2207	0.4657				
2	0.0000	0.08677	0.02582	0.8874	3.77 ± 0.01	3.62 ± 0.02	3.57 ± 0.01	3.48 ± 0.01
	0.01797	0.1047	0.007847	0.8695				
3	0.1631	0.8358	0.0000	0.00109	1.99 ± 0.01	2.04 ± 0.01	2.10 ± 0.04	2.08 ± 0.01
	0.01562	0.6882	0.1475	0.1486				
4	0.0000	0.1555	0.5427	0.3018	3.12 ± 0.02	3.02 ± 0.02	3.05 ± 0.01	2.94 ± 0.04
	0.1071	0.2626	0.4356	0.1948				
5	0.09432	0.1855	0.4144	0.3059	3.75 ± 0.02	3.60 ± 0.02	3.61 ± 0.05	3.53 ± 0.01
	0.1294	0.2205	0.3792	0.2709				
6	0.08391	0.07939	0.02364	0.8131		4.32		
	0.07759	0.07309	0.02993	0.8194				
7	0.07936	0.06952	0.1388	0.7124		4.46		
	0.1239	0.1140	0.09425	0.6679				
8	0.07792	0.07658	0.04563	0.7999		4.53		
	0.08398	0.08258	0.03957	0.7939				
9	0.02878	0.02828	0.01685	0.9261		3.54		
	0.03963	0.03913	0.005993	0.9152				
10	0.1455	0.1429	0.08517	0.6264		4.58		
	0.1240	0.1215	0.1066	0.6479				
11	0.0990	0.6838	0.05796	0.1593		2.09		
	0.02436	0.6091	0.1326	0.2339				
12	0.08184	0.4192	0.0000	0.4989		2.82		
	0.02852	0.3659	0.05333	0.5522				
13	0.1062	0.5442	0.3472	0.00241		1.91		
	0.03448	0.4724	0.4189	0.07414				

[a] Mole fractions: upper at start, lower at equilibrium at 25° C. [b] Standard deviation calculated from four or more titrations. (In experiments 6 through 13, only two samples were taken.)

The mole fractions of the other components of this mixture at equilibrium at 15° C. were: (A stands for acetate) $X_{HA} = 0.148_0$, $X_{H_2O} = 0.482_5$, $X_{EtOH} = 0.143_8$, and $X_{EtA} = 0.213_8$. From the good agreement at all temperatures, the authors assumed that the resin does not affect Q in mixtures in contact with it in the absence of soluble acids.

RESULTS

The Q values, with initial and equilibrium compositions of the mixtures, are shown in Table I. In all but one case, Q decreased slightly with temperature increase. In experiment 3, Q was constant at 2.05 ± 0.06. However, the slight increase is just above the titration error limit. This mixture is unique in having the highest ethanol content.

Jones and Lapworth (*1*) reported Q from 4 to over 8 with HCl as catalyst. Trimble and Richardson (*5*) report Q from about 3 to 14 with $HClO_4$, and 3.45 as the Q extrapolated to zero catalyst.

A multiple linear regression analysis was made on a digital computer to seek correlation between Q and mole fractions at equilibrium for experiments 1 through 13 at 25° C. The following approximate relationship summarized these results.

$$Q = 4.13 + 10.8\,X_{HA}\,X_{H_2O} - 2.53\,X_{EtOH}/(1 - X_{EtA}) \\ -1.89 \times 10^{-4}/X_{EtOH}\,X_{EtA} - 2.13\,X_{EtOH}\,X_{H_2O}$$

It reproduces the Q values within a standard deviation of 0.1 unit of the Q values, and reflects the fact that Q is high for mixtures with high acetic acid and water content, and low for high ethanol and ester content.

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Contact Angles of Mercury on Various Surfaces and the Effect of Temperature

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The contact angle of mercury on six different materials was measured as a function of temperature over the range 25° to 150° C. The materials were stainless steel, nickel, tungsten, glass, fused quartz, and Teflon. The contact angles were very high on all the substrates, ranging at equilibrium from about 130° to 145° at 25° C. Although there were significant differences between the dynamic advancing and receding angles, equilibrium was rapidly achieved in all systems, and the residual hysteresis was negligible. The temperature coefficient of the contact angle was very small in all the systems and was positive. The largest increase occurred with Teflon and amounted to about 15° of angle over the 125° C. temperature range explored.

IN THE weightless environment prevailing in space vehicles the behavior of a liquid is determined largely by its capillary properties. A controlling parameter of capillary behavior is the contact angle of the liquid against the solid material which forms its container. Thus a precise knowledge of the contact angle is necessary in the design of tankage systems for the various liquids used in spacecraft. One liquid of interest, because of its potential use as the propellant in an ion engine, is mercury. The object of this work therefore, was to determine the contact angle of mercury against various materials which might be used in tankage over a temperature range that might exist in use. Thus, mercury contact angles against stainless steel, nickel, tungsten, borosilicate glass, quartz, and Teflon were