

where C_1 and C_2 are the concentration of fatty acid in the upper and lower layers respectively, k_1 is the distribution constant of monomer in the upper and lower layers, and k_2 is the dissociation constant of dimer into monomer in the upper layer.

From the values of k_1 and k_2 and their variation with temperature, free energy change (ΔF), enthalpy change (ΔH) and entropy change (ΔS) were calculated by the ordinary thermodynamic treatment. The results obtained are given in the next table.

	Temp. °C	k_1			k_2		
		ΔF cal./mole	ΔH cal./mole	ΔS cal./mole, deg.	ΔF cal./mole	ΔH cal./mole	ΔS cal./mole, deg.
Palmitic acid	25	220			930		
	10	290	1810	4.9	1230	6990	22.1
	0	330			1460		
Myristic acid	25	360			1010		
	10	420	1890	5.2	1300	7230	21.6
	0	470			1520		
Lauric acid	25	520			1170		
	10	620	2167	5.5	1470	7380	20.9
	0	660			1680		

20. Protecting Methods against Blistering on Galvanized Steel Plate

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Many investigators have observed that the blistering on the galvanized steel plate is caused by the hydrogen absorbed during acid pickling before hot galvanizing. So, it is important to know the behavior of the hydrogen in the steel plate during and after acid pickling for the protection of blistering. The authors have investigated the absorption and the evolution of hydrogen in the steel plates by sulphuric acid pickling under various conditions.

Steel plates used for these experiments have 0.5 mm. thickness and following chemical composition: C, 0.06%; Si, 0.12%; Mn, 0.38%; P, 0.057%; S, 0.025%; and H₂, 1.6 cc./100 gr Fe. Determination of hydrogen in steel plate is performed in conformity to the "vacuum heat extraction method" established by "Gakushin", except that the Orsat's apparatus is replaced by Ambler's for gas analysis and extraction temperature is raised to 900°C.

Eight small plates cut to 15×60mm. are pickled simultaneously in 1.8 l. of 3.6~9.8% H₂SO₄ solution at 10~90°C. for various lengths of time (0~90 min.).

At first, it was ascertained that the volume of absorbed hydrogen by steel plates was not influenced by the existence of the rolled scale on them.

The volume of absorbed hydrogen increases for the initial 10 min. and decreases in longer pickling time. At 60°C., steel plates absorb the most hydrogen during 40 min. pickling with 6.8% H₂SO₄ solution.

The concentration of H₂SO₄ does not affect the degree of hydrogen absorption.

After pickling by 6.8% H₂SO₄ at 60°C. for 40 min., the pickled plates were kept at various temperatures. By holding at room temperature, the absorbed hydrogen hardly effuses, even in 20 days.

After holding the pickled steel plates in hot water of 60 and 90°C. for 90 hrs. these plates evolve respectively 30 and 40% of the initial volume of absorbed hydrogen by pickling.

In order to facilitate the detection of evolution of absorbed hydrogen, the iron sulphide powder was added to the pickling solution before pickling, as S²⁻ ion promotes the absorption of hydrogen in steel. In this case, the volume of absorbed hydrogen reaches 55.6 cc./100grFe. in comparison with 4.6 cc./100 grFe. under the same condition without iron sulphide addition. And most of these absorbed hydrogen effuses at room temperature, and the remained hydrogen in steel reaches 5.32 cc./100grFe. after 15 days.

By holding in 60 and 90°C. hot water, the plates pickled with 6.8% H₂SO₄ solution containing S²⁻ ion effuse 50 and 85% of the initial volume of absorbed hydrogen in 5 hours respectively.

"Rodine" or gelatine is added at various amounts to the pickling solution containing S²⁻ ion in order to retard the hydrogen absorption. Of these inhibitors, "Rodine" shows the most favourable result, that is, addition of Rodine 0.09 gr./l. decreases the volume of absorbed hydrogen to 1/20 of that of absorbed hydrogen without this reagent.

21. Synthesis of Some Fatty Acid Derivatives

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1. Reactions of Diethyl Decyl-malonate.

a) Synthesis of diethyl decyl-malonate. (I) $C_{10}H_{21}CH<\begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix}$

The authors have prepared (I) by the action of diethyl oxalate upon ethyl laurate in the presence of sodium ethylate according to *J. Am. Chem. Soc.*, **69**, 2354, (1947). Yield 87.3%, b.p. 183-188°C/22mmHg.