THE FREE ENERGIES OF REACTIONS OF CALCIUM CARBIDE[1]

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Although calcium carbide has been treated with a large variety of elements and compounds over a wide range of conditions, little has been done in the way of estimating the free-energy changes of the reactions which do or might occur. With the exception of those involving the formation of calcium cyanamide and the formation and decomposition of calcium carbide itself, nothing can be found in the literature on this subject.

This shortage was noted in the course of an extensive survey on the reactions of calcium carbide. Since free-energy values can be very useful in investigating new reactions, an effort was made to estimate this property for a large number of cases. About forty reagents were studied, generally with several alternative reactions for each. Among the organic reagents, only one or two members in any family were considered.

The results, while containing large probable errors, nevertheless clearly differentiate most of the reactions into those thermodynamically possible and those thermodynamically impossible. Heats of reaction and changes in heat capacity have been included to permit moderate extrapolation of results to higher temperatures.

GENERAL METHOD

The standard free energy for each reaction was found by the algebraic addition of the corresponding free energies of formation of the reactants and products. Heats of reaction and changes in heat capacity were estimated in the same manner.

Whenever available, values were taken from the literature. Special methods were used to estimate many of the entropies and specific heats. The concept that there is a definite change in heat of reaction and entropy accompanying the structural alteration of one compound to form another was widely used.

The probable errors involved in the final free-energy values were estimated in a somewhat arbitrary manner. The error resulting from several contributing errors was taken to be the square root of the sum of the squares.

HEATS OF FORMATION

Many heats of reaction of organic and inorganic compounds were taken from Bichowsky and Rossini (1), applying a correction of 200 calories per

TABLE 1

Heats of formation from heats of combustion

COMPOUND*	ΔH COMBUSTION		ΔH FORMATION
	calories		*calories*
Ethyl acetoacetate............	$-690,800$	(2)†	$-216,550$
Diethyl malonate.............	$-860,400$	(2)	$-209,570$
Acetic anhydride.............	$-431,900$	(2)	$-150,210$
Acetone......................	$-426,800$	(2)	$-61,060$
Ethyl acetate................	$-536,900$	(2)	$-113,580$
Allylene(g)..................	$-465,100$	(2)	$+45,610$
Iodobenzene..................	$-770,700$	(2)	$+34,280$
Methyl butyl ketone.........	$-895,200$	(2)	$-80,520$
sec-Butyl alcohol...........	$-634,000$	Text, p. 2	$-84,850$
n-Butyl alcohol.............	$-638,600$	(2)	$-80,250$
Dimethylethylcarbinol........	$-784,600$	(2)	$-96,870$
Dibenzyl.....................	$-1,810,600$	(2)	$+12,510$
n-Propane(g)................	$-526,300$	(2)	$-29,930$
n-Pentane(g)................	$-838,300$	(2)	$-43,170$
n-Hexane(l).................	$-989,800$	(2)	$-54,290$
Acetylenedicarboxylic acid......	$-305,900$	(3)	$-139,470$

* All substances are in the solid state unless indicated as liquid (l) or gaseous (g).
† References are to bibliography or to text of this paper.

TABLE 2

Corrections in heats of formation for structural changes

NO.	MODIFICATION IN STRUCTURE	DERIVATION	CORRECTION
			calories
1	$Ca(CN)_2(s)$ for $Ca(CN)_2(aq)$	$Ba(CN)_2(s)-Ba(CN)_2(aq)$	$+1,500$
2	$2(CaS-$ for $NaS-)$	$CaS-Na_2S$	$-23,600$
3	$2(CaC\equiv$ for $NaC\equiv)$	$CaC_2-Na_2C_2$	$-18,600$
4	$2(CaC\equiv$ for $HC\equiv)$	$CaC_2-Na_2C_2 + 2(NaC_2H-C_2H_2)$	$-76,200$
5	$2(CaOOC-$ for $HOOC-)$	$CaC_2O_4-H_2C_2O_4$	$-135,500$
6	$2(CaOC-$ for $HOC-)$	$Ca(OC_2H_5)_2-2C_2H_5OH$	$-94,720$
7	$\equiv$ for $=$	$C_2H_2-C_2H_4$	$+42,900$
8	$\equiv$ for $-$	$C_2H_2-C_2H_6$	$+74,860$
9	$C-CH_2-C$ for $C-C$	$1/2(n$-pentane-n-propane)(g)	$-6,620$
10	$C-CO-C$ for $C-CH_2-C$.	$CH_3COC_4H_9-C_6H_{14}$	$-26,230$
11	C_2H_5O- for $HO-$	$CH_3COOC_2H_5-CH_3COOH$	$+3,720$

carbon atom to convert from the diamond-carbon to the graphite-carbon basis. More were calculated as indicated in table 1 from their heats of

Heats of formation by application of corrections for structural changes

BASE COMPOUND		CORRECTION NO.†	DESIRED COMPOUND	
Compound	ΔH_f and source*		ΔH_f	Compound
	calories		*calories*	
$Ca(CN)_2$(aq)	−59,800 (1)	1	−58,300	$Ca(CN)_2$(s)
2NaSH	−113,520 (1)	2	−137,120	$Ca(SH)_2$
$2NaC_2H$	+51,000 (1)	3	+32,400	$Ca(C_2H)_2$
$HOOCC{\equiv}CCOOH$(s)	−139,470 (table 1)	5	−275,000	$Ca\left(\begin{array}{c}OOC-C\\ \|\|\|\\ OOC-C\end{array}\right)$
$2CH_3COCH_2COOC_2H_5$	−433,100 (table 1)	6	−527,820	$Ca(CH_3COCHCOOC_2H_5)_2$
$2CH_2(COOC_2H_5)_2$	−419,140 (table 1)	6	−513,860	$Ca(CH(COOC_2H_5))_2)_2$
sec-Butyl alcohol	−84,850 (table 1)	1/2 6, 1/2 4, 8	−95,450	$Ca\left(\begin{array}{c}C{=}C\\ O\end{array}CHCH_3\right)$
n-Butyl alcohol	−80,250 (table 1)	1/2 6, 1/2 4, 8	−90,850	$Ca\left(\begin{array}{c}C{=}C-CH_2\\ O-CH_2\end{array}CH_2\right)$
Dimethylethylcarbinol	−96,870 (table 1)	1/2 6, 1/2 4, 8	−107,470	$Ca\left(\begin{array}{c}C{=}C\\ O\end{array}C(CH_3)_2\right)$
$2CH_3OH$	−114,500 (1)	6	−209,220	$Ca(OCH_3)_2$
$C_2H_4Cl_2$(g)	−28,900 (1)	8	+45,960	C_2Cl_2(g)
$C_2H_4Br_2$(g)	−10,200 (1)	8	+64,660	C_2Br_2(g)
$C_2H_4I_2$(g)	+16,400 (1)	8	+91,260	C_2I_2(g)
n-Hexane(l)	−54,290 (table 1)	8	+20,570	$C_2H_5C{\equiv}CC_2H_5$(l)
n-Hexane(l)	−54,290 (table 1)	8	−31,890	$CH_3COC{\equiv}CCOCH_3$(l)
n-Propane(g)	−29,930 (table 1)	8, 9	+38,310	$CH_3C{\equiv}CCH_3$(g)
$C_6H_5CH_2CH_2C_6H_5$	+12,510 (table 1)	8	+87,370	$C_6H_5C{\equiv}CC_6H_5$
H_2SO_4(l)	−193,750 (1)	11, 11	−186,310	$(C_2H_5)_2SO_4$(l)

* Reference 1 or table 1.

† See table 2.

combustion taken from the *Handbook of Chemistry and Physics* (2) and the *International Critical Tables* (3), using −94,250 and −68,370 calories per gram-mole as the heats of formation of carbon dioxide and water, respectively. The heat of combustion of *sec*-butyl alcohol was taken as the average of those for *n*-butyl and *tert*-butyl alcohols. The heat of formation of ketene was taken from Rice and Greenberg (10). The differences between values at 18° and 25°C. were ignored.

The remaining heats of formation were estimated by applying corrections for structural changes to those of known compounds, as indicated in table 3. The corrections and the manner in which they were estimated are indicated in table 2.

HEAT CAPACITIES

Many specific heats were taken from the *Handbook of Chemistry and Physics* (2) and from the *International Critical Tables* (3) by suitable in-

TABLE 4

Specific heats of calcium compounds at 25°C.

COMPOUND	SPECIFIC HEAT	COMPOUND	SPECIFIC HEAT	COMPOUND	SPECIFIC HEAT
	cal. per gram		*cal. per gram*		*cal. per gram*
CaO..............	0.182	$Ca_3(PO_4)_2$.......	0.193	$CaSiO_3$.........	0.177
$Ca(OH)_2$.......	0.273	CaC_2...........	0.200	$CaMoO_4$........	0.165
CaF_2.............	0.207	$CaCO_3$*.........	0.196	$CaWO_4$.........	0.103
$CaCl_2$...........	0.162	$CaCO_3$†........	0.188		
$CaSO_4$...........	0.173	$Ca(OCOCH_3)_2$..	0.240	Average........	0.19

* Aragonite.   † Calcite.

terpolation and extrapolation and were converted directly to the corresponding molar heat capacities at constant pressure and 25°C.

Table 4 indicates that the average specific heat for thirteen calcium compounds is 0.19 calorie per gram, with ten of the values being within 15 per cent of the average. Accordingly, this figure was accepted for the remaining calcium compounds.

The rest of the compounds were assigned specific heats or molar heat capacities corresponding to those of similar compounds, as shown in table 5. It is seen that for liquids and solids the specific heats were assumed to be the same, while for gases the molar heat capacities were taken equal.

ENTROPIES

Kelley (4) gives entropies for a number of calcium compounds which, with the exception of those having an atom linked to calcium in two places,— that is, calcium sulfide and calcium oxide,—are listed in table 6. It is

TABLE 5

Estimated heat capacities of organic compounds

LIQUID AND SOLID COMPOUNDS			GASEOUS COMPOUNDS		
Compound	Compared to	Specific heat	Compound	Compared to	Heat capacity
$C_2H_5C{\equiv}CC_2H_5(l)$	1,5-Hexadiene(l)	0.407	C_2Cl_2	C_2H_2	10.0
$CH_3COC{\equiv}CCOCH_3(l)$	1,5-Hexadiene(l)	0.407	C_2Br_2	C_2H_2	10.0
$CH_3COBr(l)$	$CH_3COCl(l)$	0.339	C_2I_2	C_2H_2	10.0
$CH_3COI(l)$	$CH_3COCl(l)$	0.339	$CH_2{=}C{=}O$	CH_3CHO	16.2
$(C_2H_5)_2SO_4(l)$	$H_2SO_4(l)$	0.339	CH_3CH_2O	CH_3CHO	16.2
$(CH_3CO)_2O(l)$	$CH_3COOC_2H_5(l)$	0.459	$CH_3C{=}CH$	$CH_3CH_2CH_3$	17.3
$C_6H_5I(l)$	$C_6H_5Br(l)$	0.231	$CH_3C{=}CCH_3$	$(CH_3)_3CH$	20.1
$C_6H_5C{\equiv}CC_6H_5(s)$	$C_6H_5CH_2CH_2CH_2C_6H_5(s)$	0.363	$C_2H_5NH_2$	$CH_3CH_2CH_3$	17.3
$CH_3CONH_2(s)$	Urea(s)	0.320			

TABLE 6

Specific entropies of calcium compounds at 25°C.

Compound	$CaCO_3$	$CaC_2O_4 \cdot H_2O$	CaF_2	$CaSO_4$	CaH_2	$Ca(OH)_2$	$Ca_3(PO_4)_2$	Average
E.U. per gram	0.220	0.256	0.210	0.188	0.235	0.235	0.186	0.220

TABLE 7

Entropies by application of corrections for physical and structural changes

COMPOUND	CHANGE	BASE COMPOUND	S OF BASE* E.U.	CORRECTION E.U.	S OF COMPOUND E.U.
$C_2H_2(g)$	= for —	$C_2H_4(g)$	52.3 (8)	−2.7	49.6
$C_2Cl_2(g)$	2(Cl for H)	$C_2H_2(g)$	49.6 (table 7)	+18.0	67.6
$C_2Br_2(g)$	2(Br for H)	$C_2H_2(g)$	49.6 (table 7)	+23.0	72.6
$C_2I_2(g)$	2(I for H)	$C_2H_2(g)$	49.6 (table 7)	+28.0	77.6
$CH_3C{\equiv}CH(g)$	= for —	$CH_3CH{=}CH_2(g)$	63.1 (8)	−2.7	60.4
$CH_3C{\equiv}CCH_3(g)$	= for —	av. Butene-2(g)	72.1 (8)	−2.7	69.4
$C_2H_5C{\equiv}CC_2H_5(l)$	= for —	n-Hexylene(l)	68.1 (9)	−2.7	65.4
$C_2H_5Cl(g)$	Cl for H	$C_2H_6(g)$	55.0 (8)	+9.0	64.0
$C_2H_5Cl(l)$	Condensation	$C_2H_5Cl(g)$	64.0 (table 7)	−19.9	44.1
$CH_3COCl(l)$	COX for CH_2X	$C_2H_5Cl(l)$	44.1 (table 7)	−0.4	43.7
$C_2H_5Br(l)$	Condensation	$C_2H_5Br(g)$	65.0 (9)	−21.9	43.1
$CH_3COBr(l)$	COX for CH_2X	$C_2H_5Br(l)$	43.1 (table 7)	−0.4	42.7
$C_2H_5I(g)$	I for H	$C_2H_6(g)$	55.0 (8)	+14.0	69.0
$C_2H_5I(l)$	Condensation	$C_2H_5I(g)$	69.0 (table 7)	−24.0	45.0
$CH_3COI(l)$	COX for CH_2X	$C_2H_5I(l)$	45.0 (table 7)	−0.4	44.6
$C_2H_5NH_2(g)$	NH_2 for H	$C_2H_6(g)$	55.0 (8)	0.0	55.0
$C_2H_5NH_2(l)$	See text	$C_2H_5NH_2(g)$	55.0 (table 7)	−21.0	34.0
$CH_3CONH_2(l)$	COX for CH_2X	$C_2H_5NH_2(l)$	34.0 (table 7)	−0.4	33.6
$CH_3CONH_2(s)$	Freezing	$CH_3CONH_2(l)$	33.6 (table 7)	−10.0	23.6
$CH_3COCH_2COOC_2H_5(l)$	$\{$CO for CH_2 / Insert COO$\}$	n-Pentane(l)	62.0 (8)	+13.7	75.7
$CH_2(COOC_2H_5)_2(l)$	Insert 2(COO)	n-Pentane(l)	62.0 (8)	+26.4	88.4
$CH_2{\cdot}CH_2O(l)$	See text	$CH_3CHO(g)$	61.0 (9)	−0.0	61.0
$CH_2{=}C{=}O(g)$	= for —	$CH_3CHO(g)$	61.0 (9)	−2.7	58.3
$C_6H_5I(l)$	I for H	$C_6H_5H(l)$	41.9 (9)	+14.0	55.9
$C_6H_5C{\equiv}CC_6H_5(s)$	= for —	$C_6H_5CH{=}CHC_6H_5(s)$	60.0 (9)	−2.7	57.3
$(C_2H_5)_2SO_4(l)$	2(C_2H_5O for HO)	$H_2SO_4(l)$	31.3 (text)	+48.0	79.3
$CH_3COC{\equiv}CCOCH_3(l)$	2(CO for CH_2)	$C_2H_5C{\equiv}CC_2H_5(l)$	65.4 (table 7)	+1.0	66.4

seen that their average specific entropy is 0.22 E.U. per gram with a maximum deviation of 16 per cent from the average, in spite of the fact that the entropies themselves varied from 9.9 for calcium hydride to 57.7 for calcium phosphate. Accordingly, the entropies of the remaining calcium compounds were estimated using the average specific entropy.

Sulfuric acid and calcium hydroxide both can be represented as "$A(OH)_2$", and as solids they have approximately the same specific heats. Then if identical specific heat curves are assumed, sulfuric acid will have the same specific entropy of 0.235 E.U. per gram as calcium hydroxide at 25°C., exclusive of the 8.3 E.U. change on fusion at 10°C. This makes a total of 31.3 E.U. for liquid sulfuric acid.

The entropy of gaseous ethylene oxide was assumed to be the same as for gaseous acetaldehyde, its isomer.

The remaining entropies were estimated by applying corrections for structural changes to compounds of known entropy, as indicated in table 7. The corrections used were those recommended by Parks and Huffman (9), with the exception of those for the alterations "C_2H_5O—

TABLE 8

Entropies of elements in their standard states at 25°C.

Element	$\frac{1}{2}H_2$	$\frac{1}{2}F_2$	$\frac{1}{2}Cl_2$	$\frac{1}{2}Br_2$	$\frac{1}{2}I_2$	$\frac{1}{2}O_2$	S (rhombic)	$\frac{1}{2}N_2$	Ca	C (graphite)
S^0_{298}	15.615	24.02	26.62	16.3	13.3	24.52	7.6	22.89	9.95	1.3

for HO—" and "—COX for —CH_2X". The former was taken to be the difference between the entropies of liquid ethyl acetate and acetic acid, while the latter was derived similarly from the entropies of liquid acetic acid and ethyl alcohol. In several cases it was necessary to allow for the entropy of vaporization or of fusion to get the compound into its normal state. A latent heat of fusion of 40 calories per gram was assumed for acetamide. Trouton's rule was assumed to hold for ethylamine. The entropies of the compounds to which the corrections were applied were taken from table 7 or from Parks (8) or from Parks and Huffman (9).

Table 8 contains a list of atomic entropies taken from Parks and Huffman (9), save for calcium (4) and fluorine (6).

FREE ENERGIES OF FORMATION AND THEIR PROBABLE ERRORS

The free energies of formation of many of the organic compounds were taken from Parks and Huffman (9). Their figures for the limiting values of the errors involved in their estimates were taken to be the probable errors save for acetic anhydride, where the limiting value of "over 5000" was set at 7000 calories. For carbon dioxide and carbon monoxide errors of 500 calories were assumed.

TABLE 9

Thermodynamic properties of reactants and products

COMPOUND	ΔF°_{298}	ΔH_{298}	C_p
CaC₂	$-14,560 \pm 1,200$	$-14,100$ (1)*	12.9 (3)*
CaH₂	$-36,670 \pm 1,000$	$-46,000$ (1)	8.0 (table 4)
CaO	$-144,250 \pm 1,000$	$-151,700$ (1)	10.2 (3)
CaS	$-112,190 \pm 1,000$	$-113,400$ (1)	13.7 (table 4)
Ca(OH)₂	$-214,300 \pm 1,000$	$+236,000$ (1)	20.3 (3)
Ca(NH₂)₂	$-60,950 \pm 1,200$	$-91,500$ (1)	13.7 (table 4)
Ca(SH)₂	$-127,280 \pm 3,200$	$-137,120$ (table 3)	20.2 (table 4)
CaCN₂	$-73,040 \pm 1,200$	$-84,800$ (1)	15.2 (table 4)
Ca(CN)₂	$-46,930 \pm 1,600$	$-58,300$ (table 3)	17.5 (table 4)
CaF₂	$-277,800 \pm 1,000$	$-290,200$ (1)	16.52 (3)
CaCl₂	$-179,020 \pm 1,400$	$-190,600$ (1)	18.2 (3)
CaBr₂	$-162,640 \pm 2,200$	$-162,220$ (1)	38.0 (table 4)
CaI₂	$-136,860 \pm 3,000$	$-128,480$ (1)	55.9 (table 4)
CaSO₄	$-313,880 \pm 1,000$	$-340,700$ (1)	23.45 (3)
Ca(C₂H)₂	$+40,310 \pm 2,800$	$+32,400$ (table 3)	17.1 (table 4)
Ca(OCOCH₃)₂	$-305,900 \pm 1,800$	$-357,200$ (1)	30.0 (table 4)
Ca⟨OCOC≡OCOC⟩	$-251,200 \pm 14,000$	$-275,000$ (table 3)	28.9 (table 4)
Ca(OCH₃)₂	$-169,640 \pm 10,200$	$-209,220$ (table 3)	19.4 (table 4)
Ca(OC₂H₅)₂	$-171,100 \pm 16,000$	$-228,200$ (1)	24.76 (table 4)
Ca(CH₂COCHCOOC₂H₅)₂	$-412,190 \pm 17,200$	$-527,820$ (table 3)	56.7 (table 4)
Ca(CH(COOC₂H₅)₂)₂	$-368,060 \pm 20,200$	$-513,860$ (table 3)	68.1 (table 4)
Ca⟨C≡C–CH₂ ; O–CH₂⟩	$-67,500 \pm 16,000$	$-90,850$ (table 3)	20.6 (table 4)

Ca$\big\langle\!\begin{smallmatrix}C\equiv C\\O\text{—CHCH}_3\end{smallmatrix}$	$-72,100 \pm 16,000$	$-95,450$ (table 3)*	20.6 (table 4)*
Ca$\big\langle\!\begin{smallmatrix}C\equiv C\\O\text{—C(CH}_3)_2\end{smallmatrix}$	$-75,350 \pm 18,400$	$-107,470$ (table 3)	23.2 (table 4)
CO(g)	$-32,700 \pm 500$ (9)*	$-26,600$ (1)	6.94 (2)
CO$_2$(g)	$-94,100 \pm 500$ (9)	$-94,250$ (1)	8.75 (2)
CS$_2$(l)	$+17,150 \pm 2,000$ (9)	$+15,600$ (1)	17.70 (3)
H$_2$O(l)	$-56,560 \pm 500$ (7)	$-68,370$ (1)	18.0
H$_2$S(g)	$-7,840 \pm 500$ (7)	$-5,300$ (1)	8.61 (2)
NH$_3$(g)	$-3,910 \pm 500$ (7)	$-11,000$ (1)	8.90 (2)
HCl (g)	$-22,692 \pm 500$ (7)	$-22,060$ (1)	7.07 (2)
HBr(g)	$-12,540 \pm 500$ (7)	$-8,650$ (1)	6.64 (2)
HI(g)	$+315 \pm 500$ (7)	$+5,910$ (1)	6.97 (2)
H$_2$SO$_4$(l)	$-162,350 \pm 2,200$	$-193,750$ (1)	33.2 (2)
(C$_2$H$_5$)$_2$SO$_4$(l)	$-130,410 \pm 3,600$	$-186,310$ (table 3)	52.2 (table 5)
C$_2$H$_6$(g)	$+50,840 \pm 500$ (9)	$+54,300$ (1)	9.95 (2)
C$_2$H$_4$(g)	$+12,300 \pm 2,000$ (9)	$+11,400$ (1)	10.06 (2)
CH$_2$C≡CH(g)	$+47,390 \pm 4,600$	$+45,610$ (table 3)	17.3 (table 5)
CH$_3$C≡CCH$_3$(g)	$+47,100 \pm 9,200$	$+38,310$ (table 3)	20.1 (table 5)
C$_2$H$_5$C≡CC$_2$H$_5$(l)	$+49,940 \pm 12,400$	$+20,570$ (table 3)	33.4 (table 5)
CH$_3$OH(l)	$-39,960 \pm 500$ (9)	$-57,250$ (1)	19.2 (2)
C$_2$H$_5$OH(l)	$-42,200 \pm 2,000$ (9)	$+66,740$ (1)	26.8 (2)
CH$_3$CHO(g)	$-32,000 \pm 2,000$ (9)	$-44,000$ (1)	16.2 (2)
CH$_3$COCH$_3$(l)	$-37,220 \pm 2,000$ (9)	$-61,060$ (table 1)	30.6 (2)
CH$_3$COOC$_2$H$_5$(l)	$-77,600 \pm 1,000$ (9)	$-113,580$ (table 1)	40.45 (2)
(CH$_3$CO)$_2$O(l)	$-104,200 \pm 7,000$ (9)	$-150,210$ (table 1)	46.9 (table 5)
CH$_3$COOH(l)	$-94,500 \pm 2,000$ (9)	$-117,300$ (1)	28.1 (2)
CH$_3$COC≡CCOCH$_3$(l)	$-6,830 \pm 13,400$	$-31,890$ (table 3)	44.8 (table 5)
CH$_3$COCH$_2$COOC$_2$H$_5$(l)	$-168,350 \pm 7,000$	$-216,550$ (table 1)	62.0 (2)

TABLE 9—Concluded

COMPOUND	ΔF^0_{298}	ΔH_{298}	C_p
$CH_2(COOC_2H_5)_2(l)$	$-148,070 \pm 8,800$	$-209,570$ (table 1)*	69.4 (2)*
$CH_2{=}C{=}O(g)$	$-14,770 \pm 1,200$	$-14,780$ (10)	16.2 (table 5)
$CH_2CH_2O(g)$	$-8,100 \pm 1,400$	$-16,600$ (1)	16.2 (table 5)
$C_2Cl_2(g)$	$+42,460 \pm 7,400$	$+45,960$ (table 3)	10.0 (table 5)
$C_2Br_2(g)$	$+53,510 \pm 7,600$	$+64,660$ (table 3)	10.0 (table 5)
$C_2I_2(g)$	$+76,860 \pm 7,800$	$+91,260$ (table 3)	10.0 (table 5)
$C_2H_5Cl(g)$	$-12,400 \pm 1,200$	$-25,300$ (1)	12.5 (3)
$C_2H_5Br(l)$	$-6,180 \pm 3,000$ (9)	$-21,900$ (1)	23.4 (3)
$C_2H_5I(l)$	$+6,600 \pm 1,400$	$-8,000$ (1)	26.8 (3)
$CH_3COCl(l)$	$-49,400 \pm 1,200$	$-66,400$ (1)	26.2 (2)
$CH_3COBr(l)$	$-40,300 \pm 1,200$	$-54,500$ (1)	41.7 (table 5)
$CH_3COI(l)$	$-28,400 \pm 1,400$	$-41,100$ (1)	57.6 (table 5)
$C_6H_5I(l)$	$+47,180 \pm 7,800$	$+34,280$ (table 1)	47.1 (table 5)
$C_6H_5C{=}CC_6H_5(s)$	$+122,270 \pm 19,600$	$+87,370$ (table 3)	64.6 (table 5)
$C_2H_5NH_2(g)$	$+11,200 \pm 1,200$	$-12,600$ (1)	17.3 (table 5)
$CH_3CONH_2(s)$	$-46,420 \pm 1,800$	$-77,580$ (1)	18.9 (table 5)
$H_2(g)$			6.83 (2)
$N_2(g)$			5.96 (2)
$O_2(g)$			7.00 (2)
S (rhombic)			5.65 (2)
$F_2(g)$			7.00 (3)
$Cl_2(g)$			8.14 (2)
$Br_2(l)$			17.10 (2)
$I_2(s)$			13.28 (2)
Ca(s)			6.74 (2)
C(graphite)			2.04 (2)

* Sources are given in parentheses.

The free energies of formation of many of the simple inorganic compounds were taken from Lewis and Randall (7) and were arbitrarily assigned probable errors of 500 calories.

Kelley (5) calculated the free energy of calcium carbide from equilibrium measurements on its formation from calcium oxide and carbon and on its decomposition to calcium vapor and carbon. He pointed out that his results were in good agreement between themselves but not with the expected entropy for the carbide. Thus, the mean value of $-17,500$ calories at 25°C. corresponds to an entropy of 24 E.U., compared to 14.1 E.U. as estimated from table 6. From table 4 it is seen that calcium carbide has very close to the average specific heat of the other calcium compounds, indicating no abnormality. It seems much more probable that the discrepancy lies in the extrapolation of the free-energy values from 1500°C. and 2500°C. down to room temperature. Accordingly, the free energy of calcium carbide was calculated in the same manner as were those of the other calcium compounds.

The free energies of formation of all the rest of the compounds were calculated from the relation, $\Delta F = \Delta H - T\Delta S$, where T is 298° and ΔS is the entropy of formation. ΔS was found by the algebraic addition of the entropy of each compound and the entropies of its constituent atoms.

In figuring the probable errors for these free energies the following arbitrary allowances were made: (a) 1 per cent of heats of combustion and 1000 calories in heats of formation from the literature; (b) 1000 calories or 10 per cent of corrections in heats of formation for structural changes; (c) 1.5 E.U. for entropies of compounds from the literature; (d) 15 per cent of the entropy of calcium compounds based on average specific entropy; (e) 1000 calories or 20 per cent of entropy corrections for structural changes; and (f) 20 per cent of the entropy for sulfuric acid and 5 per cent for ethylene oxide. The net probable errors were taken to be the square roots of the sums of the squares of the contributing errors, but were rounded off to the nearest 200 calories.

FREE ENERGIES, HEATS, AND CHANGES IN HEAT CAPACITY OF REACTIONS

The free energies of formation, heats of formation, and heat capacities of all the compounds considered were listed in table 9, along with references indicating their source. These values then were combined algebraically to give the free energies, heats, and changes in heat capacity of reactions which were to be considered.

The probable errors in the free-energy values were obtained by taking the square roots of the sums of the squares of the errors for the products and the reactants. However, in equations 39, 40, and 41 some of the reactants and products were so related that they had some of the same

TABLE 10

Thermodynamic relations of reactions of calcium carbide

NO.	REACTION	ΔF_{298}^{0}		ΔH_{298}	ΔC_p
	Elements:				
1	$CaC_2 \rightarrow Ca + 2C$	$+14,560 \pm$	$1,200$	$+14,100$	-2.1
2	$CaC_2 + 2H_2(g) \rightarrow CaH_2 + C_2H_2(g)$	$+28,730 \pm$	$1,600$	$+22,400$	-8.6
3	$CaC_2 + H_2(g) \rightarrow CaH_2 + 2C$	$-22,110 \pm$	$1,600$	$-31,900$	-7.6
4	$CaC_2 + N_2(g) \rightarrow Ca(CN)_2$	$-32,370 \pm$	$2,000$	$-44,200$	-1.4
5	$CaC_2 + N_2(g) \rightarrow CaCN_2 + C$	$-58,480 \pm$	$1,600$	$-70,700$	-1.6
6	$CaC_2 + \frac{1}{2} O_2(g) \rightarrow CaO + 2C$	$-129,690 \pm$	$1,600$	$-137,600$	-2.1
7	$CaC_2 + \frac{5}{2} O_2(g) \rightarrow CaO + 2CO_2(g)$	$-317,890 \pm$	$1,800$	$-326,100$	-2.7
8	$CaC_2 + S \rightarrow CaS + 2C$	$-97,630 \pm$	$1,600$	$-99,300$	-0.8
9	$CaC_2 + 5S \rightarrow CaS + 2CS_2(l)$	$-63,330 \pm$	$4,200$	$-68,100$	$+8.0$
10	$CaC_2 + F_2(g) \rightarrow CaF_2 + 2C$	$-263,240 \pm$	$1,600$	$-276,100$	$+0.7$
11	$CaC_2 + Cl_2(g) \rightarrow CaCl_2 + 2C$	$-164,460 \pm$	$1,800$	$-176,500$	$+1.2$
12	$CaC_2 + Br_2(l) \rightarrow CaBr_2 + 2C$	$-148,080 \pm$	$2,600$	$-148,120$	$+12.1$
13	$CaC_2 + I_2 \rightarrow CaI_2 + 2C$	$-122,300 \pm$	$3,200$	$-114,380$	$+33.8$
14	$CaC_2 + 2Cl_2(g) \rightarrow CaCl_2 + C_2Cl_2(g)$	$-122,000 \pm$	$7,600$	$-130,540$	-1.0
15	$CaC_2 + 2Br_2(l) \rightarrow CaBr_2 + C_2Br_2(g)$	$-94,570 \pm$	$8,000$	$-83,460$	$+0.9$
16	$CaC_2 + 2I_2 \rightarrow CaI_2 + C_2I_2(g)$	$-45,440 \pm$	$8,400$	$-23,120$	$+26.2$
	Inorganic compounds:				
17	$CaC_2 + 2NH_3(g) \rightarrow Ca(NH_2)_2 + 2C + H_2(g)$	$-38,570 \pm$	$2,000$	$-55,400$	-6.1
18	$CaC_2 + 2NH_3(g) \rightarrow Ca(NH_2)_2 + C_2H_2(g)$	$+12,270 \pm$	$2,000$	$-1,100$	-7.0
19	$CaC_2 + H_2O(l) \rightarrow CaO + 2C + H_2(g)$	$-73,130 \pm$	$1,600$	$-69,230$	-9.8
20	$CaC_2 + H_2O(l) \rightarrow CaO + C_2H_2(g)$	$-22,290 \pm$	$1,800$	$-14,930$	-10.8
21	$CaC_2 + 2H_2O(l) \rightarrow Ca(OH)_2 + 2C + H_2(g)$	$-86,620 \pm$	$1,800$	$-85,160$	-17.7
22	$CaC_2 + 2H_2O(l) \rightarrow Ca(OH)_2 + C_2H_2(g)$	$-35,780 \pm$	$2,000$	$-30,860$	-18.7
23	$CaC_2 + H_2S(g) \rightarrow CaS + 2C + H_2(g)$	$-89,790 \pm$	$1,600$	$-94,000$	$+3.1$
24	$CaC_2 + H_2S(g) \rightarrow CaS + C_2H_2(g)$	$-38,950 \pm$	$1,800$	$-39,700$	$+2.1$
25	$CaC_2 + 2H_2S(g) \rightarrow Ca(SH)_2 + C_2H_2(g)$	$-46,200 \pm$	$3,600$	$-58,120$	0.0
26	$CaC_2 + 2HCl(g) \rightarrow CaCl_2 + 2C + H_2(g)$	$-119,080 \pm$	$2,000$	$-132,380$	$+2.1$
27	$CaC_2 + 2HBr(g) \rightarrow CaBr_2 + 2C + H_2(g)$	$-123,000 \pm$	$2,600$	$-130,820$	$+22.7$
28	$CaC_2 + 2HI(g) \rightarrow CaI_2 + 2C + H_2(g)$	$-122,930 \pm$	$3,400$	$-126,200$	$+40.0$
29	$CaC_2 + 2HCl(g) \rightarrow CaCl_2 + C_2H_2(g)$	$-68,240 \pm$	$2,200$	$-78,080$	$+1.1$
30	$CaC_2 + 2HBr(g) \rightarrow CaBr_2 + C_2H_2(g)$	$-72,160 \pm$	$2,800$	$-76,520$	$+21.8$
31	$CaC_2 + 2HI(g) \rightarrow CaI_2 + C_2H_2(g)$	$-72,090 \pm$	$3,400$	$-71,900$	$+39.0$
32	$CaC_2 + CO_2(g) \rightarrow CaO + CO + 2C$	$-68,290 \pm$	$1,800$	$-69,950$	-0.4
33	$CaC_2 + 2CO_2(g) \rightarrow Ca\diagdown \overset{OCOC}{\underset{OCOC}{\mathbin{\mkern-6mu\vert\vert\vert}}}$	$-48,440 \pm$	$1,400$	$-73,400$	-1.5
34	$CaC_2 + CO(g) \rightarrow CaO + 3C$	$-96,990 \pm$	$1,600$	$-111,000$	-3.6
35	$CaC_2 + \frac{1}{2} CS_2(l) \rightarrow CaS + \frac{5}{2} C$	$-106,210 \pm$	$1,800$	$-107,100$	-3.0
36	$CaC_2 + Ca(OH)_2 \rightarrow 2CaO + 2C + H_2$	$-59,640 \pm$	$2,600$	$-53,300$	-1.9
37	$CaC_2 + Ca(OH)_2 \rightarrow 2CaO + C_2H_2(g)$	$-8,800 \pm$	$2,600$	$+1,000$	-2.9
38	$CaC_2 + H_2SO_4(l) \rightarrow CaSO_4 + C_2H_2(g)$	$-86,140 \pm$	$2,800$	$-78,550$	-12.7

TABLE 10—*Continued*
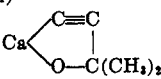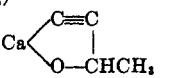
NO.	REACTION	ΔF^0_{298}	ΔH_{298}	ΔC_p
	Organic compounds:			
39	$CaC_2 + C_2H_2(g) \rightarrow Ca(C\equiv CH)_2$	$+4,030 \pm 2,400$	$-7,800$	-5.8
40	$CaC_2 + 2CH_3COCH_2COOC_2H_5(l) \rightarrow$ $Ca(CH_3COCHCOOC_2H_5)_2 + C_2H_2(g)$	$-10,090 \pm 10,600$	$-26,320$	-70.2
41	$CaC_2 + 2CH_2(COOC_2H_5)_2(l) \rightarrow$ $Ca(CH(COOC_2H_5)_2)_2 + C_2H_2(g)$	$-6,520 \pm 10,800$	$-26,320$	-73.6
42	$CaC_2 + 2C_2H_5OH(l) \rightarrow Ca(OC_2H_5)_2 +$ $C_2H_2(g)$	$-21,300 \pm 4,000$	$-26,320$	-31.8
43	$CaC_2 + 2C_2H_5OH(l) \rightarrow Ca(OH)_2 +$ $2C_2H_4(g) + C_2H_2(g)$	$-39,900 \pm 6,000$	$-11,320$	-16.1
44	$CaC_2 + C_2H_5OH(l) \rightarrow Ca(OH)_2 +$ $C_2H_5C\equiv CC_2H_5(l)$	$-65,400 \pm 13,200$	$+67,850$	$+12.8$
45	$CaC_2 + 2CH_3OH(l) \rightarrow Ca(OCH_3)_2 +$ $C_2H_2(g)$	$-24,320 \pm 10,200$	$-26,320$	-22.0
46	$CaC_2 + 2CH_3OH(l) \rightarrow Ca(OH)_2 +$ $CH_3C\equiv CCH_3(g)$	$-72,720 \pm 9,400$	$-69,090$	-10.9
47	$CaC_2 + CH_3OH(l) \rightarrow CaO +$ $CH_3C\equiv CH(g)$	$-42,340 \pm 9,400$	$-34,740$	-4.6
48	$CaC_2 + CH_3COCH_3(l) \rightarrow$ Ca$\langle$ $\begin{smallmatrix}C\equiv C\\ \\O-C(CH_3)_2\end{smallmatrix}$	$-23,570 \pm 18,600$	$-32,310$	-20.3
49	$CaC_2 + CH_3CHO(g) \rightarrow$ Ca$\langle$ $\begin{smallmatrix}C\equiv C\\ |\\O-CHCH_3\end{smallmatrix}$	$-25,540 \pm 16,200$	$-37,750$	-8.5
50	$CaC_2 + CH_2CH_2O(g) \rightarrow$ Ca$\langle$ $\begin{smallmatrix}C\equiv CCH_2\\ |\\O-CH_2\end{smallmatrix}$	$-44,840 \pm 16,000$	$-60,150$	-8.5
51	$CaC_2 + 2CH_3COOC_2H_5(l) \rightarrow$ $Ca(OC_2H_5)_2 + CH_3COC\equiv CCOCH_3(l)$	$-8,170 \pm 13,800$	$-18,830$	-24.2
52	$CaC_2 + 2CH_3COOC_2H_5(l) \rightarrow$ $\frac{1}{2}Ca(OC_2H_5)_2 +$ $\frac{1}{2}Ca(CH_3COCHCOOC_2H_5)_2 +$ $C_2H_2(g)$	$-71,040 \pm 9,000$	$-82,450$	-43.1
53	$CaC_2 + 2(CH_3CO)_2O(l) \rightarrow$ $Ca(OCOCH_3)_2 +$ $CH_3COC\equiv CCOCH_3(l)$	$-89,770 \pm 15,200$	$-74,580$	-31.9
54	$CaC_2 + 2(CH_3CO)_2O(l) \rightarrow$ $Ca(OCOCH_3)_2 + 2CH_2=C=O(g) +$ $C_2H_2(g)$	$-61,640 \pm 7,800$	$-17,950$	-34.3
55	$CaC_2 + 2CH_3COOH(l) \rightarrow$ $Ca(OCOCH_3)_2 + C_2H_2(g)$	$-51,500 \pm 4,600$	$-54,200$	-29.1
56	$CaC_2 + 2CH_3COOH(l) \rightarrow Ca(OH)_2 +$ $CH_3COC\equiv CCOCH_3(l)$	$-17,570 \pm 14,000$	$-19,190$	-4.0

TABLE 10—*Concluded*

NO.	REACTION	ΔF^{0}_{298}	ΔH_{298}	ΔC_p
	Organic compounds—Concluded:			
57	$CaC_2 + 2CH_3COCl(l) \rightarrow CaCl_2 + CH_3COC\equiv CCOCH_3(l)$	$-72,490 \pm 13,800$	$-75,590$	-3.1
58	$CaC_2 + 2CH_3COCl(l) \rightarrow CaCl_2 + 2CH_2=C=O(g) + C_2H_2(g)$	$-44,360 \pm 3,800$	$-18,960$	-5.6
59	$CaC_2 + 2CH_3COBr(l) \rightarrow CaBr_2 + CH_3COC\equiv CCOCH_3(l)$	$-74,310 \pm 13,800$	$-71,010$	-13.5
60	$CaC_2 + 2CH_3COI(l) \rightarrow CaI_2 + CH_3COC\equiv CCOCH_3(l)$	$-72,340 \pm 14,000$	$-64,070$	-27.4
61	$CaC_2 + 2C_2H_5Cl(g) \rightarrow CaCl_2 + C_2H_5C\equiv CC_2H_5(l)$	$-89,720 \pm 12,800$	$-105,330$	$+13.7$
62	$CaC_2 + 2C_2H_5Br(l) \rightarrow CaBr_2 + C_2H_5C\equiv CC_2H_5(l)$	$-85,780 \pm 14,000$	$-83,750$	$+11.7$
63	$CaC_2 + 2C_2H_5Br(l) \rightarrow CaBr_2 + 2C_2H_4(g) + C_2H_2(g)$	$-60,280 \pm 7,600$	$-27,220$	$+8.4$
64	$CaC_2 + 2C_2H_5I(l) \rightarrow CaI_2 + C_2H_5C\equiv CC_2H_5(l)$	$-85,560 \pm 13,200$	$-77,810$	$+22.8$
65	$CaC_2 + 2C_6H_5I(l) \rightarrow CaI_2 + C_6H_5C\equiv CC_6H_5$	$-94,390 \pm 25,200$	$-95,570$	$+13.4$
66	$CaC_2 + (C_2H_5)_2SO_4(l) \rightarrow CaSO_4 + C_2H_5C\equiv CC_2H_5(l)$	$-118,970 \pm 13,000$	$-119,720$	-8.2
67	$CaC_2 + 2C_2H_5NH_2(g) \rightarrow Ca(NH_2)_2 + C_2H_5C\equiv CC_2H_5(l)$	$-18,850 \pm 12,800$	$-31,630$	-0.4
68	$CaC_2 + 2CH_3CONH_2 \rightarrow Ca(NH_2)_2 + CH_3COC\equiv CCOCH_3(l)$	$+39,620 \pm 13,800$	$+45,870$	$+7.8$

constituent probable errors, which therefore should cancel out and which were eliminated.

DISCUSSION

The sixty-eight reactions considered are listed in table 10, along with their standard free energies, their heats of reaction, and their changes in heat capacity, all at 25°C.

It is agreeable to note that the well-known reactions of water and nitrogen with calcium carbide are thermodynamically feasible. Moreover, it is immediately apparent that an overwhelming majority of the reactions are in the same class. Thus alcohols, esters, anhydrides, ketones, aldehydes, ethylene oxide, and many other compounds may react with calcium carbide. Only five of the reactions have positive free energies.

Reactions which occur with the formation of carbon and hydrogen rather than acetylene have an advantage of $-50,800$ calories. In two of the reactions, those involving hydrogen and ammonia, this advantage is sufficient to change their free energies from positive to negative. The remaining positive free energies belong to the reaction with acetamide,

to the decomposition of the carbide, and to the reaction with acetylene to form the acetylide. The latter is really a borderline case.

In the reactions with the halogens there is a steep decline in the magnitude of the free energies from fluorine to iodine. However, in the hydrogen halides, the alkyl halides, and the acyl halides there is little, if any, difference between the free energies.

Many of the probable errors are large, but only a few of them are large enough to leave the sign of the free energy in doubt.

The value of the heats of reaction and changes in heat capacity is that they permit moderate extrapolation of the free energies to higher temperatures. The relation used is the familiar

$$\Delta F^0_{298} = \Delta H_0 - \Delta C_p T \ln T + IT$$

where $\Delta H_0 = \Delta H_{298} - 298 \Delta C_p$ and I balances the equation at 25°C.

As an example of the use of this relation, consider the reaction between calcium carbide and acetylene (equation 39):

$$CaC_2 + C_2H_2(g) \rightarrow Ca(C\equiv CH)_2$$
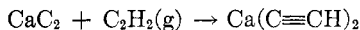
$$\Delta F^0_{298} = +4{,}030 \pm 2{,}400; \Delta H_{298} = -7{,}800; \Delta C_p = -5.8$$

Solving for H_0 and I as indicated above, the free-energy expression becomes

$$\Delta F^0_T = -6{,}070 + 5.8T \ln T + 0.85T$$

It is immediately obvious that any increase in T above 298° will only make the free energy still more positive. On the other hand, lowering T below 298° will make the value more negative. Thus, at -100°C.,

$$\Delta F^0_{173} = -750$$

Accordingly, there would seem to be hope of carrying out this reaction at low temperatures, possibly in liquid ammonia, depending on the magnitude and sign of the actual error.

SUMMARY

Free energies, heats of reaction, and changes in specific heats have been estimated for sixty-eight possible reactions of calcium carbide with some forty reagents.

An overwhelming majority of these reactions are thermodynamically possible.

REFERENCES

(1) BICHOWSKY AND ROSSINI: *Thermochemistry of Chemical Substances.* Reinhold Publishing Corporation, New York (1936).
(2) *Handbook of Chemistry and Physics*, 23rd edition. Chemical Rubber Company, Cleveland, Ohio (1933).

(3) *International Critical Tables*. McGraw-Hill Book Company, Inc., New York.
(4) KELLEY: U. S. Bur. Mines, Bull. No. 394 (1935).
(5) KELLEY: U. S. Bur. Mines, Bull. No. 407 (1935).
(6) LANDOLT-BÖRNSTEIN: *Physikalisch-chemische Tabellen.* J. Springer, Berlin (1923).
(7) LEWIS AND RANDALL: *Thermodynamics and the Free Energy of Chemical Substances.* McGraw-Hill Book Company, Inc., New York (1923).
(8) PARKS: Chem. Rev. **18**, 325 (1936).
(9) PARKS AND HUFFMAN: *Free Energies of Some Organic Compounds.* The Chemical Catalog Company, Inc., New York (1932).
(10) RICE AND GREENBERG: J. Am. Chem. Soc. **56**, 2268 (1934).

THE PRECIPITATION OF SILVER CHROMATE. III

GELATIN MEDIUM[1]

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INTRODUCTION

For the complete quantitative description of the Liesegang ring phenomenon, on the basis of a supersaturation theory, it is necessary to know the kinetics of the precipitation of the substance forming the bands. Silver chromate has been investigated in this way, in spite of expected difficulties in the kinetic interpretations of its rate of precipitation, because it is the best-known example of a material forming rhythmic bands. It has already (8) been found possible to represent the rate of precipitation of silver chromate from aqueous medium in not too complex a manner. It was then desirable to have this same information for the precipitation from gelatin medium, since quantitative data on the Liesegang phenomenon are difficult to obtain in a mobile, fluid medium, such as water. However, it is known (9) that various ions are sequestered to a greater or less extent by gelatin, and therefore it was necessary to have some information on the effective activities of the silver and chromate ions in this medium. With these data available (9), it is possible to apply successfully the analysis previously found valid for water medium to the rate of precipitation of silver chromate in gelatin medium.

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[1] Presented in part at the Seattle Meeting of the American Association for the Advancement of Science, June, 1940.