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THERMODYNAMIC PROPERTIES OF BINARY
IRON - ALUMINUM ALLOYS

BY

J. ELDRIDGE AND K. KOMAREK

FINAL REPORT

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ABSTRACT: A METHOD HAS BEEN DEVELOPED TO EQUILIBRATE METAL SPECIMENS IN AN ALL CERAMIC SYSTEM WITH A REACTIVE LOW MELTING METAL OF LOW VOLATILITY. RELATIVELY FEW EXPERIMENTS ARE NECESSARY TO OBTAIN RELIABLE RESULTS OF THERMODYNAMIC PROPERTIES OVER A WIDE RANGE OF TEMPERATURE AND CONCENTRATION. THERMODYNAMIC PROPERTIES OF SOLID IRON-ALUMINUM ALLOYS HAVE BEEN DETERMINED BY THIS METHOD BETWEEN 30 AND 75 ATOMIC % ALUMINUM AND 1100 TO 1400°K. THE ACTIVITY OF ALUMINUM SHOWS A STRONG NEGATIVE DEVIATION FROM RAOULT'S LAW AT LOW CONCENTRATIONS OF ALUMINUM BUT INCREASES RAPIDLY ABOVE 40 ATOMIC % ALUMINUM. CLOSE TO 50 ATOMIC % ALUMINUM THE BEHAVIOR OF THERMODYNAMIC PROPERTIES INDICATES A RAPID INCREASE IN ORDER AS THE COMPOSITION $FeAl_3$ IS APPROACHED. A FURTHER RAPID INCREASE OF THE ACTIVITY OF ALUMINUM OCCURS AT THE INTERMETALLIC COMPOUND $FeAl_3$. VARIOUS MOLAR AND PARTIAL MOLAR THERMODYNAMIC PROPERTIES HAVE BEEN CALCULATED FOR A TEMPERATURE OF 1200°K. THE ACCURACY AND RELIABILITY OF THE RESULTS HAS BEEN ASSESSED AND THE RESULTS COMPARED WITH PUBLISHED DATA.

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1. INTRODUCTION

THE IRON-ALUMINUM SYSTEM IS OF BOTH THEORETICAL AND PRACTICAL INTEREST FOR VARIOUS REASONS AND IT HAS BEEN THE OBJECT OF A GREAT NUMBER OF INVESTIGATIONS. MOST OF THESE STUDIES WERE CONCERNED WITH THE PHASE DIAGRAM AND THE ORDER-DISORDER REACTIONS FIRST OBSERVED BY BRADLEY AND JAY⁽¹⁾. THE RESULTS HAVE BEEN COMPILED AND PRESENTED AS A COMPLETE PHASE DIAGRAM BY HANSEN⁽²⁾ BUT THE DELINEATION OF SEVERAL PHASE BOUNDARIES WAS LEFT OPEN FOR FURTHER INVESTIGATIONS (FIG. 1). IN A RECENT STUDY LEE⁽³⁾ REDETERMINED THE SOLIDUS AND LIQUIDUS CURVES AND FOUND THAT FeAl_3 (9) HAS A CONGRUENT MELTING POINT. THE MOST PROMINENT FEATURES OF THE PHASE DIAGRAM ARE AN EXTENSIVE RANGE OF SOLID SOLUTIONS OF ALUMINUM IN α -IRON FROM 0 TO 52 AT% AL, A SERIES OF ORDER-DISORDER TRANSFORMATIONS AT LOWER TEMPERATURES WITHIN THE α -FIELD, AND SEVERAL INTERMETALLIC COMPOUNDS, NAMELY FeAl , FeAl_2 , Fe_2Al_5 , AND FeAl_3 . RECENTLY, TAYLOR AND JONES⁽⁴⁾ FOUND THAT BOTH ORDERED AND DISORDERED ALLOYS CAN EXIST IN THE α -FIELD UP TO THE SOLIDUS CURVE SEPARATED BY A GENTLY CURVED SLOPING LINE STARTING AT 18.75 AT% AL AT ROOM TEMPERATURE UP TO 37 AT% AL AT 1375°C.

ALLOYS WITHIN THE α -PHASE FIELD ARE OF SPECIAL COMMERCIAL INTEREST. THOSE CONTAINING ABOUT 25 TO 30 AT% AL ARE BEING INVESTIGATED FOR USE AS HIGH QUALITY, SOFT MAGNETIC MATERIALS WHEREBY THE ORDERING REACTIONS AND THEREBY THE MAGNETIC PROPERTIES ARE CONTROLLED BY HEAT TREATMENT. DUE TO EXCELLENT HIGH-TEMPERATURE OXIDATION RESISTANCE, ATTRACTIVE NUCLEAR PROPERTIES AND LOW COST IRON-ALUMINUM BASE ALLOYS HAVE ALSO BEEN STUDIED AS POSSIBLE NUCLEAR REACTOR COMPONENTS⁽⁵⁾. IN STEEL MAKING ALUMINUM IS BEING USED AS A DEOXIDANT. FINALLY, IT HAS BEEN PROPOSED TO PRODUCE

ALUMINUM BY CARBOTHERMIC REDUCTION OF ALUMINUM BEARING ORE AND TO EXTRACT ALUMINUM FROM THE RESULTING ALUMINUM RICH ALLOYS⁽⁶⁾.

IN VIEW OF THE IMPORTANCE OF THE IRON-ALUMINUM SYSTEM IT HAS BEEN FELT THAT A STUDY OF THE THERMODYNAMIC PROPERTIES WOULD CONTRIBUTE MATERIALLY TO THE UNDERSTANDING OF ALLOYS IN THIS SYSTEM.

BECAUSE OF ITS USE AS A DEOXIDANT IN THE STEEL INDUSTRY CHIPMAN AND COWORKERS^(7,8,9,10) HAVE STUDIED REPEATEDLY THE ACTIVITY OF ALUMINUM IN LIQUID DILUTE IRON-ALUMINUM ALLOYS. THEY MEASURED THE DISTRIBUTION OF ALUMINUM BETWEEN LIQUID IRON AND SILVER AND CALCULATED THE ACTIVITY FROM KNOWN ACTIVITY VALUES OF ALUMINUM IN SILVER AT SOME LOWER TEMPERATURE. THE RESULTS HAVE BEEN RECALCULATED BY CHOU AND ELLIOTT⁽¹¹⁾ AND WILDER AND ELLIOTT⁽¹²⁾. PEHLKE⁽¹³⁾ COMPUTED THE ACTIVITY OF ALUMINUM AT 1600°C OVER THE WHOLE CONCENTRATION RANGE FROM THE SLOPE OF THE LIQUIDUS CURVE BUT NO GREAT ACCURACY CAN BE ASSIGNED TO HIS RESULTS, SINCE THE LIQUIDUS TEMPERATURES LACK THE NECESSARY PRECISION.

THERMODYNAMIC INVESTIGATIONS OF SOLID IRON-ALUMINUM ALLOYS HAVE BEEN RESTRICTED TO THE CALORIMETRIC DETERMINATION OF HEATS OF FORMATION BY BILTZ AND HAASE⁽¹⁴⁾, OELSEN AND MIDDEL⁽¹⁵⁾, AND KUBASCHEWSKI AND DENCH⁽¹⁶⁾. AFTER THE PRESENT INVESTIGATION WAS INITIATED GROSS AND COWORKERS⁽¹⁷⁾ PRESENTED THE RESULTS OF THEIR STUDY OF THE ACTIVITIES OF ALUMINUM IN SOLID IRON-ALUMINUM ALLOYS. THE MEASUREMENTS AT 920°C WERE CARRIED OUT BY A CAPILLARY METHOD DEVELOPED BY GROSS⁽¹⁸⁾ FOR THE STUDY OF EQUILIBRIA INVOLVING ALUMINUM MONOHALIDES AND AT 1300°C BY EMPLOYING THE EFFUSION TECHNIQUE.

THE SCARCITY OF THERMODYNAMIC DATA IN THE IRON-ALUMINUM SYSTEM IS MAINLY DUE TO EXPERIMENTAL DIFFICULTIES. ALUMINUM IN THE MOLTEN OR GASEOUS STATE IS A VERY REACTIVE METAL WHICH IMPOSES SEVERE RESTRICTIONS ON THE CHOICE OF CONTAINER MATERIALS. AT LOWER TEMPERATURES ALUMINUM HAS A RATHER LOW VAPOR PRESSURE SO THAT EVAPORATION AND EQUILIBRATION WILL PROCEED BUT SLOWLY. A MAJOR OBSTACLE TO EMF-MEASUREMENTS, BESIDES THE PROBLEM TO SELECT A SUITABLE CONTAINER MATERIAL, CONSISTS IN FINDING A MOLTEN ELECTROLYTE WHICH WILL PERFORM REVERSIBLY.

FROM A REVIEW OF THE DIFFICULTIES INVOLVED IT BECAME CLEAR THAT A NEW APPROACH HAD TO BE FOUND TO OBTAIN THERMODYNAMIC PROPERTIES IN THE IRON-ALUMINUM SYSTEM. THE SCOPE OF THIS INVESTIGATION WAS TO DEVELOP A METHOD TO MEASURE ACTIVITIES OF ALUMINUM IN SOLID IRON-ALUMINUM ALLOYS OVER AN EXTENDED RANGE OF ALLOY COMPOSITION IN THE TEMPERATURE RANGE FROM ABOUT 750°C TO 1050°C . A TECHNIQUE WAS CHOSEN AND ADAPTED TO THE PROBLEM WHICH HAS BEEN ORIGINALLY APPLIED BY HERASYMENKO⁽¹⁹⁾ TO THE STUDY OF THE SILVER-CADMIUM SYSTEM. AT TEMPERATURES ABOVE 800°C , SPECIMENS WERE EQUILIBRATED WITH ALUMINUM VAPOR FROM AN ALUMINUM SOURCE KEPT AT CONSTANT TEMPERATURE IN AN EVACUATED ALL ALUMINA SYSTEM. THE SPECIMENS WERE HEATED IN A TEMPERATURE GRADIENT UNTIL EQUILIBRATION WAS COMPLETED AND THEN ANALYZED. AT TEMPERATURES BELOW 800°C SODIUM CHLORIDE WAS ADDED UTILIZING THE FORMATION OF ALUMINUM SUBCHLORIDE TO ACCELERATE THE TRANSFER OF ALUMINUM FROM THE ALUMINUM SOURCE TO THE IRON SPECIMENS. THE NECESSARY EQUATIONS HAVE BEEN WORKED OUT TO OBTAIN ACTIVITIES OF ALUMINUM. THE METHOD IS APPLICABLE TO OTHER SYSTEMS ESPECIALLY TO ALLOYS OF HIGH REFRACTORY METALS WITH OTHERS OF RELATIVELY LOW MELTING POINT AND LOW VOLATILITY.

11. APPARATUS AND EXPERIMENTAL PROCEDURE

A. MATERIALS:

THE IRON SPECIMENS WERE MADE FROM VACUUM MELTED IRON "FERROVAC E" PURCHASED FROM VACUUM METALS CORP. AND ROLLED TO A .005" THICK SHEET BY HAMILTON WATCH CO. THE COMPOSITION IN WT % WAS AS FOLLOWS: .009 C, .001 MN, .002 P, .007 S, .006 SI, .04 NI, .01 CR, .004 V, .01 MO, .007 CO, .014 CU, .01 AL, .0004 PB, .0003 N, .008 O, .00006 H.

IRON-ALUMINUM SPECIMENS WERE PREPARED FROM A .01" THICK SHEET OBTAINED FROM GENERAL PLATE DIVISION (METALS AND CONTROLS CORPORATION) SOLD UNDER THE TRADE NAME "ALFENOL". THE CHEMICAL COMPOSITION IN WT % AS GIVEN BY THE SUPPLIER WAS 16.21 AL, .014 C, .0002 P, .005 S.

THE ALUMINUM USED (ALUMINUM CORP. OF AMERICA) HAD A PURITY OF 99.99+% AND THE SODIUM CHLORIDE WAS OF ANALYTICAL GRADE (BAKER). METAL SPECIMEN TUBES AND SPACERS WERE MACHINED FROM SOLID ARMCO IRON RODS (99.9+% FE) AND HEATED FOR SEVERAL HOURS IN WET HYDROGEN. THE ALUMINA TUBES AND CRUCIBLES WERE MADE OF IMPERVIOUS RECRYSTALLIZED ALUMINA WITH AN ALUMINA CONTENT OF 99.7% (TRIANGLE RR, MORGANITE INC.).

B. APPARATUS:

INITIAL EXPERIMENTS WERE MADE IN CLOSED IRON TUBES WHILE THE BULK OF THE INVESTIGATION WAS CARRIED OUT USING HIGH PURITY ALUMINA TUBES, SEALED BY A MOLTEN ALUMINUM POOL. ALTHOUGH THE PREPARATION AND ASSEMBLAGE OF THESE TUBES DIFFERED MARKEDLY, THE EXPERIMENTAL CONDITIONS (E.G. TEMPERATURE) WERE SIMILAR; FOR THAT REASON, THE ASSEMBLAGE OF EACH KIND OF TUBE WILL BE DESCRIBED SEPARATELY BELOW, BUT A DISCUSSION OF THE EXPERIMENTAL METHOD, GERMANE TO BOTH TYPES OF TUBES, WILL BE PRESENTED TOGETHER. THE

MAIN CRITERION IN THE TUBE DESIGN WAS TO PROVIDE A CLOSED THERMODYNAMIC SYSTEM IN WHICH THIN IRON SPECIMENS, AT DIFFERENT POSITIONS IN A TEMPERATURE GRADIENT, COULD BE EQUILIBRATED WITH A GAS PHASE OF KNOWN ALUMINUM ACTIVITY RESULTING IN A DIFFUSION OF ALUMINUM INTO THE SPECIMENS UNTIL, IN EQUILIBRIUM, THE PARTIAL PRESSURE OF THE ALUMINUM IN EACH OF THE SPECIMENS EQUALED THAT OF THE PARTIAL PRESSURE OF THE ALUMINUM IN THE GAS PHASE ADJACENT TO EACH SPECIMEN. BY MAINTAINING A RESERVOIR OF ALUMINUM AT THE TEMPERATURE MINIMUM, THE ACTIVITY OF ALUMINUM IN THE GASEOUS PHASE THROUGHOUT THE STATIC SYSTEM CAN BE CALCULATED FROM A KNOWLEDGE OF THE TEMPERATURE DEPENDENCE OF THE VAPOR PRESSURE OF ALUMINUM AND IN THE PRESENCE OF NaCl OF THE EQUILIBRIUM CONSTANT FOR THE REACTION,

IN RUNS WITHOUT NaCl, THE ACTIVITY OF ALUMINUM IN A GIVEN SPECIMEN AT EQUILIBRIUM IS EQUAL TO THE RATIO OF THE PARTIAL PRESSURE OF ALUMINUM IN THE SPECIMEN (DETERMINED BY THE AL RESERVOIR TEMPERATURE) TO THE VAPOR PRESSURE OF PURE ALUMINUM AT THE TEMPERATURE OF THE SPECIMEN.

IRON REACTION TUBES

SOLID ARMCO IRON RODS, 1-1/4" DIA. x 14 TO 16" LONG, WERE DRILLED OUT TO AN INSIDE DIAMETER OF 1-1/16". IRON PLUGS WERE MACHINED WITH FLANGES TO CLOSE OFF THE TUBES AT BOTH ENDS; THE FLANGES WERE MADE TO FACILITATE SUBSEQUENT ARC-WELDING OF THE PLUGS TO THE LONG TUBE. THE TOP PLUG ALSO HAD A CONCENTRIC 1/4" I.D. x 3/8" O.D. FLANGE TO PERMIT A LONG (APPROXIMATELY 14") IRON TUBE TO EXTEND INTO THE 1-1/4" REACTION TUBE. THE INNER IRON TUBE WAS CLOSED ON THE BOTTOM END BY WELDING AND: (A) ALLOWED ACCESS FOR A THERMOCOUPLE INSIDE THE REACTION TUBE; (B) SERVED AS A VERTICAL SUPPORT FOR THE SPECIMENS. THE INNER TUBE WAS MADE OF THE

LOWEST-CARBON STEEL COMMERCIALY AVAILABLE AND WAS SUBJECTED TO A STRONGLY REDUCING H_2-H_2O GAS MIXTURE AT $1000^\circ C$ FOR SEVERAL HOURS TO LOWER THE IMPURITY CONTENT. THE BOTTOM PLUG WAS PROVIDED WITH A SHORT CAPILLARY STEEL TUBE FOR FINAL EVACUATION OF THE ASSEMBLED TUBE.

1. SPECIMEN PREPARATION. SPECIMENS WERE PREPARED FROM BOTH IRON AND IRON-16% ALUMINUM ALLOY SHEET SO THAT EQUILIBRATION COULD BE FACILITATED BY REDUCING THE AMOUNT OF ALUMINUM WHICH HAD TO BE TRANSPORTED TO THE SPECIMENS.

ANNULAR SPECIMENS 12 MM I.D. x 20 MM O.D. WERE PUNCHED FROM IRON SHEET 5 MILS THICK AND FROM IRON-ALUMINUM ALLOY SHEET 10 MILS THICK USING A HIGH ALLOY TOOL STEEL DIE. THEY WERE GROUND TO REMOVE PUNCHING BURRS, DEGREASED IN CARBON TETRACHLORIDE, RINSED IN ACETONE AND WEIGHED ON A MICROBALANCE TO WITHIN AN ACCURACY OF ± 0.01 MG.

IRON AND IRON-ALUMINUM ALLOY SPECIMENS WERE ALTERNATELY POSITIONED ALONG THE INNER TUBE, USING TRIANGULAR SPACERS $3/8$ " HIGH PREPARED FROM ELECTROLYTIC IRON SHEET. THE POSITIONS OF THE SPECIMENS WITH RESPECT TO THE INNER TUBE WERE MEASURED TO WITHIN AN ACCURACY OF ± 0.5 MM. (SEE FIGURE 2).

2. CRUCIBLES. BECAUSE LIQUID ALUMINUM IS EXTREMELY REACTIVE, CRUCIBLES OF HIGH-PURITY ALUMINA WERE USED TO CONTAIN THE ALUMINUM (OR AL-NA₂CL MIXTURE). FOR SOME RUNS HIGH-PURITY GRAPHITE CRUCIBLES WERE EMPLOYED BUT AT HIGHER TEMPERATURES AND LONGER TIMES OF EXPOSURE ALUMINUM REACTED SEVERELY TO FORM ALUMINUM CARBIDE. THIN TITANIUM SHEET WAS WRAPPED AROUND THE GRAPHITE COMPONENTS TO PREVENT IRON-GRAPHITE CONTACT. SINCE THE TEMPERATURE OF THE RESERVOIR HAD TO BE KNOWN ACCURATELY, THE

INNER IRON TUBE WAS EXTENDED DIRECTLY INTO THE MELT AND WAS PROTECTED BY A SHEATH OF EITHER ALUMINA OR GRAPHITE.

3. WELDING OPERATIONS. WITH THE EXCEPTION OF THE SEALING OF THE CAPILLARY TUBE, ALL WELDING OPERATIONS WERE DONE IN AN ARGON ATMOSPHERE UNDER REDUCED PRESSURE IN THE SPECIALLY CONSTRUCTED WELDING UNIT SHOWN IN FIGURE 3. THE PART TO BE WELDED WAS POSITIONED WITH SCREWS IN A STEEL BEAKER WHICH COULD BE RAISED AND LOWERED BY A LONG STEEL ROD. A WELDING GENERATOR SERVED AS THE POWER SOURCE WITH ONE POLE CONNECTED TO THE TUNGSTEN TIPPED ELECTRODE AND THE OTHER ONE TO THE STEEL ROD. BEFORE CLOSING THE CAPILLARY TUBE, THE REACTION TUBE WAS EVACUATED AND FLUSHED WITH OXYGEN SEVERAL TIMES. THE TUBE WAS FINALLY EVACUATED TO 0.1 MICRON (Hg) PRESSURE AND CLOSED. TRACES OF OXYGEN LEFT IN THE TUBE REACTED ON HEATING WITH ALUMINUM AND DID NOT CAUSE ANY INTERFERENCE DUE TO THERMAL DIFFUSION.

THE REST OF THE PROCEDURE IS SIMILAR FOR BOTH THE IRON AND ALUMINA TUBES; ACCORDINGLY, THE CONSTRUCTION OF THE LATTER WILL NOW BE DISCUSSED BEFORE PROCEEDING FURTHER.

ALUMINA REACTION TUBES

ALUMINA TUBES, CLOSED AT THE TOP, WERE CONVENIENTLY AND SATISFACTORILY SEALED ON THE BOTTOM (AFTER INSERTION OF THE SPECIMENS, ETC.) BY HEATING THESE INVERTED TUBES IN POOLS OF MOLTEN ALUMINUM. BECAUSE HIGH-PURITY ALUMINA IS INERT TO LIQUID AND GASEOUS AL AT THE TEMPERATURES USED IN THIS STUDY, ALL COMPONENTS OF THE REACTION TUBE WERE OF RECRYSTALLIZED HIGH-PURITY ALUMINA.

IRON AND IRON-16% ALUMINUM ALLOY SPECIMENS, PREPARED AS PREVIOUSLY DESCRIBED, WERE ALTERNATELY POSITIONED ALONG A 1/4" DIA. ALUMINA TUBE.

SPACERS OF ALUMINA, $1/2$ " TO $3/4$ " HIGH X $3/8$ " I.D. X $1/2$ O.D., WERE USED TO SEPARATE AND POSITION THE SPECIMENS AND THE POSITIONS OF THE SPECIMENS WITH RESPECT TO THE REACTION TUBE WERE MEASURED. HIGH-PURITY ALUMINUM METAL WEIGHING APPROXIMATELY 80 GRAMS WAS MACHINED TO THE CYLINDRICAL SHAPE SHOWN IN FIGURE 4. IN RUNS WITH NaCl APPROXIMATELY 8-10 GRAMS OF SODIUM CHLORIDE, DRIED FOR SEVERAL HOURS AT 500°C ., WAS PLACED ON TOP OF THE ALUMINUM. AN ALUMINA CRUCIBLE $1-1/2$ " I.D. X $1-9/16$ " O.D. X $3-1/2$ " HIGH AND A 1 " I.D. X $1-1/4$ " O.D. X 14 TO 16" ALUMINA TUBE (CLOSED ON THE TOP END) WERE ASSEMBLED WITH THE SPECIMENS AS SHOWN IN FIGURE 4.

THE ADVANTAGES OF THIS ARRANGEMENT ARE THE FOLLOWING:

- A. THE CONTENTS OF THE REACTION TUBE CAN BE THOROUGHLY DRIED IN SITU IN VACUUM AND AT TEMPERATURES UP TO THE MELTING POINT OF ALUMINUM, I.E. 659°C . THIS WILL REMOVE ANY TRACES OF MOISTURE PICKED UP BY NaCl DURING TUBE ASSEMBLY, WHICH COULD CAUSE UNDESIRABLE SIDE REACTIONS IF NOT REMOVED.
- B. THE MOLTEN ALUMINUM ACTS SATISFACTORILY AS A SEALANT TO ISOLATE THE CONTENTS OF THE TUBE FROM THE SURROUNDINGS.
- C. THE USE OF A RELATIVELY LARGE QUANTITY OF ALUMINUM PRODUCES A FLATTER TEMPERATURE MINIMUM SO THAT THE TEMPERATURE OF THE AL-NaCl INTERFACE CAN BE MORE ACCURATELY ASSESSED WHEN COMPUTING ALUMINUM ACTIVITIES.

C. EXPERIMENTAL PROCEDURE:

THE ASSEMBLED REACTION TUBE (IRON OR ALUMINA) WAS INSERTED VERTICALLY IN A MULLITE TUBE, AND A LONG QUARTZ TUBE, CLOSED AT THE BOTTOM, WAS PLACED EITHER INSIDE THE $1/4$ " DIA. INNER TUBE OF THE IRON TUBE OR ALONG THE OUTSIDE OF THE ALUMINA TUBE. THE QUARTZ TUBE ACCOMMODATED A

PLATINUM-PLATINUM-10% RHODIUM THERMOCOUPLE WHICH COULD BE RAISED OR LOWERED ALONG THE LENGTH OF THE REACTION TUBE FROM OUTSIDE THE MULLITE TUBE. THE MULLITE TUBE WAS CLOSED WITH A WATER-COOLED BRASS HEAD, USING AN APIESON WAX AS A SEALANT. THE BRASS HEAD HAD AN OPENING FOR THE QUARTZ THERMOCOUPLE PROTECTION TUBE AND A METAL-TO-GLASS CONNECTION TO A VACUUM SYSTEM CONSISTING OF A TWO-STAGE MECHANICAL PUMP, A THREE-STAGE OIL DIFFUSION PUMP, A COLD TRAP AND A McLEOD GAUGE. THE MULLITE TUBE WAS CONTINUOUSLY EVACUATED DURING THE RUN TO A PRESSURE OF BETTER THAN 2 MICRONS (Hg).

THE MULLITE TUBE WAS POSITIONED BETWEEN TWO SEPARATE RESISTANCE-WOUND TUBE FURNACES. THE BOTTOM FURNACE USED NICHROME V RESISTANCE WIRE AND THE TOP FURNACE (ALWAYS AT A HIGHER TEMPERATURE THAN THE BOTTOM) HAD A SUPER-KANTHAL WINDING. EACH FURNACE WAS CONTROLLED BY A SEPARATE SINGLE-POINT CELECTRAY CONTROLLER TO WITHIN $\pm 1^{\circ}\text{C}$.

BY SUITABLE FURNACE SETTINGS, DIFFERENT TEMPERATURE GRADIENTS WERE IMPOSED ON THE REACTION TUBES IN THE TEMPERATURE RANGE $750-1150^{\circ}\text{C}$. THE AL SURFACE OR THE AL- NaCl INTERFACE WAS ALWAYS KEPT AT THE TEMPERATURE MINIMUM AND A TOTAL TEMPERATURE GRADIENT OF APPROXIMATELY 150° TO 250°C ALONG THE ENTIRE LENGTH OF THE REACTION TUBE WAS GENERALLY USED. ON HEATING THE ALUMINA TUBES, THE ALUMINUM MELTED AND SEALED THE INTERIOR OF THE TUBE FROM THE REST OF THE SYSTEM (SEE FIGURE 5).

ACCURATE TEMPERATURE MEASUREMENTS WERE MANDATORY, SINCE A TEMPERATURE ERROR OF 1°C . WOULD LEAD TO AN ERROR IN THE CALCULATED ALUMINUM ACTIVITY OF 1 TO 5%. THE THERMOCOUPLES WERE CALIBRATED TO AN ACCURACY OF $\pm 1/2^{\circ}$ USING THE FREEZING POINTS OF ZINC, ANTIMONY AND COPPER AND FOLLOWING A PROCEDURE DESCRIBED BY THE NATIONAL BUREAU OF STANDARDS⁽²⁰⁾. THE TEMPERATURE GRADIENT WAS DETERMINED BY MEASURING THE TEMPERATURE EVERY

CENTIMETER ALONG THE OUTSIDE OF THE REACTION TUBE. SINCE THE POSITIONS OF THE SPECIMENS WERE KNOWN, THEIR TEMPERATURES COULD BE DETERMINED. TO IMPROVE THE ACCURACY OF THE TEMPERATURE MEASUREMENTS IN ALUMINA TUBES CALIBRATION RUNS WERE MADE UNDER OTHERWISE IDENTICAL CONDITIONS USING ALUMINA TUBE IN WHICH THE TOP WAS PIERCED AND THE TEMPERATURE GRADIENT COULD BE MEASURED BOTH INSIDE AND OUTSIDE THE REACTION TUBE. BY CAREFULLY DUPLICATING THE TEMPERATURE GRADIENT OF THE EXPERIMENTAL RUNS THE ACTUAL TEMPERATURE OF THE SPECIMENS COULD BE DETERMINED QUITE SATISFACTORILY.

THE LENGTH OF A RUN WAS GENERALLY ABOUT THIRTY DAYS, ALTHOUGH SOMEWHAT LONGER PERIODS WERE USED FOR LOWER TEMPERATURE RUNS. RUNS MADE WITH IRON TUBES WERE TERMINATED BY WATER QUENCHING IN ORDER TO PRESERVE THE COMPOSITIONS OF THE SPECIMENS AT THE RUN TEMPERATURE. RUNS MADE WITH ALUMINA TUBES WERE TERMINATED BY AIR-COOLING THE EVACUATED MULLITE TUBES; APPROXIMATELY 15 MINUTES WERE REQUIRED TO COOL TO TEMPERATURES AT WHICH DIFFUSION AND REACTION RATES WERE NEGLIGIBLE WITH RESPECT TO SHIFTING THE EQUILIBRIUM COMPOSITION OF THE SPECIMENS. THAT EQUILIBRIUM COMPOSITIONS WERE PRESERVED WAS ASCERTAINED BY REMOVING A SURFACE LAYER FROM THE SPECIMENS PRIOR TO CHEMICAL ANALYSES. THE ALUMINA SPECIMEN TUBES WERE USUALLY DISASSEMBLED BY INSERTING THE LOWER PART OF THE TUBE INTO A SHORT RESISTANCE FURNACE PREHEATED TO A TEMPERATURE ABOVE THE MELTING POINT OF ALUMINUM AND BY MELTING THE ALUMINUM. THE SPECIMENS WERE HEATED ONLY TO MODERATE TEMPERATURES SO THAT NO EVAPORATION OF ALUMINUM OR OXIDATION OF THE SPECIMENS OCCURRED. IN A FEW EXPERIMENTS THE ALUMINA TUBES WERE CUT OPEN WITH A DIAMOND WHEEL BUT SPECIMENS WITH A HIGH ALUMINUM CONTENT WERE SO BRITTLE THAT THEY WOULD TEND TO BREAK.

D. ANALYSIS OF SPECIMENS:

THE IRON CONTENT OF EACH SPECIMEN WAS DETERMINED BY A VOLUMETRIC TITRATION WITH STANDARD 0.015 N $K_2Cr_2O_7$ SOLUTION AND THE ALUMINUM CONTENT WAS TAKEN AS THE DIFFERENCE OF THE IRON CONTENT SUBTRACTED FROM 100%. THE ESTIMATED ERROR OF THE ANALYSIS WAS LESS THAN $\pm 0.25\%$ AL. BY WEIGHING THE SPECIMENS AFTER EQUILIBRATION THE RESULTS OF THE VOLUMETRIC ANALYSIS COULD BE CHECKED. HOWEVER, A CHECK BY WEIGHING WAS NOT POSSIBLE WITH SPECIMENS CUT FROM THE IRON-ALUMINUM SHEET SINCE ITS STARTING COMPOSITION WAS NOT SUFFICIENTLY CONSTANT.

III. EVALUATION OF EXPERIMENTAL RESULTS

AFTER EQUILIBRATION AND ANALYSIS THE ACTIVITY OF ALUMINUM OF THE SPECIMENS WAS CALCULATED USING THE TEMPERATURE OF THE SPECIMENS AND OF THE ALUMINUM SOURCE AND THE VAPOR PRESSURE OF PURE ALUMINUM.

IN THE ABSENCE OF SODIUM CHLORIDE THE ACTIVITY OF ALUMINUM IS SIMPLY GIVEN BY THE RATIO OF THE VAPOR PRESSURE OF ALUMINUM OF THE LIQUID ALUMINUM SOURCE (SINCE IT IS HELD AT THE TEMPERATURE MINIMUM IN THE CLOSED SYSTEM ITS VAPOR PRESSURE IS ALSO EQUAL TO THE PARTIAL PRESSURES OF ALL THE SPECIMENS AFTER EQUILIBRATION) AND THE VAPOR PRESSURE OF PURE ALUMINUM AT THE TEMPERATURE OF THE SPECIMEN:

$$a_{AL} = \frac{p_{AL}^{\circ} \text{ (AT TEMPERATURE OF AL SOURCE)}}{p_{AL}^{\circ} \text{ (AT TEMPERATURE OF SPECIMEN)}} \quad (1)$$

FROM A SERIES OF RUNS WITH DIFFERENT ALUMINUM SOURCE TEMPERATURES ISOTHERMAL ACTIVITY-COMPOSITION CURVES CAN BE OBTAINED.

THE ACTIVITY COEFFICIENTS OF ALUMINUM γ_{AL} AND OF IRON γ_{FE} , THE PARTIAL MOLAR FREE ENERGIES $\Delta \bar{G}_{AL}$ AND $\Delta \bar{G}_{FE}$, ENTHALPIES $\Delta \bar{H}_{AL}$ AND $\Delta \bar{H}_{FE}$, AND ENTROPIES $\Delta \bar{S}_{AL}$ AND $\Delta \bar{S}_{FE}$, AND THE MOLAR QUANTITIES CAN BE DERIVED USING WELL KNOWN EQUATIONS:

$$\gamma_{AL} = \frac{a_{AL}}{N_{AL}} \quad (2) \quad \log \gamma_{FE} = - \int_{N_{FE}}^{N_{FE}=N_{FE}} \frac{N_{AL}}{N_{FE}} d \log \gamma_{AL} \quad (3)$$

$$\Delta \bar{G}_{AL} = RT \ln a_{AL} \quad \Delta \bar{G}_{FE} = RT \ln a_{FE} \quad (4)$$

$$\Delta \bar{H}_{AL} = - RT_1 T_2 \frac{\ln (a_{AL})_2 - (a_{AL})_1}{T_2 - T_1} \quad (5)$$

$$\Delta \bar{S}_{AL} = \frac{\Delta \bar{H}_{AL} - \Delta \bar{G}_{AL}}{T} \quad (6)$$

$$\Delta G^M = N_{AL} \Delta \bar{G}_{AL} + N_{FE} \Delta \bar{G}_{FE} \quad (7)$$

$$\Delta S^M = \frac{\Delta H^M - \Delta G^M}{T} \quad (8)$$

THE EVALUATION OF ACTIVITIES IS DIFFERENT WHEN SODIUM CHLORIDE IS ADDED TO ACCELERATE THE EVAPORATION OF ALUMINUM. THE TRANSPORT OF ALUMINUM IN THE GAS PHASE IS CAUSED BY THE FORMATION OF ALUMINUM SUBCHLORIDE $AlCl$, A PHENOMENON WHICH HAS BEEN FIRST OBSERVED BY WILLMORE⁽²¹⁾. THE REACTIONS IMPLICIT IN THE FORMATION OF ALUMINUM SUBHALIDES HAVE BEEN INVESTIGATED QUITE EXTENSIVELY, ESPECIALLY BY GROSS⁽²²⁾ WHO STUDIED THE COMMERCIAL APPLICATION OF THE REACTION AND USED IT ALSO FOR EQUILIBRIUM MEASUREMENTS⁽¹⁸⁾.

AS ORIGINALLY PROPOSED ALUMINUM TRICHLORIDE AlCl_3 WAS TO BE ADDED TO THE SYSTEM TO FORM AlCl ACCORDING TO THE FOLLOWING REACTION:

EXPERIMENTAL DIFFICULTIES (E.G. THE EXTREME HYGROSCOPIC NATURE OF AlCl_3) MADE IT NECESSARY TO ADOPT THE REACTION BETWEEN ALUMINUM AND SODIUM CHLORIDE FOR THIS INVESTIGATION:

FROM EXISTING THERMODYNAMIC DATA ⁽²³⁾ THE FOLLOWING EQUATION FOR THE CHANGE IN FREE ENERGY OF REACTION 10 WAS COMPILED:

$$\Delta G^\circ_T = 101,370 + 5.9T \log T - 71.75T \quad (11)$$

BETWEEN 1074° AND 2000°K THIS EQUATION CAN ALSO BE REPRESENTED IN A MORE SIMPLIFIED FORM WITHOUT ANY LOSS IN ACCURACY:

$$\Delta G^\circ_T = 98,200 - 51.0T \quad (12)$$

BELOW 1074°K SODIUM CHLORIDE IS SOLID AND WE HAVE TO ADD THE EQUATION

TO EQUATION 10. THE CHANGE IN FREE ENERGY FOR REACTION 13 ACCORDING TO KUBASCHEWSKI ⁽²³⁾ IS:

$$\Delta G^\circ_T = 3,760 - 11.57T \log T + 1.95 \times 10^{-3}T^2 + 29.46T \quad (14)$$

$$\text{OR SIMPLIFIED: } \Delta G^\circ_T = 6,660 - 6.2T \quad (15)$$

AND THE CHANGE IN FREE ENERGY FOR THE REACTION 16

$$\text{IS } \Delta G^\circ_T = 104,860 - 57.2T. \quad (17)$$

BY APPLICATION OF THE GIBBS-HELMHOLTZ EQUATION ΔH° OF REACTION 10 CAN BE EQUATED WITH 98,200 CAL AND THAT OF REACTION 16 WITH 104,860 CAL IN THE TEMPERATURE RANGE OF OUR EXPERIMENTS.

IN OUR EXPERIMENTAL ARRANGEMENT THE LIQUID ALUMINUM WAS EITHER COVERED WITH A THIN LAYER OF LIQUID OR SOLID SODIUM CHLORIDE OR THE SODIUM CHLORIDE WAS KEPT IN A SEPARATE ALUMINA CRUCIBLE WITHIN THE SPECIMEN TUBE AT THE SAME TEMPERATURE AS THE ALUMINUM. IT HAS BEEN FOUND THAT WHENEVER SODIUM CHLORIDE WAS LIQUID IT COULD NOT BE KEPT IN THE SPECIMEN TUBE FOR MORE THAN A FEW DAYS. SINCE JUST BELOW THE MELTING POINT SODIUM CHLORIDE COULD BE RETAINED FOR MORE THAN A MONTH, THE REASON FOR THE LOSS OF LIQUID SALT IS MOST PROBABLY DUE TO THE DIFFERENCE IN SURFACE TENSION BETWEEN SODIUM CHLORIDE AND ALUMINUM. LIQUID SODIUM CHLORIDE WETS THE ALUMINA SURFACE MUCH BETTER THAN ALUMINUM (WE OBSERVED ONLY AT THE VERY HIGHEST TEMPERATURES A WETTING OF ALUMINA BY AL) AND WILL CREEP OUT OF THE SPECIMEN TUBE AS A THIN FILM BETWEEN THE ALUMINA WALL AND THE MOLTEN ALUMINUM. EQUILIBRATION IN RUNS WITH SODIUM CHLORIDE WAS THEREFORE ASSURED ONLY AT TEMPERATURES BELOW THE MELTING POINT OF THE SALT.

THE EVALUATION OF RUNS WITH SODIUM CHLORIDE IS BASED ON THE FOLLOWING PRINCIPLE:

THE GAS MIXTURE IN THE SPECIMEN TUBE CONTAINS CERTAIN AMOUNTS OF GASEOUS NaCl , Al , AlCl_3 , AND Na ACCORDING TO THE EQUILIBRIUM BETWEEN THESE SPECIES IN THE GAS PHASE. DIRECTLY ABOVE THE SURFACE OF Al-NaCl , THE PARTIAL PRESSURE OF ALUMINUM P_{Al} WILL EQUAL THAT OF THE VAPOR PRESSURE OF PURE ALUMINUM. AT EACH SPECIMEN P_{Al} WILL BE DETERMINED BY THE EQUILIBRIUM BETWEEN THE GASEOUS SPECIES AT THE PARTICULAR TEMPERATURE. THE SPECIMENS WILL REACT WITH THE ALUMINUM VAPOR UNTIL THE ACTIVITY OF ALUMINUM IS THE SAME IN THE ALLOY PHASE AND IN THE GAS PHASE. THE ACTIVITY WILL BE A FUNCTION BOTH OF THE TEMPERATURE OF THE Al-NaCl INTERFACE AND OF THE TEMPERATURE OF THE SPECIMEN.

THE LOCAL PARTIAL PRESSURE OF ALUMINUM, I.E. P_{AL} NEAR THE SPECIMEN, IS OBTAINED BY THE FOLLOWING CALCULATIONS:

THE EQUILIBRIUM CONSTANT OF THIS REACTION IS:

$$K'(T) = \frac{P_{ALCL} \cdot P_{NA}}{P_{AL} \cdot P_{NaCl}} \quad (20)$$

AND FROM THE CHANGE IN THE STANDARD FREE ENERGY

$$\Delta G^\circ = -26,690 - 14.68T \log T + 53.51T \quad (21)$$

WE CAN SEE THAT WITH INCREASING TEMPERATURE THE REACTION WILL SHIFT ONLY VERY SLIGHTLY TO THE LEFT.

FROM EQUATION 20 WE OBTAIN THE PARTIAL PRESSURE OF ALUMINUM

$$P_{AL}(T) = \frac{P_{ALCL} \cdot P_{NA}}{K'(T) \cdot P_{NaCl}} \quad (22)$$

AT $T = T_1$, THE PARTIAL PRESSURE OF AL IS EQUAL TO THE PARTIAL PRESSURE OF AL OVER PURE AL (WHERE T_1 IS THE RESERVOIR TEMPERATURE AND T IS THE SPECIMEN TEMPERATURE).

$$P_{AL}^\circ(T_1) = \frac{P_{ALCL} \cdot P_{NA}}{K'(T_1) \cdot P_{NaCl}} \quad (23)$$

SINCE THE PARTIAL PRESSURE OF ALUMINUM IS SEVERAL ORDERS OF MAGNITUDE LESS THAN THAT OF THE OTHER REACTANTS, ITS CONTRIBUTION TO THE TOTAL PRESSURE MAY BE NEGLECTED AND THE TOTAL PRESSURE OF THE REACTANTS THROUGHOUT THE TUBE SET EQUAL TO $P = P_{NaCl} + P_{ALCL} + P_{NA}$. SINCE $AlCl_{(G)}$ AND $Na_{(G)}$ ARE FORMED IN EQUAL STOICHIOMETRIC PROPORTIONS, $P_{ALCL} = P_{NA} =$ CONSTANT SINCE A SLIGHT SHIFT OF $K'(T)$ WITH TEMPERATURE WILL NOT AFFECT P_{ALCL} AND P_{NA} DUE TO THE SMALLNESS OF P_{AL} . THE PARTIAL PRESSURE OF SODIUM

CHLORIDE CAN VARY BETWEEN WIDE LIMITS WITHOUT AFFECTING THE CALCULATIONS AS LONG AS P_{NaCl} IS MUCH LARGER THAN P_{AL} , I.E. THE NaCl RESERVOIR COULD BE KEPT AT SOME LOWER TEMPERATURE (E.G. RUN I-K).

TAKING $\Delta H^{\circ 1}$ AS VIRTUALLY INDEPENDENT OF T, VAN'T HOFF'S EQUATION CAN BE APPLIED. BY DIVIDING EQUATION 22 BY EQUATION 23 AND NOTING THAT THE PARTIAL PRESSURES OF THE COMPONENTS, OTHER THAN THAT OF ALUMINUM, ARE VIRTUALLY CONSTANT WITHIN THE TUBE, THE FOLLOWING EQUATION IS OBTAINED:

$$\frac{P_{\text{AL}}(T)}{P_{\text{AL}}^{\circ}(T_1)} = \frac{K'(T_1)}{K'(T)} = \text{EXP} - \left[\frac{\Delta H^{\circ 1}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (24)$$

THE LOCAL ACTIVITY OF ALUMINUM OF A SPECIMEN IS:

$$a_{\text{AL}} = \frac{P_{\text{AL}}(T)}{P_{\text{AL}}^{\circ}(T)} \quad (25)$$

TO OBTAIN a_{AL} FROM EQUATION 24 WE HAVE TO EXPRESS THE PARTIAL PRESSURE OF AL OVER PURE LIQUID AL AS A FUNCTION OF TEMPERATURE:

$$P_{\text{AL}}^{\circ}(T) = P_{\text{AL}}^{\circ}(T_1) \text{ EXP} - \left[\frac{\Delta H^{\circ}_{\text{EVAP. AL}}}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right] \quad (26)$$

COMBINING EQUATIONS 24 AND 26 WE GET:

$$\begin{aligned} \frac{P_{\text{AL}}(T)}{P_{\text{AL}}^{\circ}(T_1)} \cdot \frac{P_{\text{AL}}^{\circ}(T_1)}{P_{\text{AL}}^{\circ}(T)} &= \frac{P_{\text{AL}}(T)}{P_{\text{AL}}^{\circ}(T)} = a_{\text{AL}}(T) = \\ &= \text{EXP} - \left[\frac{\Delta H^{\circ 1}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \cdot \text{EXP} - \left[\frac{H^{\circ}_{\text{EVAP. AL}}}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right] \\ a_{\text{AL}}(T) &= \text{EXP} - \left[\frac{\Delta H^{\circ 1} + \Delta H^{\circ}_{\text{EVAP. AL}}}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right] \quad (27) \end{aligned}$$

TO USE THE KNOWN VALUE OF ΔH° FOR THE REACTION 10 WITH LIQUID SODIUM CHLORIDE (I.E., 98,200 CAL/MOLE), THE SUM OF THE ENTHALPY CHANGES

IN EQUATION 27 MUST BE COMBINED WITH THE ENTHALPY CHANGE OF EVAPORATION OF SODIUM CHLORIDE. SINCE THE HEAT CAPACITIES OF LIQUID AND GASEOUS NaCl ARE KNOWN⁽²³⁾, THE FOLLOWING RELATION IS VALID FOR AL-NaCl RESERVOIR TEMPERATURES FROM 801-900°C. (I.E., THE HEAT OF EVAPORATION OF NaCl WAS CALCULATED FOR THIS TEMPERATURE RANGE AND FOUND TO HAVE A NEARLY CONSTANT VALUE OF 42,950 CALORIES):

$$\Delta H^{\circ} + \Delta H^{\circ}_{\text{EVAP. AL}} = \Delta H^{\circ} - \Delta H^{\circ}_{\text{EVAP. NaCl}} = 55,250 \text{ CALORIES} \quad (28)$$

FOR EXPERIMENTS WITH SOLID SODIUM CHLORIDE A COMBINATION OF H° OF REACTION 16 (I.E. 104,860 CALORIES) WITH ΔH° OF SUBLIMATION OF SODIUM CHLORIDE WILL GIVE THE SAME VALUE. THUS FOR ALL RUNS WITH SODIUM CHLORIDE IN THE CONDENSED STATE THE FOLLOWING EQUATION IS APPLICABLE FOR CALCULATING THE ACTIVITY OF ALUMINUM IN THE SPECIMENS:

$$\begin{aligned} \log a_{\text{AL}} &= - \frac{55,250}{4.575} \left(\frac{1}{T_1} - \frac{1}{T} \right) \\ &= -12,080 \left(\frac{1}{T_1} - \frac{1}{T} \right) \end{aligned}$$

WHERE T_1 IS THE RESERVOIR TEMPERATURE AND T THE SPECIMEN TEMPERATURE.

IV. EXPERIMENTAL RESULTS

FROM A CURSORY GLANCE AT THE IRON-ALUMINUM PHASE DIAGRAM (FIG. 1) ONE CAN EXPECT THAT THE ACTIVITY OF ALUMINUM WILL SHOW A RATHER PRONOUNCED NEGATIVE DEVIATION FROM RAOULT'S LAW IN THE REGION OF SOLID SOLUTIONS OF ALUMINUM IN IRON AND THAT THE ACTIVITY WILL INCREASE MARKEDLY AT ONE OR MORE OF THE INTERMETALLIC COMPOUNDS TO APPROACH IDEALITY AS THE COMPOSITION APPROACHES THAT OF PURE ALUMINUM.

IRON REACTION TUBES:

WITH THE MATHEMATICAL RELATIONSHIPS PREVIOUSLY DERIVED THE ACTIVITY OF ALUMINUM WAS CALCULATED USING EITHER EQUATION 1 OR EQUATION 29. THE EQUATION FOR THE VAPOR PRESSURE OF ALUMINUM AS A FUNCTION OF TEMPERATURE WAS TAKEN FROM KUBASCHEWSKI⁽²³⁾. THIS VALUE HAS BEEN ACCEPTED IN ALL RECENT COMPILATIONS^(24,25,26). THE RESULTS FOR TWO RUNS ARE LISTED IN TABLE 1 AND 2 AND PLOTTED IN FIG. 6. IN RUN 1 (TABLE 1) NaCl WAS USED AS AN ACCELERATOR, IN RUN 3 (TABLE 2) PURE ALUMINUM WAS EVAPORATED. COLUMN 3 (TABLE 2) GIVES THE VAPOR PRESSURE OF PURE ALUMINUM AT EACH SPECIMEN TEMPERATURE. IT SHOULD BE EMPHASIZED THAT FIG. 6 IS NOT AN ISOTHERMAL ACTIVITY-COMPOSITION PLOT.

IT CAN BE SEEN FROM FIG. 6 THAT THE QUALITATIVE EXPECTATION OF A STRONG NEGATIVE DEVIATION FROM RAOULT'S LAW IS NOT BORNE OUT. ALTHOUGH THE DATA SHOW NO SYSTEMATIC DEVIATION WITH RESPECT TO THE INITIAL ALUMINUM CONTENT OF THE SPECIMENS THE RESULTS MUST BE IN SERIOUS ERROR. TO ACHIEVE EQUILIBRATION OF IRON SPECIMENS IN IRON TUBES THE DIFFUSION OF ALUMINUM IN IRON HAS TO BE THE RATE DETERMINING STEP AS COMPARED WITH THE RATE OF MASS TRANSFER OF ALUMINUM FROM THE RESERVOIR TO THE SPECIMENS. THE INSIDE WALL OF THE SPECIMEN TUBE WOULD THEN ALSO BECOME EQUILIBRATED WITH RESPECT TO ALUMINUM AND WHATEVER ALUMINUM WOULD DIFFUSE INTO THE WALL WOULD NOT AFFECT THE PARTIAL PRESSURE OF ALUMINUM WITH THE CLOSED TUBE. UNDER THESE CONDITIONS IT SHOULD BE POSSIBLE TO APPROACH EQUILIBRIUM IN THE THIN SPECIMENS. VARIATIONS OF TIME AND TEMPERATURE AND ADDITION OF NaCl DID NOT IMPROVE THE RESULTS SO THAT EXPERIMENTS IN IRON TUBES WERE FINALLY DISCONTINUED AND ALL THE DATA HAD TO BE DISCARDED. IT WAS CONCLUDED THAT UNDER ALL EXPERIMENTAL CONDITIONS THE RATE OF EVAPORATION

OF ALUMINUM AND NOT THE DIFFUSION INTO IRON WAS THE RATE DETERMINING STEP AND EQUILIBRATION COULD NOT BE ACHIEVED IN IRON TUBES. FURTHER EVIDENCE IS PROVIDED BY THE FACT THAT IN RUN 3 THE 5 MIL IRON AND 10 MIL IRON - 16% ALUMINUM SPECIMENS LIE ON A SMOOTH CURVE. IF DIFFUSION HAD CONTROLLED THE REACTION THE TWO TYPES OF SPECIMENS SHOULD LIE ON SEPARATE CURVES.

ALUMINA REACTION TUBES:

THE RESULTS OBTAINED FROM SUCCESSFUL RUNS IN ALUMINA REACTION TUBES ARE LISTED IN TABLES III TO VIII AND IN FIG. 7 AND 8 AS NONISOTHERMAL ACTIVITY-COMPOSITION PLOTS WITH THE NUMBER INDICATING THE SPECIMEN TEMPERATURE. RUN I-K WAS MADE IN AN EXCEPTIONALLY LONG (24") ALUMINA TUBE, AND IT WAS NOT POSSIBLE TO KEEP THE VERY TOP OF THE TUBE AT A HIGHER TEMPERATURE THAN THE AL-NaCl RESERVOIR AT THE BOTTOM. AS A RESULT, SOLID SODIUM CHLORIDE AND DROPLETS OF ALUMINUM (1/8" DIA. MAX.) CONDENSED AT THE TOP OF THE ALUMINA TUBE. THUS, THE ALUMINUM-SODIUM CHLORIDE SOURCE TEMPERATURE FOR THE UPPERMOST SPECIMENS WAS THAT OF THE TOP OF THE TUBE, WHILE THE CORRESPONDING TEMPERATURE FOR THE LOWER SPECIMENS WAS THAT OF THE SURFACE OF THE ALUMINUM AT THE BOTTOM OF THE TUBE. ALTHOUGH ALL THE NaCl IN THE TUBE CONDENSED AT THE TOP, THE PARTIAL PRESSURE OF NaCl WAS KNOWN TO BE NOT CRITICAL AS FAR AS AFFECTING THE CALCULATED ACTIVITY OF ALUMINUM AS A FUNCTION OF RESERVOIR AND SPECIMEN TEMPERATURE. IN VIEW OF THE UNCERTAINTIES INVOLVED, DATA OF RUN I-K HAVE NOT BEEN INCLUDED IN FIG. 7 AND WERE GIVEN NO WEIGHT IN THE FINAL EVALUATION. HOWEVER, FROM TABLE III IT CAN BE SEEN THAT ACTIVITIES FOR THE UPPERMOST AND THE LOWEST SPECIMENS CALCULATED AS OUTLINED ABOVE AGREE VERY WELL WITH THE RESULTS FROM OTHER RUNS. ACTIVITY VALUES FOR SPECIMENS IN THE MIDDLE OF THE TUBE ARE AMBIGUOUS SINCE NO DEFINITE AL-SOURCE TEMPERATURE CAN BE ASSIGNED TO THEM.

FOR RUN I-N BOTH IRON AND IRON - 16% ALUMINUM SPECIMENS WERE USED IN ALTERNATE POSITIONS AND THEIR ACTIVITIES IN FIG. 7 FALL ON A SMOOTH CURVE (Fe-16% AL SPECIMENS HAVE THE TEMPERATURE UNDERLINED). ALTHOUGH THIS BY ITSELF IS NOT ENOUGH TO BE INDICATIVE OF COMPLETE EQUILIBRATION THE RESULTS AGREE VERY WELL WITH THOSE OF OTHER RUNS. DIFFERENT SPECIMEN THICKNESS AND STARTING COMPOSITION HAS THEREFORE NO INFLUENCE ON THE FINAL RESULTS.

ALL THE OTHER RUNS SHOW VERY LITTLE SCATTER (WITH THE POSSIBLE EXCEPTION OF RUN I-S) AND COULD BE PLOTTED ON SMOOTH CURVES IN FIG. 7. AT HIGHER ALUMINUM CONTENTS THE DATA SHOW QUITE AN INCREASE IN SCATTER AS SEEN IN FIG. 8. THESE SPECIMENS WERE VERY CLOSE TO THE ALUMINUM SOURCE, INCREASED APPRECIABLY IN THICKNESS DURING THE EXPERIMENT AND AS A CONSEQUENCE WARPED QUITE CONSIDERABLY. ALL THESE FACTORS MADE ACCURATE MEASUREMENTS DIFFICULT. THE DATA HAVE THEREFORE BEEN PLOTTED AS SHOWN IN FIG. 8 AND NO FURTHER ATTEMPT HAS BEEN MADE TO CORRECT THE RESULTS FOR DIFFERENCES IN TEMPERATURE. THE AVERAGE CURVE DRAWN THROUGH THE POINTS SHOULD NEVERTHELESS GIVE A GOOD APPROXIMATION OF THE ACTIVITY OF ALUMINUM IN THESE ALLOYS AT ABOUT 1200°K.

ISOTHERMAL ACTIVITY-COMPOSITION PLOTS CAN BE OBTAINED FROM FIG. 7 BY EITHER SELECTING ISOTHERMAL SPECIMENS FROM THE CURVES OR LOCATING THESE POINTS BY INTERPOLATION AND DRAWING THE ACTIVITY-COMPOSITION CURVE FOR THE SELECTED TEMPERATURE. WHEN DATA ARE NOT NUMEROUS IT IS PREFERABLE TO CALCULATE PARTIAL MOLAR ENTHALPY VALUES AT CERTAIN COMPOSITIONS BY SELECTING THE MOST ACCURATE CURVE (RUN I-P IN FIG. 7) AS THE REFERENCE CURVE AND APPLYING VAN'T HOFF'S EQUATION (EQUATION 5) TO THE DIFFERENCE IN ACTIVITY BETWEEN THE REFERENCE CURVE AND THE OTHER CURVES.

SINCE THE $\Delta \bar{H}_{AL}$ VALUES CAN BE TAKEN AS CONSTANT FOR A LIMITED RANGE OF TEMPERATURE THE RESULTS THUS OBTAINED CAN BE AVERAGED AND THESE AVERAGE VALUES USED IN EQUATION 5 TO CALCULATE ACTIVITIES AT OTHER TEMPERATURES, AGAIN RELATIVE TO THE ACTIVITIES OF THE REFERENCE CURVE. RESULTS OF THESE CALCULATIONS ARE SHOWN IN TABLE IX. THE AVERAGE VALUES IN COLUMN 6 WITH LIQUID ALUMINUM AS STANDARD STATE ARE THE ARITHMETIC MEAN OF RUNS 1-N, 1-O, AND 1-R. RUN 1-S WAS NOT INCLUDED SINCE THE DATA SHOW MORE SCATTER AND NaCl WAS USED AS ACCELERATOR. THE AGREEMENT, HOWEVER, WITH RESULTS FROM OTHER RUNS IS GOOD ENOUGH TO CONCLUDE THAT RELIABLE VALUES CAN BE OBTAINED USING NaCl. THE DATA IN COLUMN 7 ARE THOSE GIVEN BY HULTGREN AND COWORKERS⁽²⁷⁾ IN FORM OF THE EQUATION

$$\Delta \bar{H}_{AL} = (-66,000 + 56,000 N_{FE}) N_{FE}^2 \quad (30)$$

THESE RESULTS ARE VALID AT 298°K AND FOR SOLID ALUMINUM AS THE STANDARD STATE. SINCE

$$\Delta \bar{H}_{AL(s)} - \Delta H_{F(AL)} = \left(\bar{H}_{AL(s)} - H_{AL(s)}^{\circ} \right) - \left(H_{AL(L)}^{\circ} - H_{AL(s)}^{\circ} \right) = \bar{H}_{AL(s)} - H_{AL(L)}^{\circ} \quad (31)$$

THE HEAT OF FUSION OF ALUMINUM $H_{F(AL)}$ AT 1200°K (2,000 CAL/G-ATOM) CALCULATED FROM EQUATION

$$\Delta H_{F(T)} = 2.06T - 1.48 \times 10^{-3}T^2 + 1,870 \quad (32)$$

WAS SUBTRACTED TO GIVE THE VALUES IN COLUMN 8 NOW REFERRING TO LIQUID ALUMINUM AS THE STANDARD STATE.

ISOTHERMAL ALUMINUM ACTIVITY-COMPOSITION CURVES FOR 1200°, 1300° AND 1400°K DERIVED FROM THE AVERAGE $\Delta \bar{H}_{AL}$ DATA IN TABLE IX ARE SHOWN IN FIG. 9. THE CORRESPONDING PLOT FOR THE ACTIVITY COEFFICIENT IS SHOWN IN FIG. 10. THE CURVES HAVE BEEN EXTRAPOLATED TO ZERO CONCENTRATION PARTLY BY APPROXIMATION, PARTLY BY FOLLOWING THE CURVATURE SUGGESTED BY

GROSS' DATA⁽¹⁷⁾. THE ACCURACY OF THE DATA BELOW 30 ATOMIC % AL IS THEREFORE NOT VERY HIGH. WITH THE EXTRAPOLATED ACTIVITY COEFFICIENTS $\Delta \bar{H}_{AL}$ VALUES HAVE BEEN ESTIMATED FOR THIS CONCENTRATION RANGE AND LISTED IN TABLE IX (COLUMN 6). MAKING USE OF EQUATION 2 TO 8, VARIOUS THERMODYNAMIC PARAMETERS HAVE BEEN CALCULATED FOR IRON-ALUMINUM ALLOYS FROM 0 TO 50 ATOMIC % AL AT 1200°K (TABLE X). ENTHALPY AND FREE ENERGY VALUES HAVE BEEN PLOTTED IN FIG. 11 AND ENTROPY VALUES IN FIG. 12. THESE PLOTS ARE VALID FOR A TEMPERATURE OF 1200°K AND REFER TO SOLID ALUMINUM AS THE STANDARD STATE. TO OBTAIN ENTROPIES FOR SOLID ALUMINUM AS THE STANDARD STATE A SIMILAR CORRECTION HAS BEEN APPLIED AS FOR ENTHALPY VALUES (EQUATION 31). THE ENTROPY CHANGE ON FUSION WAS CALCULATED FROM

$$\Delta S_{F(T)} = 4.75 \log T - 2.96 \times 10^{-3}T - 8.67 \quad (33)$$

V. ERRORS

THE RELIABILITY AND ACCURACY OF THE RESULTS IS AFFECTED BY ERRORS INHERENT IN THE METHOD OR IN THE MEASUREMENTS PERFORMED. IT IS ASSUMED THAT THE FOLLOWING FACTORS ARE POSSIBLE SOURCES OF ERRORS AND MIGHT INTRODUCE AN ELEMENT OF UNCERTAINTY:

- (A) TEMPERATURE MEASUREMENT
- (B) POSITION OF SPECIMENS
- (C) ANALYSIS OF SPECIMENS
- (D) INCOMPLETE EQUILIBRATION
- (E) THERMODYNAMIC DATA
- (F) SIDE REACTIONS
- (G) THERMAL DIFFUSION

IN THE SUBSEQUENT PARAGRAPHS THE INFLUENCE AND MAGNITUDE OF ERRORS DUE TO THESE FACTORS IS DISCUSSED.

THE ACCURACY OF THE TEMPERATURE MEASUREMENTS IS AFFECTED BY THE PERFORMANCE OF THE CONTROLLERS AND THE THERMOCOUPLES. BOTH CONTROLLERS WERE OPERATING WITHIN $\pm 1^{\circ}\text{C}$ AND THE TEMPERATURE GRADIENT, ONCE A STEADY STATE WAS REACHED, DID NOT CHANGE MORE THAN 1 TO 2°C OVER THE PERIOD OF A RUN (1 MONTH). THE THERMOCOUPLES WERE CALIBRATED TO WITHIN $\pm 0.5^{\circ}\text{C}$.

THE POSITION OF THE SPECIMENS WAS MEASURED TO WITHIN ± 0.5 MM WHICH IS EQUIVALENT TO AN UNCERTAINTY OF $\pm 0.5^{\circ}\text{C}$ IN THE STEEPEST PART OF THE TEMPERATURE GRADIENT BUT THIS UNCERTAINTY WAS INCREASED DURING THE TEMPERATURE MEASUREMENTS DUE TO THE DIFFERENCE IN THERMAL EXPANSION OF THE COMPONENT PARTS OF THE SYSTEM. AN ACCURATE ESTIMATE OF THIS ERROR WAS NOT POSSIBLE BUT ITS MAGNITUDE IS MOST PROBABLY NOT GREATER THAN THAT DUE TO THE TEMPERATURE MEASUREMENTS.

THE ERROR IN THE ANALYSES OF THE SPECIMENS WAS ABOUT $\pm 0.25\%$. THE IMPURITY LEVEL IN THE MATERIALS USED WAS LOW ENOUGH SO AS NOT TO AFFECT THE RESULTS. A POSSIBLE CHANGE IN THE SURFACE CONCENTRATION OF THE SPECIMENS DURING QUENCHING WAS ELIMINATED BY REMOVING A THIN SURFACE LAYER PRIOR TO THE ANALYSES.

SINCE IT CAN BE ASSUMED THAT THE ERRORS WILL TO AN EXTENT CANCEL EACH OTHER OUT IT IS ESTIMATED THAT THE EFFECTS DISCUSSED ABOVE WILL INTRODUCE A COMBINED UNCERTAINTY EQUIVALENT TO $\pm 2^{\circ}\text{C}$ OF THE SPECIMEN TEMPERATURE. SINCE A SMOOTH CURVE WAS DRAWN THROUGH THE POINTS OF BOTH THE TEMPERATURE GRADIENT AND THE ACTIVITY-COMPOSITION PLOT THE ASSUMPTION OF A PARTIAL CANCELLATION OF ERRORS SEEMS TO BE JUSTIFIED. AN ERROR OF $\pm 2^{\circ}\text{C}$ WILL HAVE DIFFERENT EFFECTS ON THE ACTIVITY VALUES DEPENDING ON THE ALUMINUM CONTENT OF THE SPECIMENS. AT 35 ATOMIC % AL THE ACTIVITIES WILL BE ACCURATE TO $\pm 2.5\%$ AND THE MAGNITUDE OF THE ERROR WILL INCREASE TO CLOSE TO $\pm 10\%$ FOR SPECIMENS CONTAINING 75 ATOMIC % AL.

THE COMPLETION OF EQUILIBRATION WAS ASCERTAINED BY VARYING THE LENGTH OF A RUN. AFTER ONE MONTH THE COMPOSITION OF THE SPECIMENS REMAINED CONSTANT EVEN FOR THE RUNS AT THE LOWEST TEMPERATURE. NO ERRATIC DIFFERENCES IN COMPOSITION BETWEEN RUNS AT THE LOWEST AND HIGHEST TEMPERATURE WHICH WOULD INDICATE INCOMPLETE EQUILIBRATION COULD BE OBSERVED AS CAN BE SEEN FROM THE CALCULATED $\Delta \bar{H}_{AL}$ VALUES (TABLE IX). FURTHERMORE, VALUES OBTAINED FROM SPECIMENS OF DIFFERENT THICKNESS DID NOT SHOW ANY SYSTEMATIC DEVIATIONS.

ALL THE CALCULATIONS ARE BASED ON THERMODYNAMIC DATA TAKEN FROM LITERATURE AND ARE THEREFORE SUBJECT TO REVISION WHENEVER MORE ACCURATE DATA WILL BECOME AVAILABLE. THE EXPERIMENTS WITH ALUMINUM ARE BASED ON THE VAPOR PRESSURE OF ALUMINUM AND THOSE WITH SODIUM CHLORIDE AND ALUMINUM DEPEND ALSO ON THE EQUILIBRIUM CONSTANT OF THE REACTION BETWEEN THE DIFFERENT SPECIES IN THE GAS PHASE. SINCE THE AGREEMENT BETWEEN RESULTS OBTAINED BY BOTH METHODS IS VERY CLOSE, A SUBSTANTIAL SHIFT IN THE DATA DUE TO MORE ACCURATE THERMODYNAMIC EQUATIONS IS NOT TO BE EXPECTED.

ACCORDING TO BREWER⁽²⁸⁾ ALUMINUM IS CAPABLE OF FORMING TWO GASEOUS SUBOXIDES, Al_2O AND AlO , AT ELEVATED TEMPERATURES. UNDER REDUCING CONDITIONS ONLY Al_2O NEEDS TO BE CONSIDERED. ALTHOUGH IT IS UNCERTAIN IF IN THE TEMPERATURE RANGE OF OUR EXPERIMENTS EQUILIBRIUM BETWEEN $Al_{(g)}$, $Al_2O_{(g)}$, AND $Al_2O_{3(s)}$ IS ESTABLISHED, A KNOWLEDGE OF THE POSSIBLE EFFECT OF THIS SIDE REACTION ON THE ACTIVITY VALUES IS OF GREAT INTEREST. THE FOLLOWING CALCULATIONS ARE BASED ON DATA TAKEN FROM COUGHLIN⁽²⁹⁾ AND WILL ILLUSTRATE THE MAGNITUDE OF THE EFFECT:

SELECTING RUN I-P WITH AN ALUMINUM SOURCE TEMPERATURE OF 1120°K

(LOG p°_{AL} (ATM) = -8.35) WE OBTAIN:

$$\begin{aligned}
\Delta G^\circ_{1120} &= -36,844 & p_{\text{Al}_2\text{O}} &= 1.78 \times 10^{-9} \text{ ATM} \\
p_{\text{TOTAL}} = p_{\text{Al}_2\text{O}} + p_{\text{AL}} &= 6.25 \times 10^{-9} \text{ ATM} & p_{\text{AL}}/p_{\text{Al}_2\text{O}} &= \frac{4.47 \times 10^{-9}}{1.78 \times 10^{-9}} = 2.5
\end{aligned}$$

WHEN THE SPECIMENS ARE EQUILIBRATED THE TOTAL PRESSURE P_{TOTAL} IN THE SPECIMEN TUBE WILL BE CONSTANT.

FOR THE SPECIMEN AT 1275°K (SPECIMEN NUMBER 11) THE FOLLOWING RESULTS ARE OBTAINED:

$$\begin{aligned}
\Delta G^\circ_{1275} &= -39,564 & p_{\text{AL}} &= 6.25 \times 10^{-9} - p_{\text{Al}_2\text{O}} = 4.8 \times 10^{-9} \text{ ATM} \\
p_{\text{Al}_2\text{O}} &= 1.45 \times 10^{-9} \text{ ATM} & p_{\text{AL}}/p_{\text{Al}_2\text{O}} &= 3.4
\end{aligned}$$

WITH INCREASING TEMPERATURE THE PARTIAL PRESSURE OF ALUMINUM IN EQUILIBRIUM WITH $p_{\text{Al}_2\text{O}}$ WILL SHIFT TO SLIGHTLY HIGHER VALUES. THIS IN TURN WILL CAUSE A SLIGHT INCREASE IN THE ACTIVITY VALUES COMPARED TO THOSE CALCULATED ON THE BASIS OF A UNIFORM PARTIAL PRESSURE OF ALUMINUM THROUGHOUT THE SPECIMEN TUBE.

FOR SPECIMEN #11 IN OUR EXAMPLE, THE ACTIVITY a_{AL} WOULD BE .0192 INSTEAD OF .0178, AN INCREASE OF 8%. AS THE SPECIMEN TEMPERATURE APPROACHES THAT OF THE ALUMINUM RESERVOIR THE CORRECTION BECOMES INCREASINGLY

SMALLER SO THAT THE ACTIVITY OF SPECIMENS HIGH IN ALUMINUM IS NOT AFFECTED BY THIS SIDE REACTION. THE RESULTS OF OUR EXPERIMENTS HAVE BEEN CORRECTED TAKING INTO ACCOUNT THE FORMATION OF Al_2O_3 .

IN THE PRESENCE OF SODIUM CHLORIDE OTHER SIDE REACTIONS ARE POSSIBLE, ESPECIALLY THE FORMATION OF $AlCl_3(g)$ AND $FeCl_2(g)$. SINCE THE ATMOSPHERE IS HIGHLY REDUCING, THE AMOUNT OF $AlCl_3$ IN THE GAS PHASE WILL BE SMALL. A CALCULATION FOR $1000^\circ K$ USING EQUATION

$$AlCl_3(g) + 2Al(g) = 3AlCl(g)$$

$$\Delta G^\circ = -48,880 + 5.84T \log T - 28.31T \quad (35)$$

GAVE A RATIO $p_{AlCl}/p_{AlCl_3} = 2000$. THE CONCENTRATION OF $AlCl_3$ IN THE GAS PHASE WAS THEREFORE NEGLECTED.

THE PARTIAL PRESSURE OF $FeCl_2(g)$ IN THE GAS PHASE HAS BEEN CALCULATED TO BE OF THE SAME ORDER OF MAGNITUDE AS THAT OF ALUMINUM IN THE CASE OF PURE IRON SPECIMENS. SINCE THE ACTIVITY OF IRON IN THE SURFACE LAYER OF THE SPECIMENS DECREASES RAPIDLY WITH THE ABSORPTION OF ALUMINUM THE PARTIAL PRESSURE OF $FeCl_2$ WILL DECREASE ACCORDINGLY AS THE EXPERIMENT PROGRESSES. THE AMOUNT OF IRON LOST BY THE SPECIMENS DUE TO THIS SIDE REACTION WAS WITHIN THE DIFFERENCE OF THE IRON CONTENT AS DETERMINED BY CHEMICAL ANALYSIS AND BY WEIGHING OF THE SPECIMENS BEFORE AND AFTER THE RUN. IN ADDITION, NO IRON WAS FOUND IN THE ALUMINUM AT THE BOTTOM OF THE SPECIMEN TUBE AFTER THE RUN. THE REACTION BETWEEN THE SPECIMENS AND THE GAS PHASE TO FORM $FeCl_2(g)$ WAS THEREFORE UNIMPORTANT AND DID NOT AFFECT THE EQUILIBRATION OF THE SPECIMENS.

A SYSTEM CONSISTING OF SPECIES WITH DIFFERENT MOLECULAR WEIGHT WILL SHOW WHEN SUBJECTED TO A TEMPERATURE GRADIENT THE PHENOMENON OF THERMAL DIFFUSION, I.E., THE CONCENTRATION OF THE SPECIES WITH A SMALLER

MOLECULAR WEIGHT WILL BE HIGHER AT THE HIGHER TEMPERATURE THAN AT THE LOWER ONE. SINCE OUR SPECIMEN TUBE IS A STATIC SYSTEM, THERMAL DIFFUSION WAS PROBABLY FULLY OPERATIVE. FOR A BINARY MIXTURE GILLESPIE⁽³⁰⁾ HAS DERIVED THE FOLLOWING EQUATION:

$$\frac{d \ln X_1}{dT} = \frac{X_2 (\sqrt{M_2} - \sqrt{M_1})}{2 (X_1 \sqrt{M_1} - X_2 \sqrt{M_2})} \quad (36)$$

WHERE X_1 AND X_2 ARE THE MOLE FRACTIONS AND M_1 AND M_2 THE MOLECULAR WEIGHTS. REPLACING THE MOLE FRACTIONS BY THE PARTIAL PRESSURES AND REMEMBERING THE $P_{TOT} = \text{CONSTANT}$ THROUGHOUT THE SPECIMEN TUBE WE GET

$$\frac{\log (P_{AL})_2 - \log (P_{AL})_1}{\log T_2 - \log T_1} = \frac{P_{AL_2O} (\sqrt{M_{AL_2O}} - \sqrt{M_{AL}})}{2 (P_{AL} \sqrt{M_{AL}} - P_{AL_2O} \sqrt{M_{AL_2O}})} \quad (37)$$

FOR A GAS PHASE CONSISTING OF $AL_{(G)}$ AND $AL_2O_{(G)}$.

APPLIED TO THE PREVIOUS EXAMPLE (RUN I-P) TAKING A MEDIAN

$$P_{AL_2O} = 1.65 \times 10^{-9} \text{ ATM}, (P_{AL})_1 = 4.6 \times 10^{-9} \text{ ATM}, T_1 = 1120^\circ K, \text{ AND } T_2 = 1275^\circ K$$

$$\log (P_{AL})_2 - \log (P_{AL})_1 = .004 \text{ OR } (P_{AL})_2 = 4.63 \times 10^{-9} \text{ ATM}$$

DUE TO THERMAL DIFFUSION P_{AL} WOULD INCREASE VERY SLIGHTLY WITH TEMPERATURE (FROM 4.6 TO 4.63×10^{-9} ATM) BUT THE EFFECT ON THE ACTIVITY OF ALUMINUM IS SO SMALL THAT IT CAN BE NEGLECTED. SINCE RESULTS FOR THE RUNS WITH SODIUM CHLORIDE ARE IN GOOD AGREEMENT WITH THOSE USING ALUMINUM ALONE THERMAL DIFFUSION IS ALSO ONLY OF MINOR INFLUENCE.

SUMMING UP, WE CAN SAY THAT THE TOTAL ERROR IN THE ACTIVITIES OF ALUMINUM IN THE RANGE OF SOLID SOLUTION (UP TO 50 ATOMIC % AL) SHOULD NOT EXCEED $\pm 5\%$. THE ERROR INCREASES WITH INCREASING ALUMINUM CONTENT WHICH IS REFLECTED IN THE INCREASE IN SCATTER OF THE POINTS IN FIG. 8. THE GOOD AGREEMENT BETWEEN THE INDIVIDUAL RUNS AND GROSS' RESULTS IS A CONFIRMATION OF THIS ASSUMPTION.

VI. DISCUSSION AND CONCLUSION

AS EXPECTED FROM THE QUALITATIVE CONSIDERATION OF THE PHASE DIAGRAM THE ACTIVITY OF ALUMINUM EXHIBITS A VERY STRONG NEGATIVE DEVIATION FROM RAOULT'S LAW IN THE RANGE OF SOLID SOLUTION OF ALUMINUM IN α -IRON. (FIG. 9). DUE TO THE LACK OF DATA BELOW 30 ATOMIC % ALUMINUM THE EXPECTED EFFECT CAUSED BY THE BEGINNING OF ORDERING IN ALLOYS AT ABOUT 30-35 ATOMIC % ALUMINUM COULD NOT BE OBSERVED. HOWEVER, THE RAPID INCREASE OF THE ACTIVITY OF ALUMINUM WITH INCREASING CONCENTRATION BEYOND 35 ATOMIC % ALUMINUM LEADS TO A VERY LARGE VALUE IN $d a_{AL}/d N_{AL}$ NEAR THE PHASE BOUNDARY. THIS, IN ADDITION TO THE PRONOUNCED DROP IN $\Delta \bar{S}_{AL}$ (FIG. 12) IN THE SAME CONCENTRATION RANGE INDICATES A SHARP INCREASE IN ORDER AS THE COMPOSITION FeAl (CsCl - STRUCTURE) IS APPROACHED. THE STOICHIOMETRIC COMPOSITION FeAl SEEMS TO LIE WITHIN THE ONE PHASE FIELD.

AS MENTIONED BEFORE, ACTIVITIES AND ACTIVITY COEFFICIENTS BELOW 30 ATOMIC % ALUMINUM HAVE BEEN OBTAINED BY EXTRAPOLATION AND THE ACCURACY OF THESE RESULTS IS THEREFORE NOT VERY HIGH. THE SAME HOLDS TRUE FOR ALL DERIVED THERMODYNAMIC PROPERTIES IN THIS CONCENTRATION RANGE LISTED IN TABLE X AND PLOTTED IN FIG. 11 AND 12. ESPECIALLY THE AVERAGE $\Delta \bar{H}_{AL}$ VALUES (TABLE IX) SEEM TO BE TOO HIGH AS COMPARED WITH THOSE PUBLISHED BY HULTGREN⁽²⁷⁾. LESS NEGATIVE $\Delta \bar{H}_{AL}$ VALUES IN THE RANGE OF LOW CONCENTRATIONS OF ALUMINUM WOULD SHIFT THE $\Delta \bar{S}_{AL}$ AND ΔS^M CURVE (FIG. 12) TO MORE POSITIVE VALUES, I.E. WOULD DECREASE THE DEVIATION FROM THE IDEAL CURVES OF $\Delta \bar{S}_{AL}^{ID}$ AND ΔS^{MID} .

A COMPARISON OF OUR DATA WITH THOSE OF OTHER INVESTIGATORS SHOWS, IN GENERAL, VERY GOOD AGREEMENT. IN FIG. 10 THE ACTIVITY COEFFICIENTS DETERMINED BY GROSS⁽¹⁷⁾ AT 1193°K ARE PLOTTED AND COINCIDE WITH THE CURVE

CALCULATED FROM OUR RESULTS FOR 1200°K. SINCE GROSS OBTAINED SATISFACTORY AGREEMENT BY EXTRAPOLATING CHIPMAN'S RESULTS^(7,8,9,10) FOR LIQUID IRON-ALUMINUM ALLOYS OUR DATA AGREE ALSO WITH THOSE OF CHIPMAN. HULTGREN⁽²⁷⁾ PRESENTED DATA FOR $\Delta\bar{H}_{AL}$, $\Delta\bar{H}_{FE}$ AND ΔH^M AT 298°K BY EVALUATING THE HEATS OF FORMATION OF VARIOUS INVESTIGATORS^(14,15,16). THE $\Delta\bar{H}_{AL}$ FIGURES FOR SOLID AND LIQUID ALUMINUM AS THE STANDARD STATE ARE SHOWN IN TABLE IX. TO COMPARE OUR RESULTS WITH THOSE COMPILED BY HULTGREN⁽²⁷⁾ $\Delta\bar{c}_{pAL}$ HAS TO BE TAKEN AS ZERO. IN VIEW OF THE UNCERTAINTY OF THIS ASSUMPTION THE AGREEMENT IS RATHER GOOD, WITH OUR RESULTS BEING SLIGHTLY MORE NEGATIVE. IT IS DOUBTFUL IF BETTER AGREEMENT CAN BE EXPECTED SINCE THE ACCURACY OF ENTHALPY DATA DERIVED FROM EQUILIBRIUM MEASUREMENTS IS LESS THAN THE ACCURACY OF DATA OBTAINED BY CALORIMETRY. THERE IS ALSO GOOD AGREEMENT BETWEEN THE INTEGRAL ENTHALPY OF MIXING ΔH^M (FIG. 11) AND HULTGREN'S VALUE IN TABLE IX.

THE ACTIVITIES OF ALUMINUM IN ALLOYS WITH MORE THAN 50 ATOMIC % ALUMINUM SHOW TOO MUCH SCATTER (FIG. 8) SO THAT AN EVALUATION OF ISOTHERMAL ACTIVITY-COMPOSITION CURVES AND A CALCULATION OF OTHER THERMODYNAMIC PROPERTIES HAS NOT BEEN ATTEMPTED. THE DATA AGREE, HOWEVER, SATISFACTORILY WITH THOSE OBTAINED BY GROSS⁽¹⁷⁾ AND CAN BE FITTED INTO A CURVE GIVING APPROXIMATE ACTIVITIES OF ALUMINUM FOR THESE ALLOYS AROUND 1200°K. THE REMARKABLE FEATURE OF THIS CURVE IN FIG. 8 IS THE SHARP INCREASE OF THE ACTIVITY IN THE COMPOSITION RANGE OF THE INTERMETALLIC COMPOUND $FeAl_3$. THE DATA FOR THIS COMPOUND SUGGEST THAT $FeAl_3$ IS STABLE OVER A LIMITED COMPOSITION RANGE.

THE RESULTS OF THIS INVESTIGATION DEMONSTRATE THAT THE METHOD DEVELOPED CAN GIVE RELIABLE RESULTS WHEN PROPER PRECAUTIONS ARE TAKEN.

ALTHOUGH FURTHER EXPERIMENTS WITH SODIUM CHLORIDE WILL BE NEEDED, THE DATA OBTAINED SO FAR ARE IN GOOD AGREEMENT WITH THOSE DERIVED FROM EXPERIMENTS WITH ALUMINUM ALONE. ADDITIONS OF NaCl SHOULD MAKE IT POSSIBLE TO EXTEND MEASUREMENTS TO LOWER TEMPERATURES.

THE MAIN ADVANTAGE OF THE EXPERIMENTAL METHOD USED IN THIS INVESTIGATION IS THE SMALL NUMBER OF RUNS NEEDED TO OBTAIN THERMODYNAMIC PROPERTIES OVER A WIDE RANGE OF CONCENTRATION AND TEMPERATURE. AS A MATTER OF FACT ONLY TWO VERY ACCURATE RUNS WITH DIFFERENT RESERVOIR TEMPERATURES ARE NECESSARY TO ACHIEVE THIS OBJECTIVE BY APPLICATION OF EQUATION 5.

THE EXPERIMENTS CAN BE MODIFIED TO DETERMINE ACTIVITIES IN ALLOYS BELOW 30 ATOMIC % ALUMINUM WITH AN ALUMINUM SOURCE OF LOWER ALUMINUM ACTIVITY. THIS CAN BE ACCOMPLISHED BY THE USE OF LONGER SPECIMEN TUBES, GREATER TEMPERATURE GRADIENTS OR BY REPLACING ALUMINUM WITH AN ALUMINUM-IRON ALLOY (PREFERABLY IN THE FeAl-FeAl_2 PHASE FIELD). IN THE LATTER CASE CARE HAS TO BE TAKEN THAT THE SUPPLY OF THIS ALLOY IS LARGE ENOUGH AND THE FINAL COMPOSITION IS STILL WITHIN THE TWO-PHASE FIELD TO HAVE A CONSTANT ALUMINUM ACTIVITY IN THE VAPOR PHASE THROUGHOUT THE RUN. OTHERWISE BOTH THE SPECIMENS AND THE ALUMINUM SOURCE WOULD HAVE TO BE EQUILIBRATED AND AFTER THE RUN, ANALYZED.

THE METHOD CAN BE APPLIED TO OTHER SYSTEMS ESPECIALLY TO COMBINATIONS OF REACTIVE, HIGH MELTING METALS (Ti, Zr, Hf, V, Nb, Ta, W, Mo) AND LOW MELTING METALS WITH A COMPARATIVELY LOW VAPOR PRESSURE (Al, Sn, Pb). THE MATERIAL OF THE CERAMIC SPECIMEN TUBE CAN ALSO BE ADJUSTED TO THE PARTICULAR SYSTEM. FOR REACTIVE METALS WHERE THE POSSIBLE FORMATION OF VOLATILE SUBOXIDES (E.G. Al_2O) MIGHT LEAD TO AN OXYGEN PICKUP

BY THE SPECIMENS THE USE OF BORON NITRIDE (BN) AS A SPECIMEN TUBE MATERIAL COULD SOLVE THE PROBLEM. AT THE PRESENT AN INVESTIGATION OF THE TITANIUM-ALUMINUM SYSTEM IS BEING CARRIED OUT AND THE RESULTS OF THIS STUDY SHOULD PROVE THE APPLICABILITY OF THE METHOD DEVELOPED TO REACTIVE METAL SYSTEMS.

VII. SUMMARY

THERMODYNAMIC PROPERTIES OF SOLID IRON-ALUMINUM ALLOYS HAVE BEEN DETERMINED IN THE TEMPERATURE RANGE BETWEEN 900 AND 1100°C AND FROM 30 TO 75 ATOMIC % ALUMINUM. A METHOD WAS DEVELOPED IN WHICH IRON SPECIMENS HEATED IN A TEMPERATURE GRADIENT WERE EQUILIBRATED WITH ALUMINUM VAPOR FROM AN ALUMINUM SOURCE KEPT AT THE TEMPERATURE MINIMUM OF AN EVACUATED VERTICAL ALL ALUMINA SYSTEM. THE ALUMINA SYSTEM CONTAINING THE SPECIMENS WAS SEALED BY A POOL OF LIQUID ALUMINUM WHICH SERVED SIMULTANEOUSLY AS THE SOURCE OF ALUMINUM VAPOR. AT LOWER TEMPERATURES THE TRANSFER OF ALUMINUM TO THE SPECIMENS WAS ACCELERATED BY ADDITION OF SODIUM CHLORIDE. NECESSARY EQUATIONS HAVE BEEN WORKED OUT TO CALCULATE ALUMINUM ACTIVITIES FROM MEASURED QUANTITIES AND DATA PUBLISHED IN LITERATURE.

THE ACTIVITY OF ALUMINUM IN IRON-ALUMINUM ALLOYS SHOWS A PRO-
NOUNCED NEGATIVE DEVIATION FROM RAOULT'S LAW. AS THE COMPOSITION FeAl IS APPROACHED THERMODYNAMIC PARAMETERS INDICATE A SHARP INCREASE IN ORDER IN THE RANGE OF SOLID SOLUTIONS OF ALUMINUM IN IRON. THE COMPOSITION OF FeAl IS WITHIN THE ONE-PHASE FIELD. USING THE GIBBS-DUHEM EQUATION PARTIAL MOLAR PROPERTIES OF IRON AND INTEGRAL MOLAR PROPERTIES HAVE BEEN CALCULATED FROM 0 TO 50 ATOMIC % ALUMINUM AT 1200°K.

THE RESULTS HAVE BEEN COMPARED WITH DATA PUBLISHED IN LITERATURE AND GOOD AGREEMENT WAS FOUND. THE METHOD SHOULD BE APPLICABLE TO SYSTEMS WHICH CAN BE INVESTIGATED ONLY WITH DIFFICULTY BY OTHER EXPERIMENTAL PROCEDURES. ONE MAIN ADVANTAGE IS THE SMALL NUMBER OF EXPERIMENTS NECESSARY TO OBTAIN RESULTS OVER A WIDE RANGE OF COMPOSITION AND TEMPERATURE. THE VARIOUS SOURCES OF ERRORS HAVE BEEN DISCUSSED TO ASSESS THE ACCURACY OF THE RESULTS AND THE RELIABILITY OF THE METHOD.

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TABLE I

RUN I (ALUMINUM-SODIUM CHLORIDE)

SPECIMEN No.	TEMPERATURE °K.	-LOG a_{AL}	a_{AL}	AL CONTENT ATOMIC PERCENT
20	1178	0.654	0.222	17.27
19	1190	.754	.176	13.15
18	1201	.848	.142	10.37
17	1211	.936	.116	7.36
16	1221	1.018	.0960	4.69
15	1233	1.106	.0784	3.37
14	1240	1.182	.0657	3.56
13	1252	1.270	.0537	2.70
12	1260	1.332	.0476	1.46
11	1267	1.396	.0402	0.35
10	1272	1.438	.0369	0.69
9	1277	1.471	.0338	0.49
8	1281	1.496	.0319	1.29
7	1284	1.521	.0301	0.22
6	1287	1.546	.0287	0.64

RESERVOIR TEMPERATURE OF 1110°K.

TABLE II

RUN 3 (ALUMINUM)

SPECIMEN No.	TEMPERATURE °K	p_{AL} 10^{-4} MM	a_{AL}	AL CONTENT ATOMIC PERCENT
SPACER	1330	6.30	0.168	18.57
20	1331	6.60	.161	18.00
19*	1352	9.55	.121	13.94
18-	1356	10.7	.0990	11.98
17*	1367	13.5	.0785	9.90
16	1375	15.8	.0670	8.62
15*	1382	17.8	.0595	7.36
14-	1387	19.5	.0540	7.50
13*	1391	21.4	.0495	6.14
12-	1395	23.4	.0460	6.04
11*	1398	24.0	.0440	4.50
10-	1401	25.0	.0424	5.25

* INITIAL COMPOSITION OF SPECIMEN: Fe-16% AL; OTHER SPECIMENS: PURE IRON.

AL RESERVOIR TEMPERATURE: 1250°K ($p_{AL}^{\circ} = 1.06 \cdot 10^{-4}$ MM).

TABLE III

RUN I-K (ALUMINUM-SODIUM CHLORIDE)

<u>SPECIMEN No.</u>	<u>TEMPERATURE °K</u>	<u>-LOG a_{AL}^{**}</u>	<u>a_{AL}</u>	<u>AL CONTENT ATOMIC PERCENT</u>
<u>RUN I-K'</u>				
K-1	1134	0.220	0.628	76.71
K-1*	1155	.413	.386	75.65
K-2-	1175	.591	.256	71.40
K-2*	1196	.772	.169	51.66
K-3-	1216	.937	.116	50.00
K-3*	1233	1.075	.0845	48.79
K-4-	1246	--	--	--
K-4*	1258	1.270	.0537	42.21
K-5-	1269	1.353	.0444	38.77
K-5*	1279	1.427	.0374	34.92
<u>RUN I-K''</u>				
K-11*	1209	2.052	.00887	35.31
K-12-	1193	1.918	.0121	41.40
K-12*	1168	1.701	.0199	45.07

* INITIAL COMPOSITION OF SPECIMENS, Fe-16% AL; OTHER SPECIMENS: PURE IRON.

** ACTIVITY VALUES FOR SPECIMENS NO. K-1 TO K-5* WERE CALCULATED USING A RESERVOIR TEMPERATURE OF 1111°K. (RUN I-K'); THE ACTIVITY VALUES FOR SPECIMENS NO. K-11* TO K-12* WERE CALCULATED USING A RESERVOIR TEMPERATURE OF 1003°K. (RUN I-K'').

TABLE IV

RUN I-N (ALUMINUM)

SPECIMEN No.	TEMPERATURE °K.	p°_{AL} 10^5 MM	a_{AL}	AL CONTENT ATOMIC PERCENT
N-1	1080	0.107	0.726	76.64
N-1*	1086	.126	.618	76.42
N-2-	1100	.200	.389	--
N-2*	1118	.339	.229	72.48
N-3-	1139	.725	.107	71.25
N-3*	1161	1.15	.0676	50.2
N-4-	1175	1.66	.0468	49.2
N-4*	1183	2.04	.0380	46.36
N-5-	1192	2.57	.0302	45.10
N-5*	1198	3.02	.0257	43.71
N-6	1203	3.47	.0224	43.17
N-6*	1205	3.63	.0214	41.30
N-7-	1205	3.63	.0214	42.55
N-7*	1203	3.47	.0224	41.7

* INITIAL COMPOSITION OF SPECIMENS, Fe-16% AL; OTHER SPECIMENS: PURE
- IRON

AL RESERVOIR TEMPERATURE 1070°K. ($p^{\circ}_{AL} = 7.76 \cdot 10^{-7}$ MM).

TABLE V

RUN 1-0 (ALUMINUM)

SPECIMEN No.	TEMPERATURE °K	p°_{AL} 10^5 MM	a_{AL} 10^2	AL CONTENT ATOMIC PERCENT
1	1183.1	2.09	74.16	72.2
2	1201.6	3.39	45.72	72.4
3	1227.1	6.31	24.56	71.7
4	1252.6	11.22	13.81	66.7
5	1275.6	19.05	8.14	48.7
6	1294.1	28.18	5.50	45.4
7	1306.1	38.02	4.08	42.7
8	1316.1	46.77	3.31	41.8
9	1324.6	56.23	2.76	39.2
10	1330.1	61.66	2.51	38.3
11	1332.1	66.07	2.35	37.1
12	1331.1	66.07	2.35	36.7

AL RESERVOIR TEMPERATURE: 1173°K ($p^{\circ}_{AL} = 1.55 \times 10^{-5}$ MM)

TABLE VI

RUN I-P (ALUMINUM)

<u>SPECIMEN No.</u>	<u>TEMPERATURE °K</u>	<u>p_{AL}° 10^5 MM</u>	<u>a_{AL} 10^2</u>	<u>AL CONTENT ATOMIC PERCENT</u>
1	1136.1	0.56	60.71	75.8
2	1154.6	0.96	35.43	75.3
3	1179.6	1.86	18.32	70.9
4	1204.1	3.55	9.64	50.5
5	1223.1	5.25	6.55	48.7
6	1238.1	7.94	4.37	46.0
7	1247.1	10.23	3.42	43.5
8	1261.6	13.49	2.66	41.2
9	1269.1	16.60	2.19	39.3
10	1273.1	18.62	1.97	38.0
11	1275.1	19.05	1.92	37.4
12	1273.6	18.62	1.97	37.5

AL RESERVOIR TEMPERATURE: 1120°K ($p_{AL}^{\circ} = 3.4 \times 10^{-6}$ MM)

TABLE VIII

RUN 1-S (ALUMINUM-SODIUM CHLORIDE)

<u>SPECIMEN No.</u>	<u>TEMPERATURE °K</u>	<u>LOG a_{AL}</u>	<u>a_{AL} 10²</u>	<u>AL CONTENT ATOMIC PERCENT</u>
1	1055.6	$\overline{1}.396$	24.89	69.6
2	1083.1	$\overline{1}.106$	12.76	65.6
3	1116.1	$\overline{2}.780$	6.03	50.2
4	1144.7	$\overline{2}.514$	3.27	47.9
5	1168.6	$\overline{2}.297$	1.98	41.9
6	1187.6	$\overline{2}.116$	1.31	38.8
7	1202.1	$\overline{2}.007$	1.02	34.6
8	1215.1	$\overline{3}.898$	0.79	33.0
9	1225.1	$\overline{3}.814$	0.65	28.6
10	1231.6	$\overline{3}.766$	0.58	27.4
11	1235.3	$\overline{3}.741$	0.55	25.5
12	1237.1	$\overline{3}.717$	0.52	26.4

AL-NACL RESERVOIR TEMPERATURE: 1003 °K.

TABLE IX

RELATIVE PARTIAL MOLAR ENTHALPY OF ALUMINUM ($\Delta \bar{H}_{AL}$)

CONC. (N_{AL})	RUN No.				AVERAGE VALUE	$\Delta \bar{H}_{AL}(27)$	
	I-N	I-O	I-R	I-S		$AL(s)$	$AL(L)$
.10	--	--	--	--	-17,900	-12,700	-14,700
.20	--	--	--	--	-17,200	-13,600	-15,600
.30	--	--	--	--	-16,300	-13,100	-15,100
.35	--	-16,500	-15,800	-17,500	-16,100	-12,500	-14,500
.40	-16,000	-13,900	-14,900	-16,000	-14,900	-11,700	-13,700
.45	-15,400	-11,800	-13,100	-15,500	-13,400	-10,600	-12,600
.50	-12,400	--	-12,200	-14,000	-12,300	-9,500	-11,500

TABLE X

THERMODYNAMIC PROPERTIES OF IRON-ALUMINUM ALLOYS
AT 1200°K

THERMODY- NAMIC PROPERTY	CONCENTRATION (N_{AL})							STANDARD STATE
	.10	.20	.30	.35	.40	.45	.50	
$\Delta \bar{H}_{AL}$	-17,900	-17,200	-16,300	-16,100	-14,900	-13,400	-12,300	AL(L)
$\Delta \bar{H}_{AL}$	-15,700	-15,000	-14,100	-13,900	-12,700	-11,200	-10,100	AL(s)
LOG a_{AL}	-3.015	-2.550	-2.182	-1.987	-1.771	-1.467	-1.119	
LOG γ_{AL}	-2.015	-1.850	-1.660	-1.532	-1.373	-1.119	-0.818	
$\Delta \bar{G}_{AL}$	-16,550	-14,000	-12,000	-10,900	-9,720	-8,050	-6,140	AL(L)
$\Delta \bar{G}_{AL}^{XS}$	-17,190	-14,640	-12,640	-11,540	-10,360	-8,690	-6,780	AL(s)
$\bar{G}_{AL}$	-11,070	-10,160	-9,110	-8,410	-7,540	-6,140	-4,500	
$\Delta \bar{S}_{AL}$	-1.12	-2.67	-3.58	-4.33	-4.33	-4.45	-5.13	AL(L)
$\Delta \bar{S}_{AL}$	+1.28	-0.27	-1.18	-1.93	-1.93	-2.05	-2.73	AL(s)
$\Delta \bar{S}_{AL}^{ID}$	+4.57	+3.20	+2.50	+2.09	+1.82	+1.59	+1.38	AL(s)
$\bar{S}_{AL}^{XS}$	-3.29	-3.47	-3.68	-4.02	-3.75	-3.64	-4.11	AL(s)
LOG γ_{FE}	-.0047	-.0273	-.0951	-.1628	-.2773	-.4481	-.7211	
LOG a_{FE}	-.0507	-.1243	-.2501	-.3498	-.4993	-.7081	-1.0221	
$\Delta \bar{G}_{FE}$	-280	-680	-1,370	-1,920	-2,740	-3,890	-5,600	
ΔG^M	-1,980	-3,490	-4,750	-5,290	-5,820	-6,020	-6,190	AL(s)
$\Delta \bar{H}_{FE}$	-50	-200	-650	-930	-1,510	-2,220	-3,280	
ΔH^M	-1,620	-3,160	-4,680	-5,460	-5,980	-6,260	-6,690	AL(s)
ΔS^M	+.30	+.275	+.06	-.14	-.13	-.20	-.42	AL(s)

FIGURE 1. IRON-ALUMINUM PHASE DIAGRAM

FIGURE 2. IRON REACTION TUBE WITH POSITIONED SPECIMENS PRIOR TO FINAL ASSEMBLY AND WELDING.

FIGURE 3. UNIT FOR ARC WELDING IRON REACTION TUBES

FIGURE 4. ALUMINA REACTION TUBE (BEFORE MELTING ALUMINUM)

FIGURE 5. ALUMINA REACTION TUBE (AFTER MELTING ALUMINUM)

FIGURE 6. ACTIVITY OF ALUMINUM AS A FUNCTION OF COMPOSITION AS DETERMINED BY EXPERIMENTAL RUNS IN IRON REACTION TUBES

FIGURE 7. ACTIVITY OF ALUMINUM AS A FUNCTION OF COMPOSITION AS DETERMINED BY EXPERIMENTAL RUNS IN ALUMINA REACTION TUBES

FIGURE 8. ACTIVITY OF ALUMINUM IN IRON-ALUMINUM ALLOYS FROM 30 TO 100 ATOMIC PERCENT ALUMINUM

FIGURE 9. ACTIVITY OF ALUMINUM IN IRON-ALUMINUM ALLOYS FROM 0 TO 50 ATOMIC PERCENT ALUMINUM

FIGURE 10. ACTIVITY COEFFICIENTS OF ALUMINUM IN IRON-ALUMINUM ALLOYS FROM 0 TO 50 ATOMIC PERCENT ALUMINUM

FIGURE 11. THERMODYNAMIC PROPERTIES OF IRON-ALUMINUM ALLOYS AT 1200°K

FIGURE 12. MOLAR AND PARTIAL MOLAR ENTROPY OF IRON-ALUMINUM ALLOYS AT 1200°K