like mixtures at equal pressures with and without packing. As observed by Gibson and Hinshelwood[7] in their study of the hydrogen–oxygen reaction, packing retards the oxidation at the higher pressures and accelerates it at the lower pressures.

TABLE II

OVER-ALL REACTION RATE OF 75:22 CH_4–O_2 MIXTURES AT VARIED PRESSURES IN PACKED SILICA TUBE AT 600°

Expt.	Press., mm.	Initial compn., % CH_4	Initial compn., % O_2	Contact time, sec.	Compn. of off-gas, % CO_2	Compn. of off-gas, % CO	$-\Delta(CH_4)/\Delta t$ moles/cc. sec.
6:29	150	74.8	21.9	56.1	0.24	0.43	3.44×10^{-10}
6:26	300	75	22.0	118	.74	.18	4.21×10^{-10}
3:20	450	73.7	22.1	222	1.31	.20	5.44×10^{-10}
3:21	522	73.7	22.1	293	2.78	.21	9.22×10^{-10}
3:23	575	75.1	22.3	355	5.10	.13	13.72×10^{-10}

TABLE III

COMPARISON OF OXIDATION RATES OF 76:22 METHANE–OXYGEN MIXTURES IN UNPACKED AND PACKED TUBES

Press., mm.	Reaction tube surface/volume ratio, $cm.^{-1}$	$-\Delta(CH_4)/\Delta t$, moles/cc. sec. 1.37 cm. unpacked (interpolated) 3.5	$-\Delta(CH_4)/\Delta t$, moles/cc. sec. 1.37 cm. packed (20)	$-\Delta(CH_4)/\Delta t$, moles/cc. sec. Tube I annulus (average) 23.5	Ratio of rates: packed to unpacked
740		12.0×10^{-9}		1.5×10^{-9}	0.12
575		2.2×10^{-9}	1.37×10^{-9}		.61
522		1.4×10^{-9}	0.92×10^{-9}		.65
450		0.81×10^{-9}	$.54 \times 10^{-9}$		.67
300		$.18 \times 10^{-9}$	$.42 \times 10^{-9}$		2.3
150		$.022 \times 10^{-9}$	$.34 \times 10^{-9}$		15

Apparently the homogeneous reaction predominating in the absence of packing is propagated in chains of some length, as may be inferred from the sensitivity of the rate to pressure. The retardation at atmospheric pressure produced by packing indicates breakage of the reaction chains at the walls. That a distinct heterogeneous mechanism prevails in the packed tube is evidenced by the relatively slight influence of pressure on the rate.

Acknowledgment.—The author is indebted to Dr. L. S. Kassel for generous advice and criticism in the course of this investigation.

Summary

1. The influence of contact time, pressure, and of packing upon the oxidation of 76:22 methane–oxygen mixtures in silica tubes at 600° has been studied by a flow method.

2. In the absence of packing, a chain mechanism predominates, the apparent reaction order being 3.5 at 450 to 575 mm. pressure, and increasing rapidly with pressure.

3. In the packed tube the reaction is approximately first order; its rate exceeds that of the reaction in the unpacked tube when the pressure is 300 mm. or lower.

PITTSBURGH, PA. RECEIVED AUGUST 14, 1933

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[7] Gibson and Hinshelwood, *Proc. Roy. Soc.* (London), **A118**, 170 (1928); **A119**, 591 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

Thermodynamics of Solid Solutions. I. Perfect Solutions

BY HARRY SELTZ

Binary systems which solidify with the formation of solid solutions can be classified as follows. 1. Complete miscibility in the solid state: (a) all points on the liquidus and solidus curves lie between the melting points of the two components. (b) The liquidus and solidus curves pass through a maximum. (c) The liquidus and solidus curves pass through a minimum. 2. Partial miscibility in the solid state: (a) the two series of solid solutions form an eutectic. (b) The two series of solid solutions show a transition.

Roozeboom,[1] following the thermodynamic treatment of Gibbs, showed the forms of the free energy curves, for liquid and solid states, which would give rise to the above types of solid solution formations. This treatment is entirely qualitative and is difficult to apply quantitatively owing to the fact that the partial molal free energy of a constituent of a solution approaches minus infinity as its concentration approaches zero. The purpose of this paper is to attempt to apply the concept of fugacity or activity to this problem, following the methods which G. N. Lewis[2] and his collaborators have developed so successfully in the treatment of liquid solutions.

Theoretical

If a binary solution contains n_A moles of a component "A" and n_B moles of a component "B" and the total free energy of the solution is F, the partial molal free energies of the components,

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[1] Roozeboom, *Z. physik. Chem.*, **30**, 385 (1899).

[2] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York.

designated by $\overline{F}_A$ and $\overline{F}_B$, are defined by the equations

$$\overline{F}_A = (\delta F/\delta n_A)_{P,T,n_B}$$
$$\overline{F}_B = (\delta F/\delta n_B)_{P,T,n_A}$$

For two solution phases (in this case one liquid and one solid solution) to exist in equilibrium, the partial molal free energies of the separate components must be equal in the two phases: $\overline{F}_A = \overline{F}'_A$ and $\overline{F}_B = \overline{F}'_B$, where the prime is used to designate the solid solution phase. The fugacity, f, of a constituent of a solution is related to its partial molal free energy by the relation $\overline{F} = RT \ln f + B$, where B is a constant at a given temperature. Further, the fugacity is equal to the partial vapor pressure of the component when the vapor is a perfect gas. A state of equilibrium between a liquid and solid solution can now be defined in terms of fugacity in place of partial molal free energy; $f_A = f'_A$ and $f_B = f'_B$ where the subscripts and primes are used as above. Obviously, the fugacity of a constituent of a solution approaches zero as its concentration approaches zero. At higher concentrations the value of the fugacity, except for perfect solutions, cannot be predicted, since it is determined by the very nature of the solution components. A perfect binary liquid solution is defined as one which at all temperatures obeys Raoult's law over the entire range of composition

$$f_A = N_A f^0_A$$
$$f_A = N_B f^0_B$$

where N_A and N_B are the mole fractions and f^0_A and f^0_B are the fugacities of pure components "A" and "B" at the temperature in question.

Similarly we can conceive of a completely miscible series of solid solutions which obeys Raoult's law

$$f'_A = N'_A f^{0'}_A$$
$$f'_B = N'_B f^{0'}_B$$

Two solid organic isomers which form a complete series of solid solutions might exhibit such ideal behavior, or two similar metals with almost identical atomic weights and space lattice constants might be expected to show relatively small deviations, for example: palladium–silver, platinum–gold, nickel–copper. Solid solutions of gold and silver might also be included except for the great difference in atomic weights and the resulting mass effect. Indeed, electromotive force measurements by Wachter[3] on gold–silver electrodes show marked negative deviations from ideal behavior at lower temperatures. Calculations to temperatures between the melting points of gold and silver, using the partial molal relative heat contents given in this paper, still indicate considerable deviations from Raoult's law.

Calculation of Liquidus and Solidus Curves for Perfect Liquid and Solid Solutions.—Assuming perfect solution behavior for both liquid and solid phases in a binary system it is possible to develop a relation for calculating the complete liquidus and solidus curves for the system. The thermodynamic equation for change of fugacity of a pure substance with change of temperature is

$$\frac{\delta \ln f}{\delta T} = \frac{H^* - H}{RT^2}$$

where H^* is the heat content of the gasified substances expanded to perfect gas behavior (no further Joule–Thomson effect). In the present application H is the heat content of the pure solid or liquid phase. For the solid phase $\ln f'$ changes more rapidly with the temperature than $\ln f$ for the liquid phase, since H for the liquid is greater than H' for the solid by an amount equal to the heat of fusion.

Consider an ideal system, as defined above, with the melting point of "B," T_B, higher than the melting point of "A," T_A. At a temperature between T_A and T_B the fugacity curves of the two components in the solid and liquid phases can be represented as shown by the full lines in the lower part of Fig. 1, using the symbols as defined above. For equilibrium between a liquid and solid solution phase at this temperature, as previously stated, $f_A = f'_A$ and $f_B = f'_B$. At the same time, however, the compositions of the equilibrium liquid and solid phases must be such that $N_B = (1 - N_A)$ and $N'_B = (1 - N'_A)$. Thus, on the figure, the liquid with composition N_B can exist in equilibrium with a solid of composition N'_B, and, as can readily be seen, these will be the only compositions which can exist in equilibrium at this temperature. At higher temperatures the fugacities of all the pure phases will increase, but the $f^{0'}$ values will increase more rapidly than the f^0 values, so that $f^{0'}_B$ will approach f^0_B while $f^{0'}_A$ will diverge further from f^0_A. This condition is represented by the dotted lines in the lower part of Fig. 1. The equilibrium compositions of liquid (N_B) and solid phases (N'_B) are shifted toward the "B" component as shown in the diagram.

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(3) Wachter, This Journal, **54**, 4609 (1932).

N_B and N'_B can be determined graphically at any temperature by constructing, above the fugacity curves (Fig. 1), another pair of curves on which we plot for each component the difference between the *abscissas* of liquid and solid fugacity curves against the mole fraction of "B" in the liquid phase. This curve for the "A" component is labeled ΔN(A) and for the "B" component, ΔN(B). The intersection of these "difference curves" gives directly the equilibrium composition of the liquid phase, N_B, at this temperature, and by dropping a perpendicular to the liquid curves at this intersection and drawing horizontal lines to intersect the respective solid curves the composition of the solid solution phase, N'_B, is determined. This is illustrated in Fig. 1.

Obviously this graphical method might be used for solutions which are not perfect, if the fugacity curves for the two phases are determined experimentally. In most cases the actual fugacities cannot be found, but the relative fugacities or activities can be used in exactly the same manner, providing the activities in the liquid and solid phases for each component are referred to the same standard state, most conveniently to either the pure solid or liquid. This treatment will be discussed in a later communication.

Derivation of the Equations for N_B and N'_B

From the graphical treatment given above for perfect solutions, it is now possible to develop complete equations for calculating N_B and N'_B at temperatures between the melting points of the two components. From Fig. 1

$$ab = 1 - (f^0_A/f^{0'}_A)$$

$$\Delta N(\mathrm{A}) = (1 - N_B)\,[1 - (f^0_A/f^{0'}_A)]$$

$$cd = 1 - (f^{0'}_B/f^0_B)$$

$$\Delta N(\mathrm{B}) = N_B\left(1 - \frac{f^{0'}_B}{f^0_B}\right)\Big/\frac{f^{0'}_B}{f^0_B}$$

Solving for the intersection in terms of N_B

$$(1 - N_B)\left(1 - \frac{f^0_A}{f^{0'}_A}\right) = N_B\left(1 - \frac{f^{0'}_B}{f^0_B}\right)\Big/\frac{f^{0'}_B}{f^0_B}$$

$$N_B = \left(1 - \frac{f^0_A}{f^{0'}_A}\right)\Big/\left(\frac{f^0_B}{f^{0'}_B} - \frac{f^0_A}{f^{0'}_A}\right) \qquad (1)$$

Further

$$\frac{\delta \ln f^0_A}{\delta T} = \frac{H^*_A - H_A}{RT^2}$$

$$\frac{\delta \ln f^0_A}{\delta T} = \frac{H^*_A - H'_A}{RT^2}$$

$$\mathrm{d} \ln \frac{f^0_A}{f^{0'}_A} = \frac{H'_A - H_A}{RT^2}\,\mathrm{d}T$$

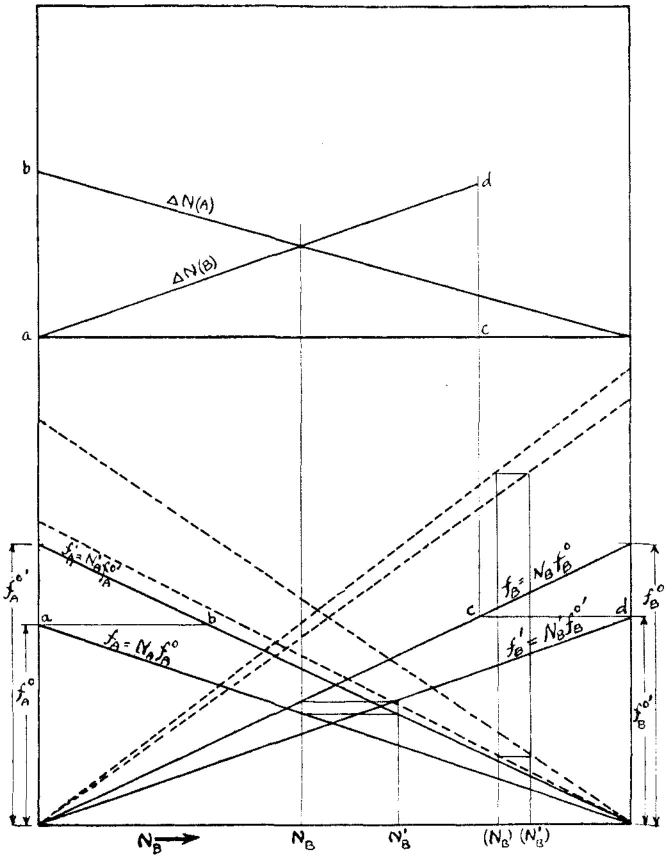

Fig. 1.

Integrating

$$\ln \frac{f^0_A}{f^{0'}_A} = \frac{H_A - H'_A}{RT} + \text{constant}$$

But $H_A - H'_A$ is equal to the molal heat of fusion of "A," designated by ΔH_A.

To evaluate the constant, at the melting point, T_A

$$f^0_A = f^{0'}_A$$

$$\text{Constant} = -\,\Delta H_A/RT_A$$

Thus

$$\frac{f^0_A}{f^{0'}_A} = \frac{e^{\Delta H_A/RT}}{e^{\Delta H_A/RT_A}}$$

or

$$f^0_A/f^{0'}_A = k_A\,e^{\Delta H_A/RT}$$

where

$$k_A = 1/e^{\Delta H_A/RT_A} \qquad (2)$$

In a similar manner

$$f^0_B/f^{0\prime}_B = k_B\, e^{\Delta H_B/RT} \qquad (3)$$

where

$$k_B = 1/e^{\Delta H_B/RT_B}$$

(These equations do not take into account the change of the heats of fusion $(H' - H)$ with change of temperature, which in most cases can be neglected.)

Substituting (2) and (3) in equation (1)

$$N_B = \frac{1 - k_A\, e^{\Delta H_A/RT}}{k_B\, e^{\Delta H_B/RT} - k_A\, e^{\Delta H_A/RT}} \qquad (4)$$

For the corresponding composition of the solid, N'_B

$$f_B = N_B f^0_B$$
$$f'_B = N'_B f^{0\prime}_B$$

but for equilibrium

$$f'_B = f_B$$

and

$$N'_B = N_B(f^0_B/f^{0\prime}_B)$$

and from equation (3)

$$N'_B = N_B k_B\, e^{\Delta H_B/RT} \qquad (5)$$

Assuming values for the heats of fusion and melting points for two hypothetical substances "A" and "B," calculations employing the above equations give the familiar lens type phase diagram, with all points on the liquidus and solidus curves lying between the melting points of the pure components and with the liquid phase richer at each temperature in the lower melting component.

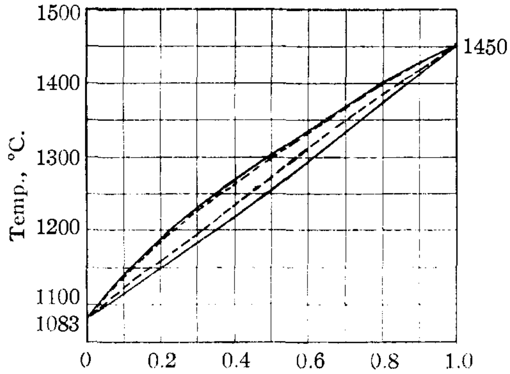

Fig. 2.—Solidus and liquidus curves for the copper–nickel system: ———— observed, — — — — calculated.

In Figs. 2, 3 and 4 experimental curves for three systems are compared with the theoretical curves from the above equations. The full lines represent the experimental curves and the dotted lines the calculated. The necessary heats of fusion were taken from the "International Critical Tables." As is to be expected, none of these systems show absolute agreement with the ideal curves. The copper–nickel system appears to approach most closely to such ideal behavior, since the experimental solidus curve can well be in error by ten or fifteen degrees. In binary liquid metal systems Hildebrand[4] and others have shown that Raoult's law is not obeyed over the entire composition range, and certainly more marked deviations would occur in solid solutions. On the other hand, the development here presented will apply as a limiting condition. Investigations of the activities of the components of several systems for both liquid and solid phases are being carried out in this Laboratory in an attempt to study the nature and origin of these deviations in solid solutions, and to apply the graphical treatment described above to locate

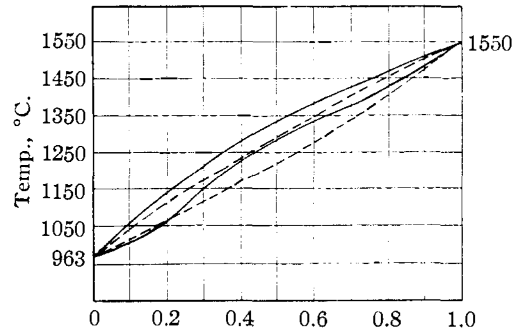

Fig. 3.—Solidus and liquidus curves for the silver–palladium system: ———— observed, — — — — calculated.

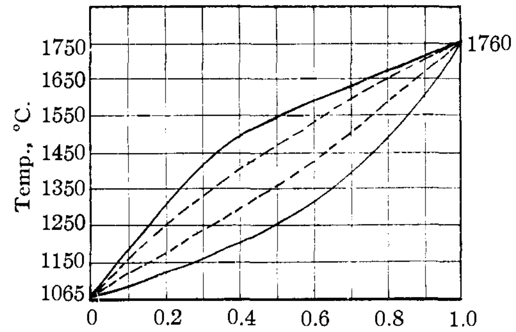

Fig. 4.—Solidus and liquidus curves for the gold–platinum system: ———— observed, — — — — calculated.

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[4] Hildebrand and Sharma, THIS JOURNAL, 51, 462 (1929).

accurately the liquidus and solidus curves. It is obvious, also, that this method can be used in the reverse manner to determine the activities of the constituents of solid solutions from their activities in the liquid phase and the known liquidus and solidus curves.

The experimental data for the copper–nickel system, Fig. 2, were taken from the work of Guertler and Tammann;[5] for the silver–palladium system, Fig. 3, from the work of Ruer,[6] and for the gold–platinum system, Fig. 4, from the work of Doerinckel.[7] The heats of fusion, per gram atom, used in the calculations were: Cu, 2655 cal.; Ni, 4280 cal.; Ag, 2795 cal.; Pd, 3850 cal.; Au, 3130 cal.; Pt, 5250 cal.

Summary

1. A graphical method is developed for determining the liquidus and solidus curves for binary systems which solidify with the formation of solid solutions, from the fugacities or activities of the components in the two phases.

2. Equations are derived for calculating the liquidus and solidus curves from the temperatures and heats of fusion of the two pure solids and the assumption that both solutions are perfect.

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[5] Guertler and Tammann, *Z. anorg. Chem.*, **52**, 25 (1907).

[6] Ruer, *ibid.*, **51**, 315 (1906).

[7] Doerinckel, *ibid.*, **54**, 333 (1907).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURE EXPERIMENT STATION]

The Solubility of Potassium Acid Tartrate. I.[1] In Tartaric Acid and Dipotassium Tartrate Solutions

BY D. C. CARPENTER AND G. L. MACK

A large number of investigators have reported values for the solubility of potassium acid tartrate in pure water at various temperatures, but agreement between the results is not particularly good. Low values are obtained by shaking unsaturated solutions with excess salt, while high values are the result of crystallizing salt from supersaturated solutions. The two investigations[2] in which both methods were used show medial results, in essential agreement with those presented in this paper. In both of these cases, however, insufficient time was allowed for equilibrium to be established. With mechanical shaking, undersaturated solutions reach equilibrium much sooner than supersaturated ones, but without agitation the reverse is true. The time required for equilibrium to be established varies considerably with the temperature. Thus at 25° twenty-four hours is amply sufficient, while at 0° equilibrium is not attained in less than seven days.

Experimental Part

Preparation of Materials.—Potassium acid tartrate was prepared from C. P. potassium hydroxide and tartaric acid by slowly adding the calculated amount of a solution of the former to a cooled solution of the latter, stirring meanwhile. Potassium acid tartrate crystallized out promptly and was filtered off on a Buchner funnel and washed with successive amounts of cold water. The salt was recrystallized three times from hot water and finally dried at 100° and stored in a desiccator over phosphorus pentoxide. The purity of the salt was determined by a potassium analysis.

Anal. Calcd. for $KHC_4H_4O_6$: K, 20.78. Found: K, 20.74, 20.78.

Dipotassium tartrate was prepared by slowly adding a solution of C. P. potassium hydroxide to a cold solution of tartaric acid until a test portion showed a P_H of 6.35 with brom thymol blue indicator. The solution was concentrated over a steam-bath and set aside for crystallization of the salt $K_2C_4H_4O_6 \cdot 0.5H_2O$. The salt was recrystallized from hot water three times, dried *in vacuo* at 40° to constant weight and bottled. Purity of the salt was established by a potassium analysis.

Anal. Calcd. for $K_2C_4H_4O_6 \cdot {}^1/_2H_2O$: K, 33.24. Found: K, 33.25, 33.32, 33.28, av. 33.28.

The tartaric acid used in this work was a sample of the acid of C. P. Baker analyzed grade. This was not further purified inasmuch as the equivalent weight was found to be 75.108, 75.005 and 74.998, mean 75.037 (calcd., 75.035), against standard alkali with brom thymol blue indicator.

Experimental Method

Concentrated stock solutions of dipotassium tartrate and of tartaric acid were prepared from the pure compounds, for use in preparing the various concentrations of each required in the solubility studies recorded below.

Appropriate quantities (usually 5 to 10 ml.) of these stock solutions were added as required to an excess of potassium acid tartrate in a clean dry 125-ml. Erlenmeyer flask

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 5.

[2] Noyes and Clement, *Z. physik. Chem.*, **13**, 412 (1894); Klapproth, *Z. anal. Chem.*, **61**, 1 (1922).