Equilibrium of Water between Gelatin Solution and Ice

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Synopsis

The equilibration of water between aqueous gelatin solution and physically separate cakes of ice was observed.   Typically, the water content of the solutions reached a nearly steady value several times before final equilibrium, reasons for which are discussed. The equilibrium gelatin concentrations were found to be 72 ± 1%, 77 ± 2%, and 80 ± 3% at −10, −21, and −33°C., respectively, in moderately good agreement with predictions based on the vapor pressure measurements of Bull at higher temperatures.

Introduction

The purpose of this study was to determine whether a reproducible equilibrium exists between aqueous gelatin solution and ice.   The method was to place together blocks of ice and trays of the solution in the form of powder or shavings (minimum dimension <1 mm.) within sealed containers at the desired temperatures.

It was hoped that the solution and ice phases would remain segregated— that due to the difficulty of ice formation within gelatin solution water in excess of the equilibrium amount would migrate as vapor to the ice blocks rather than freeze within the bulk of the solution.   Equilibrium was to be assumed when the trays of solution reached constant weight.

Materials

Central Scientific Co. granular pigskin gelatin was used, the ash content of which was stated to be 0.6%.

Procedure

Gelatin solutions prepared several weeks before and stored under refrigeration were sliced or ground at subfreezing temperature and weighed into aluminum foil trays.   A few of the samples were then hard frozen in Dry Ice; a few others were melted by storing in small sealed containers at 2°C. for several hours; then all samples and some blocks of ice were put into vacuum jars in rooms refrigerated at the experimental temperatures. Air was withdrawn from the vacuum jars at the start of the experiments and after each weighing to permit unhindered movement of water vapor be-

J. E. TANNER

tween the ice and the solution phases.   Failure to do this slowed the rate of equilibration by an order of magnitude.

Weighings were performed in a room at $-20°C.$, care being taken not to breathe on the gelatin or bring moist hands nearby.   Occasionally the samples were warmed to room temperature in small sealed containers for

TABLE I

Equilibration of Aqueous Gelatin Solutions in a Saturated Atmosphere

Temperature, °C.	Sample	Initial concentration, %	Steady intermediate concentrations, %	Final concentration, %
-10	1	30	None	$>69^{1}/_{2}$
	2	73		$72^{1}/_{2}$
		88	73	
	3	91	$71^{1}/_{2}$	
		69		$71^{1}/_{2}$
	Probable value 72 $\pm$ 1%			
-21	1	30	48, 73	
	2	73	76	
		89	$81^{1}/_{2}$	
	3[a]	91	$78^{1}/_{2}$	
		77		77
	4[b]	29	$>36, 63, 68$	70
		69	74	77
	5[a,b]	33	40, 66, 79	80
		78		77
	6[c]	32	$49, 71^{1}/_{2}, 74$	76
		93	80	78
	7[a,c]	32	$49, 69^{1}/_{2}, 73^{1}/_{2}$	76
		94	80	78
	Probable value 77 $\pm$ 2%			
-33	1	43	57, 73, 76	
	2	58	71	
		84		83
	3	69	76	
		80		80
	4	84		82
		85		81
	5	90	83	
		87	$83^{1}/_{2}$	84
	6[b]	52	68	77
	7[b]	52	$66^{1}/_{2}, 74^{1}/_{2}, 76$	77
	8[c]	52	71, 74	$76^{1}/_{2}$
		$91^{1}/_{2}$	86	81
	9[c]	52	71, 74	76
		91	86	80
	Probable value 80 $\pm$ 3%			

[a] See Figure 1.
[b] Hard frozen before the start.
[c] Melted before the start.

several hours, for reasons explained below. Small weight losses usually occurred, but if no further change occurred in the subsequent period at the experimental temperature, equilibrium was assumed to have been attained.

After equilibration, some of the samples were dried and others were moistened in a humid atmosphere to provide new starting points, and the experiment was repeated. At the finish all samples were dried at 70°C. in open air for a week, then over a molecular sieve in an evacuated desiccator at 70°C. for 4 days to determine the final moisture content. The moisture content (including any internal ice) during the preceding interval was back-calculated from this point.

Results

Table I summarizes the history of each sample, giving prior treatment, starting (gelatin) concentrations, premature steady concentrations, and those taken as final. Also listed is a judgment of the most probable value of the equilibrium concentration for each temperature. Progress of three of the samples during the experiment is shown in Figure 1. The temperature fluctuations noted were unintentional.

The results of this study are compared in Figure 2 with freezing points calculated from the vapor pressures of electrodialyzed gelatin solutions at 25° and 40°C. determined by Bull.[1] The expected freezing temperatures were calculated by means of the relation

$$\ln (p/p_0) = \int_{T_f}^{273} - (\Delta H/RT^2)dT$$

where T_f is the expected freezing temperature, p/p_0 is the measured vapor pressure of the solution relative to pure water, R is the molar gas constant, and ΔH is the heat of fusion of ice, taken as $1440 - 9.55 (273 - T)$ cal./mole.
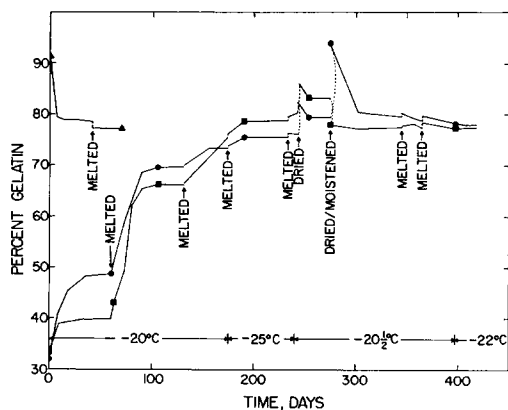

Fig. 1. Equilibration of aqueous gelatin solutions in a water-saturated atmosphere: (▲) sample 3; (■) sample 5; (●) sample 7.
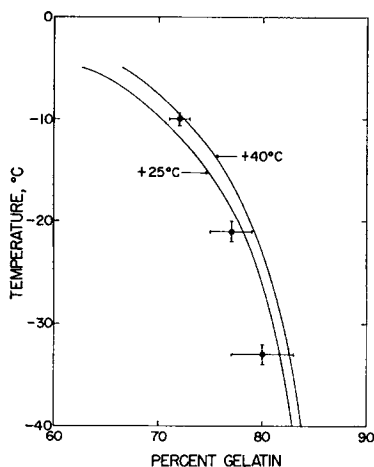
Fig. 2. Freezing temperatures of gelatin solutions: (✦) values from this study; (——) calculated from vapor pressure lowering.[1]

Discussion

Typically the solution concentrations did not progress all the way from the initial concentration to that which was finally taken as the equilibrium concentration at any one sitting in the cold room, but leveled off at intermediate values (see Fig. 1). In all cases they could be made to progress further by being warmed above 0°C. for a short time.

In many cases this was due to ice formation within the gel solution, since within a few hours of cooling to the experimental temperatures the solutions developed a whitish opacity.* Unfortunately, after this had happened a few times with a given sample the opacity persisted even above the melting temperature so that it was no longer possible to tell by eye whether ice was present.

A priori such internal ice would not be expected to sublime in a saturated atmosphere. However nucleation was observed to take place in 1-2 hr., whereas the leveling off of the concentration occurred after several weeks. This might mean only that after nucleation crystal growth took place so slowly that vaporization could compete effectively. What is more probable, considering the relative proximity of ice and of the vapor phase to most points in the solution is that some of the ice formed initially redissolved later, the water diffusing to the surface and distilling off. Such a process would be necessary to explain the behavior of the initially 30% sample (sample 1) at −10°C., which progressed nearly to the assumed equilibrium concentration without any sign of premature leveling off. MacKenzie[5] has, in fact, observed that ice formed within gelatin films will, over a longer period of time disappear and re-form at the surface, when vaporization is blocked by aluminum foil.

* A general discussion of crystallization patterns and other freezing phenomena in gelatin solutions may be found in the literature.[2-4]

The implied lower thermodynamic stability of ice formed internally may be due partly to stress from the gelatin molecules which have been pushed aside and partly to the consequent smallness of the crystallites. The fact that any leveling off at all took place before equilibrium would indicate that some of the ice crystals managed to reach sufficient size to have stability nearly equal to that of ice in bulk.

It was noted that the occasional warmings also aided equilibration at the higher concentrations, including those above equilibrium. This could merely have been the result of leveling out concentration gradients in these very viscous media.

Conclusion

An equilibrium exists between gelatin solutions and ice which is fairly reproducible, and the concentration values are in moderately good agreement with predictions based on vapor pressure-lowering measurements.

References

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3. Persidsky, M. D., and B. J. Luyet, *Biodynamica*, **8,** No. 161, 107 (1959).
4. Luyet, B., J. Tanner, and G. Rapatz, *Biodynamica*, **9,** No. 173, 21 (1962).
5. MacKenzie, A. P., private communication.

Résumé

L'equilibre de l'eau entre des solutions aqueuses de gélatine et des agrégats de glace physiquement séparés a été observé. Typiquement, la teneur en eau des solutions atteint une valeur approximativement stationnaire longtemps avant l'équilibre final et les raisons de ce comportement sont discutées. Les concentrations à l'équilibre dans la gélatine sont égales à 72 ± 1%, 77 ± 2% et 80 ± 3% à −10°, −21° et −33°C, respectivement, ceci en accord suffisant avec les prédictions basées sur les mesures de pression de vapeur à des températures plus élevées.

Zusammenfassung

Die Gleichgewichtsverteilung von Wasser zwischen einer wässrigen Gelatinlösung und physikalisch getrennten Eisstücken wurde beobachtet. In typischer Weise erreichte der Wassergehalt des Lösung einen nahezu stationären Wert in einem Bruchteil der Zeit, die für das endgültige Gleichgewicht notwendig war; die Gründe für dieses Verden diskutiert. Die Gleichgewichtskonzentration an Gelatin betrug 72 ± 1%, 77 ± 2%, und 80 ± 3% bei −10, −21 und −33°C; dies steht in meit guter Übereinstimmung mit den auf den Dampfdruckmessungen von Bull bei höheren Temperaturen beruhenden Voraussagen.