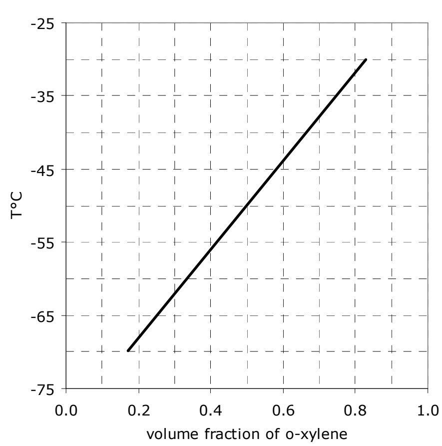
Cooling Bath Compositions

System	°C	System	°C
p-Xylene/N_2	13	Carbitol acetate/CO_2	-67
p-Dioxane	12	*t*-Butyl amine/N_2	-68
Cyclclohexane/N_2	6	Acetone/CO_2	-72
Benzene/N_2	5	Trichloroethylene/N_2	-73
Formamide/N_2	2	Butyl acetate/N_2	-77
Aniline/N_2	-6	Acetone/CO_2	-77
Cycloheptane/N_2	-12	Isoamyl acetate/N_2	-79
Benzonitrile/N_2	-13	Acrylonitrile/N_2	-82
Ethylene glycol/CO_2	-15	Sulfur dioxide/CO_2	-82
o-Dichlorobenzene/N_2	-18	Ethyl acetate/N_2	-84
Tetrachloroethane/N_2	-22	Ethyl methyl ketone/N_2	-86
Carbon tetrachloride/N_2	-23	Acrolein/N_2	-88
Carbon tetrachloride/CO_2	-23	Nitroethane/N_2	-90
o-Dichlorobenzene/N_2	-25	Heptane/N_2	-91
Nitromethane/N_2	-29	Cyclopentane/N_2	-93
o-Xylene/N_2	-29	Hexane/N_2	-94
Bromobenzene/N_2	-30	Toluene/N_2	-95
Iodobenzene/N_2	-31	Methanol/N_2	-98
Thiophene/N_2	-38	Diethyl ether/CO_2	-100
3-Heptanone/CO_2	-38	*n*-Propyl iodide/N_2	-101
Acetonitrile/N_2	-41	*n*-Butyl iodide/N_2	-103
Pyridine/N_2	-42	Cyclohexene/N_2	-104
Acetonitrile/CO_2	-42	Isooctane/N_2	-107
Chlorobenzene/N_2	-45	Ethyl iodide/N_2	-109
Cyclohexanone/CO_2	-46	Carbon disulfide/N_2	-110
m-Xylene/N_2	-47	Butyl bromide/N_2	-112
n-Butyl amine/N_2	-50	Ethyl bromide/N_2	-119
Diethyl carbitol/CO_2	-52	Acetaldehyde/N_2	-124
n-Octane/N_2	-56	Methyl cyclohexane/N_2	-126
Chloroform/CO_2	-61	*n*-Pentane/N_2	-131
Chloroform/N_2	-63	1,5-Hexadiene/N_2	-141
Methyl iodide/N_2	-66	*i*-Pentane/N_2	-160

from "The Chemist's Companion," Gordon, A. J.; Ford, R. A.; Wiley: New York, ***1972***



T°C	% o-xyl	% p-xyl
-30	83	17
-35	75	25
-40	66	34
-45	58	42
-50	50	50
-55	42	58
-60	33	67
-65	25	75
-70	17	83

Figure 1. Cooling bath temperatures for mixtures of o- and p-xylene and dry ice (from Phipps & Hume, *J. Chem. Educ.* **1968**, *45*, 664)

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General Purpose Low Temperature Dry-Ice Baths

A great many methods have been described for the preparation and maintenance of low temperature baths, and the field has been extensively reviewed recently.[1] Among the simpler techniques, the liquid nitrogen-organic solvent slush bath has become increasingly popular and a compilation of 86 such baths has been published by Rondeau.[2]

We have found it convenient to employ an even simpler bath composed of solid carbon dioxide and organic solvents or solvent mixtures having a freezing point above −78°C. Solid lumps of dry ice in a Dewar flask containing one of several solvent systems afford a bath of reasonably uniform temperature and low viscosity. Such a bath is not, of course, a system at equilibrium; a layer of solid solvent appears to form over the dry ice and a steady state is obtained with slow evolution of gaseous CO_2. The baths are generally reproducible to ±1°C if they are agitated intermittantly and if only a small excess of dry ice is used (e.g., 2–4 cc per 200 ml in a standard 265 ml (one pint) Dewar flask). Many of the solvents cited by Rondeau may be employed, although the bath temperature is not always the melting point of the solvent. Carbon tetrachloride (−23°C), 3-heptanone (−38°C), cyclohexanone (−46°C) and chloroform (−61°C) provide reproducible low viscosity baths at the temperature indicated.

Many solvents which have appropriate melting points may be unsatisfactory because they solidify, or become highly viscous at low temperatures (e.g., *n*-octane, alcohols) or are noxious. Certain solvents, however, when mixed in the right proportions provide a considerable range of stable bath temperatures together with low viscosity. Of especial interest to this laboratory has been the attainment of temperatures throughout the liquid range of ammonia (−78° to −33°C), and we have found that most of this range can be covered with mixtures of *ortho* and *meta*-xylene. Pure *o*-xylene is not useful since it forms a thick sludge at its melting point (−26°C) but mixtures of *o*- and *m*-xylene give low viscosity baths with an approximately linear temperature dependence on composition (see figure). Analytical grade acetonitrile gives a useful bath at −42°C, while temperatures between −42°C and −51°C are obtainable with acetonitrile containing 0–3% acrylonitrile. Technical grade acetonitrile was found to give a reproducible bath at −46°C. Some mixtures do not give baths in which the temperature varies normally with composition. Mixtures of 3-heptanone or cyclohexanone with acetone act as if they were acetone-dry ice baths containing the solidified higher-melting ketone. A similar result ensues for mixtures of *n*-octane and *iso*-octane.

Because of the simplicity of the technique, the easy availability of dry ice and its low cost, and the readiness with which a desired temperature may be obtained, the use of dry ice baths is worth consideration even where equipment for handling liquid nitrogen is available.

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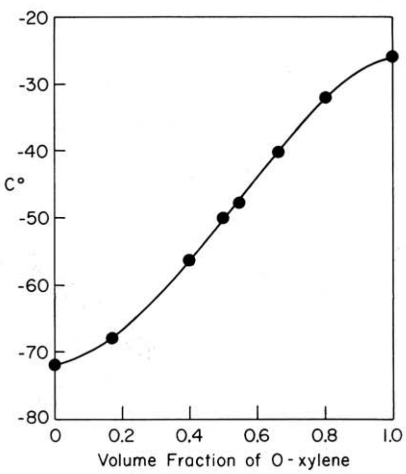

Steady state temperature of dry-ice—o-xylene, *m*-xylene mixtures.

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Slush Baths

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The preparation of constant temperature slush baths is described and 86 common slush baths are tabulated in order of decreasing temperature from 13° to −160° C. Some experimental applications of these cooling agents are also described.

THE ACCOMPANYING TABLE lists 86 common solvents and their slush bath temperatures in order of decreasing temperature from 13° to −160° C. A slush bath can be defined as a coolant consisting of a low melting liquid which has been partially frozen by mixing with liquid nitrogen. It is prepared by slowly pouring liquid nitrogen into a Dewar flask containing the solvent while continuously stirring the mixture until the desired consistency is obtained. When properly mixed, the consistency of the crystallized solvent is that of a fluid slush which will maintain a constant temperature as long as the bath is kept slushy by occasionally blending in more liquid nitrogen.

Rondeau and Harrah (*2*) made use of an ethyl bromide slush bath in measuring the melting point of 3-hexyne. The temperature rise of this particular slush was approximately 0.2° C. per minute when left standing at room temperature in an uncovered 47 × 125 mm. Dewar flask.

With certain solvents, such as diethylene glycol and some of the alcohols, a heavy sirup is formed. Although not as convenient to handle, a viscous bath is still useful for cooling purposes. The solvents in Table I that form a highly viscous coolant have been marked with an asterisk.

The temperatures listed in the table are given to the nearest degree centigrade. Measurements were made with a calibrated toluene thermometer for temperatures above −95° C. and with a calibrated pentane thermometer for readings below −95° C. All of the solvents used were reagent grade chemicals. In general, the purer the compound, the narrower its slush bath temperature range; however, the variation in temperature with purity has not been studied.

Slush baths are especially useful in degassing liquids and fractionating mixtures. Newton (*1*) has designed a low temperature reflux condenser in which the liquid can be refluxed under vacuum at a temperature where its vapor pressure is negligible. The method requires the use of a constant temperature cooling bath to maintain the desired temperature. The convenience of a table of slush bath temperatures in using such a technique is readily apparent.

Volatile mixtures can be separated in a vacuum system by fractional condensation through a series of three traps cooled to successively lower temperature. Here again, the judicious selection of the proper slush bath temperature determines the efficiency of the separation.

Table I. Materials for Low Temperature Slush Baths (with Liquid Nitrogen)

Solvent	Temp., ° C.	Solvent	Temp., ° C.
p-Xylene	13 ±1°	Ethyl acetate	−84
p-Dioxane	12	*n*-Hexyl bromide	−85
Cyclohexane	6	Methyl ethyl ketone	−86
Benzene	5	Acrolein	−88
Formamide	2	Amyl bromide	−88
Aniline	−6	*n*-Butanol [a]	−89
Diethylene glycol [a]	−10	*s*-Butanol [a]	−89
Cycloheptane	−12	Isopropyl alcohol [a]	−89
Methyl benzoate	−12	Nitroethane	−90
Benzonitrile	−13	Heptane	−91
Benzyl alcohol	−15	*n*-Propyl acetate	−92
Propargyl alcohol	−17	2-Nitropropane	−93
1,2-Dichlorobenzene	−18	Cyclopentane	−93
Tetrachloroethylene	−22	Ethyl benzene	−94
Carbon tetrachloride	−23	Hexane	−94
1,3-Dichlorobenzene	−25	Toluene	−95
Nitromethane	−29	Cumene	−97
o-Xylene	−29	Methanol	−98
Bromobenzene	−30	Methyl acetate	−98
Iodobenzene	−31	Isobutyl acetate	−99
m-Toluidine	−32	Amyl chloride	−99
Thiophene	−38	Butyraldehyde	−99
Acetonitrile	−41	Propyl iodide	−101
Pyridine	−42	Butyl iodide	−103
Benzyl bromide	−43	Cyclohexene	−104
Cyclohexyl chloride	−44	*s*-Butyl amine	−105
Chlorobenzene	−45	Isooctane	−107
m-Xylene	−47	1-Nitropropane	−108
n-Butyl amine	−50	Ethyl iodide	−109
Benzyl acetate	−52	Propyl bromide	−110
n-Octane	−56	Carbon disulfide	−110
Chloroform	−63	Butyl bromide	−112
Methyl iodide	−66	Ethyl alcohol [a]	−116
tert-Butyl amine	−68	Isoamyl alcohol [a]	−117
Trichloroethylene	−73	Ethyl bromide	−119
Isopropyl acetate	−73	Propyl chloride	−123
o-Cymene	−74	Butyl chloride	−123
p-Cymene	−74	Acetaldehyde	−124
Butyl acetate	−77	Methyl cyclohexane	−126
Isoamyl acetate	−79	*n*-Propanol [a]	−127
Acrylonitrile	−82	*n*-Pentane	−131
n-Hexyl chloride	−83	1,5-Hexadiene	−141
Propyl amine	−83	*iso*-Pentane	−160

[a] High viscosity slush.

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D. Salt-Ice Cooling Mixtures

This table lists salt/ice cooling mixtures that can be obtained by mixing the salt (at about room temperature) with water or ice at the specified temperature in the amount noted. In actual practice, these temperatures are often difficult to reach and may depend on rate of stirring and on how finely crushed the ice is.

Substance	Initial Temperature (°C)	g/100g H_2O	Final Temperature (°C)
Na_2CO_3	-1 (ice)	20	-2.0
NH_4NO_3	20	106	-4.0
$NaC_2H_3O_2$	10.7	85	-4.7
NH_4Cl	13.3	30	-5.1
$NaNO_3$	13.2	75	-5.3
$Na_2S_2O_3 \cdot 5H_2O$	10.7	110	-8.0
$CaCl_2 \cdot 6H_2O$	-1 (ice)	41	-9.0
KCl	0 (ice)	30	-10.9
KI	10.8	140	-11.7
NH_4NO_3	13.6	60	-13.6
NH_4Cl	-1 (ice)	25	-15.4
NH_4NO_3	-1 (ice)	45	-16.8
NH_4SCN	13.2	133	-18.0
NaCl	-1 (ice)	33	-21.3
$CaCl_2 \cdot 6H_2O$	0 (ice)	81	-21.5
H_2SO_4 (66.2%)	0 (ice)	23	-25
NaBr	0 (ice)	66	-28
H_2SO_4 (66.2%)	0 (ice)	40	-30
C_2H_5OH (4°)	0 (ice)	105	-30
$MgCl_2$	0 (ice)	85	-34
H_2SO_4 (66.2%)	0 (ice)	91	-37
$CaCl_2 \cdot 6H_2O$	0 (ice)	123	-40.3
$CaCl_2 \cdot 6H_2O$	0 (ice)	143	-55