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(5) Heat is transferred from the warm hand (system/surroundings) to the cold hand (surroundings/system). Cold hand: > 0, warm hand: < 0

1.3 Is the earth an isolated, closed, or open system?

Answer: The earth is an open system because energy and matter can be exchanged between earth and space.

2 State functions and the laws of thermodynamics

2.1 A triathlete performs 1000 kJ of work and loses 400 kJ of heat while swimming in cold water. How does the internal energy of the triathlete change? How much does the pool (50 m length, 20 m width, 2 m depth) warm up? C_p (H_2O) = 4.18 kJ kg^{-1} K^{-1}, ρ (H_2O) = 1 g cm^{-3}.

Answer: The work performed by the triathlete (system) on the surroundings is δw = -1000 kJ. The heat transferred from the triathlete (system) to the surroundings (water) is δq = -400 kJ. The overall change in internal energy is $\Delta U = \delta w + \delta q$ = -1400 kJ.

The pool volume is $V = 50 \cdot 20 \cdot 2$ m^3 = 2000 m^3 = $2 \cdot 10^9$ cm^3. This volume corresponds to a water mass of $m_{water} = 2 \cdot 10^6$ kg. The transfer of 1400 kJ leads to a temperature change ΔT of

$$\Delta T = \frac{\delta q}{C_p m_{water}} = \frac{400\ kJ \cdot kg \cdot K}{4.18\ kJ \cdot\ 2 \cdot 10^6 kg} = 4.8 \cdot 10^{-5}\ \mathrm{K}$$

2.2 Isothermal expansion of an ideal gas does not change its internal energy. What is the associated change in enthalpy?

Answer: The enthalpy is defined as $H = U + pV$. U is constant. pV is also constant (Boyle-Mariotte law), and the enthalpy does not change: H = const.

Biophysical Chemistry 1st edition Klostermeier Solutions Manual

2.3 During normal breathing, humans exchange about 0.5 L of air in their lungs. Calculate the amount of worked that is performed during one exhalation against atmospheric pressure. How many grams of ATP need to be hydrolyzed for breathing during a day (30 breath cycles per minute, $\Delta G^{0\prime}$ (ATP hydrolysis) = -31 kJ mol^{-1}, M = 507.18 g mol^{-1}). A 100 g bar of chocolate provides about 500 kJ of energy. How long does the energy last just for breathing?

Answer: The work per exhalation can be calculated as $w = -p\Delta V$ = -1.013·10^5 Pa·0.5·10^{-3} m^3 = -51 J. The number of exhalations per day is 30 min^{-1}·60·24 min = 43 200, which gives a total work for breathing per day of w = 43 200·51 J = -2188 kJ. To obtain 2188 kJ from ATP hydrolysis, n = -31 kJ mol^{-1}/-2188 kJ = 70.6 mol have to be hydrolyzed. 70.6 mol correspond to a mass m = 507.18 g mol^{-1} / 70.6 mol ≈ 35.8·10^3 g = 35.8 kg ATP.

The energy in a bar of chocolate supports 500 kJ/51 J = 9872 breathing cycles. 9872 breath cycles correspond to 9872/30 min^{-1} ≈ 329 min = 5h 29 min.

2.4 A diver grabs a bottle of compressed air. The pressure gauge states p = 200·10^5 Pa (200 bar). Just after the descent into the dive, the pressure is reduced to 190·10^5 Pa. Why? The diver has directly descended to 30 m depth. What are the pressure and the temperature of the surrounding water? $T_{air,surface}$ = 30°C.

Answer: The initial pressure decrease is too large to be caused by the few breaths the diver has taken. The temperature of the water is lower than the temperature at the surface, and the pressure decreases proportionally to the temperature (2nd law of Gay-Lussac).

The pressure at 30 m is 1.013·10^5 Pa from the air and 1.013·10^5 Pa per 10 m of water column, which gives p_{tot} = 4.052·10^5 Pa. The water temperature can be calculated from the change in gas pressure according to the 2nd law of Gay-Lussac as

$$T_{water,30\,m} = T_{air,surface} \cdot \frac{190 \cdot 10^5 Pa}{200 \cdot 10^5 Pa} = 0.95 \cdot T_{air,surface} = 288.0\,K = 14.8°C$$

Biophysical Chemistry 1st edition Klostermeier Solutions Manual

2.5 The diver breathes enriched air that contains 32% (m/m_{tot}) oxygen and 68% (m/m_{tot}) nitrogen (at $p = p^0 = 10^5$ Pa and $T = T_0 = 25$°C). A partial oxygen pressure of > 1.6 10^5 Pa is lethal for humans. Is it safe for the diver to dive down to the sea bed at 40 m? The diver starts with a 15 L tank of enriched air at $p = p^0$. The air needed during descent and ascent can be neglected. How long can the diver stay at 45 m with his air supply for 0.5 L breathing volume and 30 breathing cycles min^{-1}?

Answer: 1000 g of air contain 320 g oxygen and 680 g nitrogen. From the molar masses $M(O_2) = 32$ g mol^{-1} for and $M(N_2) = 28$ g mol^{-1}, we obtain the amount of oxygen and nitrogen as $n(O_2) = 320$ g / 32 g $mol^{-1} = 10 \cdot$mol, and $n(N_2) = 680$ g / 28 g $mol^{-1} = 24.3$ mol. The mole fractions are $x(O_2) = n(O_2)/n_{tot} = 0.29$ and $x(N_2) = 0.71$.

From Raoult's law, the partial pressures can be calculated as $p(O_2) = x(O_2) \cdot p = 0.29 \cdot 10^5$ Pa and $p(N_2) = 0.71 \cdot 10^5$ Pa under standard conditions. $p(O_2)$ exceeds 1.6 10^5 Pa at a pressure of $p = p_{lethal}(O_2)/x(O_2) = 1.6\ 10^5$ Pa/0.29 = 5.5 10^5 Pa, which corresponds to environmental pressure below 40 m. Hence, it is safe for the diver to descend to the sea bed.

The 15 L of gas at $200 \cdot 10^5$ Pa correspond to 592 L at $5.065 \cdot 10^5$ Pa, the environmental pressure at 40 m depth. 592 L are sufficient for 1184 breath cycles, or 39.5 min.

2.6 On a winter day (T = -10°C) you adjust the pressure of your car tires to $1.8 \cdot 10^5$ Pa. What is the pressure in summer (T = 30°C)?

Answer: We assume the volume of the tires as constant. The final pressure is

$$p_{final} = p_{initial} \cdot \frac{T_{final}}{T_{initial}} = 1.8 \cdot 10^5\ Pa \cdot \frac{303.15\ K}{263.15\ K} = 2.1 \cdot 10^5\ Pa$$

2.7 The enthalpy change for the reaction of glucose ($C_6H_{12}O_6$) to CO_2 and H_2O is -2800 kJ mol^{-1}, for the reaction of ethanol to water it is -1370 kJ mol^{-1}. What is the enthalpy change during fermentation of glucose to ethanol? Is fermentation a useful metabolic pathway?

Answer: The reaction schemes are

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(1) $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ H_2O + 6\ CO_2$ $\Delta H^0_1 = -2800$ kJ mol^{-1}

(2) $C_2H_5OH + 3\ O_2 \rightarrow 3\ H_2O + 2\ CO_2$ $\Delta H^0_2 = -1370$ kJ mol^{-1}

(3) $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$

We can express the reaction scheme (3) as (1)-2·(2) and calculate ΔH^0_3 from the Hess law: $\Delta H^0_3 = (\Delta H^0_1 - 2\Delta H^0_2 = -2800$ kJ mol^{-1} - 2·(-1370 kJ mol^{-1}) = -60 kJ mol^{-1}. Fermentation thus only provides the organism with a small fraction of the energy compared to the complete oxidation to CO_2 and H_2O.

2.8 The heat capacity of water ($C_p = 75$ J mol^{-1} K^{-1}) is much higher than the heat capacity of air ($C_p = 20$ J mol^{-1} K^{-1}). Calculate the temperature change when 10 kJ of heat is transferred to 1 m^3 of water or air. $\rho(H_2O) = 1$ g cm^{-3}; ρ(air) = 1.2 mg cm^{-3}.

Answer: 1 m^3 = 10^6 cm^3 water corresponds to 10^6 g water = 10^6 g/18 g mol^{-1} = 55.5·10^3 mol. The mean molar mass of air is M_{air} = (0.21·32 + 0.79·28) g mol^{-1} = 28.84 g mol^{-1}. 1 m^3 = 10^6 cm^3 of air corresponds to 1.2·10^3 g air or 1.2·10^3 g/28.84 g mol^{-1} = 41.6 mol. The temperature change of water is

$$\Delta T_{H_2O} = \frac{\delta q}{C_p} = \frac{10\ kJ \cdot mol \cdot K}{75\ J \cdot\ 55.5 \cdot 10^3\ mol} = 2.4 \cdot 10^{-3}\ \mathrm{K}$$

For air, the temperature change is

$$\Delta T_{air} = \frac{\delta q}{C_p} = \frac{10\ kJ \cdot mol \cdot K}{20\ J \cdot\ 41.6\ mol} = 12\ \mathrm{K}$$

2.9 Calculate the change in entropy for the conversion of 1 mol ice (H_2O(s), 0°C) into vapor (H_2O(g), 100°C) at constant pressure. Sublimation enthalpy $\Delta H_{subl} = 47$ kJ mol^{-1}, vaporization enthalpy $\Delta H_{vap} = 41$ kJ mol^{-1}, $C_p = 75$ J mol^{-1} K^{-1}.

Answer: The melting enthalpy can be calculated from the Hess law as ΔH_{melt}: $\Delta H_{melt} = \Delta H_{sub} - \Delta H_{vap} = 6$ kJ mol^{-1}. The entropy change during melting is $\Delta S_{melt} = \Delta H_{melt}/T = 6$ kJ mol^{-1}/273.15 K = 22.0 J mol^{-1} K^{-1}. The entropy change during heating from 0°C

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to 100°C is $dS = C_p/T \cdot dT$. By integration, we obtain $\Delta S_{heat} = C_p \ln(373.15\ K/273.15\ K) = 23.4\ kJ\ mol^{-1}\ K^{-1}$. The entropy change during evaporation is $\Delta S_{vap} = \Delta H_{vap}/T = 41\ kJ\ mol^{-1}/373.15\ K = 110\ J\ mol^{-1}\ K^{-1}$. The sum of these entropy changes is ΔS_{tot} (1 mol) = 155 J mol^{-1} K^{-1}.

2.10 Calculate the entropy change when 200 kJ of heat are transferred to water at 0°C and 100°C (isothermal conditions). Explain the difference from the statistical interpretation of entropy.

Answer: The entropy change at 0°C is ΔS (0°C) = 200 kJ / 273.15 K = 732 J K^{-1}, the entropy change at 100°C is ΔS(100°C) = 200 kJ / 373.15 K = 536 J K^{-1}. At 373.15 K, the disorder of water is higher than at 273.15 K. Therefore, adding the same amount of heat produces less additional disorder at higher temperature.

2.11 Our metabolism generates heat of about 100 J s^{-1}. Calculate the change in entropy of the surrounding per hour at 25°C.

Answer: 1 h corresponds to 3600 s. The transferred heat is q = 100 J s^{-1}·3600 s = 3.6·10^5 J. The associated change in entropy is

$$\Delta S = \frac{q}{T} = \frac{3.6 \cdot 10^5\ J}{298.15\ K} = 1.2\ kJ\ K^{-1}$$

2.12 0.1 mol of a reactant react to products in an isobaric reaction at 25°C and 10^5 Pa. During the reaction, 20 kJ of heat are transferred to the surroundings. Calculate ΔG^0, ΔH^0, and ΔS^0 for this process.

Answer: The heat released is q = 200 kJ mol^{-1} at standard pressure and temperature. ΔH is the heat exchanged at constant pressure. The heat is released from the system, and is therefore negative:

$$\Delta H = \Delta H^0 = -200\ kJ\ mol^{-1}$$

ΔS is the exchanged heat (under reversible conditions) divided by the temperature:

$$\Delta S = \Delta S^0 = \frac{-200\ kJ\ mol^{-1}}{298.15\ K} = -671\ J\ mol^{-1}\ K^{-1}$$

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From the Gibbs-Helmholtz equation, we obtain

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 = 0\ kJ\ mol^{-1}$$

2.13 Calculate the reaction enthalpy, entropy, and free energy, ΔH^0_r, ΔS^0_r, and ΔG^0_r, for the amidation of glutamate to glutamine (1) at standard temperature, (2) at 37°C, and (3) at 75°C (a) taking into account the temperature dependence of ΔH and ΔS, and (b) assuming that ΔH and ΔS are temperature-independent. What can you conclude about the importance of C_p? What does the result mean for organisms that live at moderate temperature (37°C; mesophilic organisms) and thermophilic organisms that live at 75°C?

Glutamine: ΔH^0_f = -826 kJ mol^{-1}, $C_{p,m}$ = 184 J mol^{-1} K^{-1}, S_m = 195 J mol^{-1} K^{-1}

Glutamate: ΔH^0_f = -1010 kJ mol^{-1}, $C_{p,m}$ = 175 J mol^{-1} K^{-1}, S_m = 188 J mol^{-1} K^{-1}

H_2O: ΔH^0_f = -290 kJ mol^{-1}, $C_{p,m}$ = 75 J mol^{-1} K^{-1}, S_m = 70 J mol^{-1} K^{-1}

NH_4^+: ΔH^0_f = -133 kJ mol^{-1}, $C_{p,m}$ = 80 J mol^{-1} K^{-1}, S_m = 113 J mol^{-1} K^{-1}

Answer: The reaction scheme is

glutamate + NH_4^+ → glutamine + H_2O

Under standard conditions, we can calculate the reaction enthalpy, entropy, and free energy as well as the change in heat capacity as

$$\Delta H^0_r = \sum \Delta H^0_f(products) - \sum \Delta H^0_f(reactants) = +27\ kJ\ mol^{-1}$$

$$\Delta S^0_r = \sum \Delta S_m(products) - \sum \Delta S_m(reactants) = -36\ J\ mol^{-1}\ K^{-1}$$

$$\Delta C^0_p = \sum C_p\ (products) - \sum C_p\ (reactants) = -4\ J\ mol^{-1}\ K^{-1}$$

$$\Delta G^0_r = \Delta H^0_r - T\Delta S^0_r = +37.7\ kJ\ mol^{-1}$$

For temperature-dependent ΔH and ΔS, we use Kirchhoff's law

$$\Delta H_R(T) = \Delta H^0 + \Delta C_p(T - T_0)$$

and obtain ΔH_r (310.15 K) = 27.0 kJ mol^{-1}, ΔH_r (348.15 K) = 27.2 kJ mol^{-1}. The temperature-dependent change in entropy is

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$$\Delta S_R(T) = \Delta S^0 + \Delta C_p ln \frac{T}{T_0}$$

which gives ΔS_r (310.15 K) = -35.8 J mol^{-1} K^{-1}, ΔS_r (348.15 K) = -35.4 J mol^{-1} K^{-1}. From the Gibbs-Helmholtz equation, $\Delta G_r = \Delta H_r - T \cdot \Delta S_r$, we obtain ΔG_r (310.15 K) = 38.2 kJ mol^{-1}, ΔG_r (348.15 K) = 39.5 kJ mol^{-1}.

For temperature-independent ΔH and ΔS, $\Delta H_r = \Delta H^0_r$ and $\Delta S_r = \Delta S^0_r$. The change in free energy is again calculated from the Gibbs-Helmholtz equation: ΔG_r (310.15 K) = 38.2 kJ mol^{-1}, and ΔG_r (348.15 K) = 39.5 kJ mol^{-1}.

Changes in heat capacity during chemical reactions are often very small, and the temperature-dependence of ΔH, ΔS, and ΔG is also small. Thermophilic organisms therefore do not necessarily face special energetic challenges.

2.14 The energy of one photon is $E = h \cdot \nu = hc/\lambda$. How many photons of light with λ = 680 nm have to be absorbed to synthesize an ATP molecule (degree of efficiency 100%)? In what wavelength range is one photon sufficient for the synthesis of two ATP molecules? $\Delta G^{0\prime}$ of ATP synthesis: -31 kJ mol^{-1}.

Answer: The energy of one photon is $E = hc/\lambda$ = 6.626·10^{-34} J s·3·10^8 m s^{-1}/680·10^{-9} m = 2.92·10^{-19} J.

The energy required for synthesis of one molecule of ATP is 31 kJ mol^{-1}/N_A = 1.93·10^{-19} J. Absorption of one photon of 680 nm is sufficient for synthesis of one molecule of ATP.

For the synthesis of two ATP molecules, 3.87·10^{-19} J is required. $E = hc/\lambda > 3.87 \cdot 10^{-19}$ J gives λ < 514 nm.

Biophysical Chemistry 1st edition Klostermeier Solutions Manual

2.15 Protein-protein interactions reduce the number of particles from two to one, which corresponds to a decrease in entropy. Why can the interaction nevertheless be entropically favorable and under what conditions?

Answer: Water is excluded from the area that is covered upon complex formation. This release of water is associated with an increase in entropy that is often larger than the loss of entropy due to the association of the two proteins. The effect is larger for hydrophobic than for hydrophilic interfaces.

2.16 How much does an ionic interaction between two oppositely charged side chains contribute to protein stability at the surface and in the interior of the protein?

Answer: In both cases, the two side chains are flexible and interact with water molecules in the unfolded state. In the folded state, the charged side chains in the hydrophobic interior of the protein are conformationally restricted. Further restriction of the side chains in a salt bridge only causes a small extra loss of entropy (slightly unfavorable). The water molecules bound to the side chains in the unfolded state are released upon folding, associated with an increase in entropy (favorable). The electrostatic interaction is associated with a decrease in enthalpy (favorable), but interactions with water are lost (slightly unfavorable). Overall, formation of the salt bridge in the interior is energetically favorable. The charged side chains that remain on the surface are not conformationally restricted, and formation of the salt bridge is entropically unfavorable. Furthermore, these side chains can still interact with water in the folded state, and the entropy increase and enthalpy decrease due to water release is small. As a consequence, the contribution of the salt bridge on the surface to protein stability is small.

Biophysical Chemistry 1st edition Klostermeier Solutions Manual

2.17 You mix 10 mL glycerol and 90 mL water to obtain a 10% glycerol solution. The density of the mixture is ρ_{mix} = 1.02567 g cm^{-3}. What are the mole fraction of glycerol and the volume of the mixture? What is the reason for the volume change? What can you conclude for the necessity to take volume changes into account when stabilizing proteins by using 10% glycerol buffers? *M*(glycerol) = 92.09 g mol^{-1}, *M*(H_2O) = 18 g mol^{-1}, ρ(glycerol) = 1.25802 g cm^{-3}, ρ(H_2O) = 0.99708 g cm^{-3}.

Answer: 10 mL of glycerol correspond to 10 cm^3. The mass is m = ρ(glycerol)·V(glycerol) = 92.09 g cm^{-3}·10 cm^3 = 12.5802 g. 12.5802 g are *n* = 12.6 g / 92.09 g mol^{-1} = 0.1366 mol. For water, the volume is *V* = 90 cm^3, the mass is *m* = 89.7372 g, and the amount is *n* = 4.9854 mol. The mole fraction of glycerol is

$$x(glycerol) = \frac{n(glycerol)}{n(glycerol) + n(H_2O)} = 0.0267$$

The volume of the mixture is $V_{mix} = m_{tot}/\rho_{mix}$ = 102.3174 g / 1.02567 g cm^{-3} = 99.76 cm^3 = 99.76 mL. It is smaller because the partial molar volumes of water and glycerol are smaller than their molar volumes. However, the volume reduction is 0.24/100 = 0.24%, and can be neglected.

2.18 Calculate the difference between and μ^0 and $\mu^{0\prime}$ for protons in aqueous solutions.

Answer: The chemical potential is a state function. Its value must therefore be independent of the reference state. With the reference state 1 M (solute), the chemical potential is

$$\mu_I(H^+) = \mu^0(H^+) + RTln\left(\frac{c}{1M}\right)$$

With the reference state pH 7 (10^{-7} M), the chemical potential is

$$\mu_{II}(H^+) = \mu^0(H^+) + RTln\left(\frac{c}{10^{-7}M}\right)$$

The difference is

$$\mu_I(H^+) - \mu_{II}(H^+) = RTln\left(\frac{c}{1M}\right) - RTln\left(\frac{c}{10^{-7}M}\right) = RTln\left(\frac{10^{-7}M}{1M}\right) = 40\ kJ\ mol^{-1}$$

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2.19 Is mixing of two liquids to an ideal solution a spontaneous process?

Answer: Compare the free energy *G* of the individual, unmixed components and of the mixture.

G before mixing is

$$G_{unmixed} = n_A\mu_A^* + n_B\mu_B^*$$

(* for pure component). The free energy of the mixture is

$$G_{mixture} = n_A\mu_A + n_B\mu_B = n_A(\mu_A^* + RTlnx_A) + n_B(\mu_B^* + RTlnx_B)$$

The difference is

$$\Delta G_{mix} = G_{mixture} - G_{unmixed} = RT(n_A lnx_A + n_B lnx_B) = nRT(x_A lnx_A + x_B lnx_B)$$

with $n_A = x_A \cdot n$ and $n_B = x_B \cdot n$. Both mole fractions are smaller than unity, $x_A < 1$, $x_B < 1$, hence the logarithmic terms are both negative. ΔG is therefore negative for all mixing ratios of A and B, and mixing is a spontaneous process.

2.20 A polysaccharide solution ($c(PS) = 10$ g L^{-1} in H_2O) has an osmotic pressure of $5 \cdot 10^3$ N m^{-2}. What is the molar mass of the polysaccharide? What is the vapor pressure of the solution compared to pure water?

Answer: The osmotic pressure is $\pi = cRT$ with $c = n/V$ = and $n = m/M$. By combining these equations and converting the concentration $c = 10$ g $L^{-1} = 10\,000$ g m^{-3} we obtain

$$m_m(PS) = \frac{RT}{p} \cdot \frac{m}{V} = 4957\ g\ mol^{-1}$$

The vapor pressure of the solvent in the ideal solution is

$$p(H_2O) = x_{H_2O} \cdot p_{H_2O}^*$$

(Raoult's law). The mole fraction of the polysaccharide is

$$x(PS) = \frac{n(PS)}{n(PS) + n(H_2O)}$$

For a dilute (ideal) solution, we can approximate

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$$x(PS) \approx \frac{n(PS)}{n(H_2O)} = \frac{2.02\ \text{mmol}}{55.5\ \text{mol}} = 3.63 \cdot 10^{-5}$$

The mole fraction of water is $x_{H2O} = 1 - x_{PS} = 0.9999637$. Hence, the vapor pressure is reduced by 0.00363% = 0.0363‰.

2.21 Giant sequoia trees reach a height of more than 100 m. They have to transport water into the top of their crown. Can this be explained by the osmotic pressure due to the solutes in the cytoplasm? $\rho(H_2O) = 1\ \text{g cm}^{-3}$.

Answer: We can formulate the equilibrium between upward osmotic pressure and downward pressure due to gravitation as $\pi = cRT = \rho gh$. With the water density $\rho = 1\ \text{g cm}^{-3}$, we obtain $c = \rho gh/RT = 0.4$ mM, which is rather high. In fact, capillary forces provide the driving force for transport.

2.22 What concentration of NaCl is required to prevent ice formation at $T = -1$°C and at $T = -5$°C? ΔH_{melt} (H_2O) = 6 kJ mol^{-1}. The solubility of NaCl in H_2O is 359 g L^{-1}, the molar mass M is 58.44 g mol^{-1}. What is the maximum reduction in freezing point that can be achieved by a saturated NaCl solution?

Answer: From

$$\Delta T = x_B \frac{RT_{melt}^2}{\Delta H_{melt}}$$

we obtain $x_B = 0.009$ for -1°C and $x_B = 0.048$ for -5°C. With the approximation that $n_B << n(H_2O)$, this corresponds to a 0.5 M NaCl solution to prevent ice formation at -1°C, while at -5°C, a 2.68 M solution is required. A saturated solution with 359 g L^{-1} has a concentration of $c = 359\ \text{g L}^{-1} / 58.44\ \text{g mol}^{-1} = 6.14$ M. With the approximation that $n_B << n(H_2O)$, this corresponds to a mole fraction of $x_B \approx 6.14\ \text{M} / 55.5\ \text{M} = 0.11$. The maximum decrease in freezing temperature is $\Delta T = -11.4$°C.

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