

- Starting with the First Law, derive the useful entropy equations for ideal gases:
 - $dS = (C_V/T)dT + (nR/V)dV$
 - $dS = (C_P/T)dT - (nR/p)dp$
- Can the equations developed in the preceding question be used to calculate entropy changes for irreversible processes? Explain.
- 1.00 mol of He gas (assumed to be ideal) initially at 400 K expands from 1.15 L to 4.65 L. Calculate q , w , ΔU , ΔH , and ΔS if the expansion is performed adiabatically and reversibly.
- 1.00 mol of He gas (assumed to be ideal) initially at 400 K expands adiabatically from 1.15 L to 4.65 L. 1000 J of work is done on the surroundings ($w = -1000$ J). Is the expansion reversible? Justify your answer.
- Assuming that CO₂ is an ideal gas, calculate ΔU , ΔH and ΔS for the process

$$1.00 \text{ mol CO}_2 (\text{g}, 298.15 \text{ K}, 1 \text{ bar}) \rightarrow 1.00 \text{ mol CO}_2 (\text{g}, 1000.0 \text{ K}, 1 \text{ bar})$$

Data: $C_{pm}^\circ(\text{CO}_2, \text{g}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 26.648 + (0.042262 \text{ K}^{-1})T - (0.00001425 \text{ K}^{-2})T^2$
- One mole of water is vaporized reversibly at 100 °C and 1.01325 bar. The enthalpy of vaporization is 40.69 kJ mol⁻¹.
 - What is ΔS for the water?
 - What is ΔS for the surroundings?
- Two blocks of the same material of identical mass but different initial temperatures (T_A and T_B) are brought into thermal contact and reach the same final temperature. Volume changes and heat losses to the surroundings are negligible.
 - Show that the entropy change for the process is

$$\Delta S = C_V \ln \left(\frac{(T_A + T_B)^2}{4T_A T_B} \right)$$
 - How does this equation demonstrate the important result that internal heat flow from high to low temperature in an isolated system is a spontaneous process?

... page 2

8. Science students (and most Canadians) know that liquid water is unstable below 0 °C and spontaneously freezes, forming ice. But why are ice and liquid water in equilibrium *only at 0 °C*, not over a range of temperatures, such as liquid/solid slush mixtures from say 0 °C to – 20 °C?

a) The freezing point of water is 0.00 °C (273.15 K) at 1 bar. Calculate ΔH and ΔS for freezing one mole of liquid water at 0.00 °C and 1 bar. Explain why this process is **reversible**.

b) Water (and many other liquids) can be “supercooled” below the freezing point. Calculate ΔH and ΔS for freezing one mole of supercooled liquid water at –10.00 °C (263.15 K) and 1 bar. Use the Second Law to prove that this process is **spontaneous**.

Data for water at 0.00 °C and 1 bar:

$$\begin{aligned} \Delta H_{\text{fusion,m}}^{\circ} &= 6009 \text{ J mol}^{-1} \\ C_{\text{pm}}^{\circ}(\text{H}_2\text{O}, l) &= 75.99 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_{\text{pm}}^{\circ}(\text{H}_2\text{O}, s) &= 36.93 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Repeating these calculations (*not required here!*) shows that freezing liquid water at 1 bar is spontaneous at any temperature below 0 °C. This result helps to explain the “sharpness” of freezing points – a single temperature at a given pressure for a pure substance.

9. Your instructor refuses to give up trying to convince you that partial derivatives are interesting, important, easy to understand, and incredibly useful.

In this question, partial derivatives are used to develop the principle of **least-squares** (also called **regression**, **curve fitting**, or **line of best fit**), a powerful technique for the analysis of experimental data widely available in computer software packages, even MicroSoft Excel.

Suppose the following set of $N = 5$ data points is represented by the linear function

$$f(x) = a_0 + a_1x$$

x_i	$f(x_i)_{\text{measured}}$
0.0	0.11
0.9	0.79
1.7	1.79
2.5	2.62
3.9	3.85

with intercept a_0 and slope a_1 . How can a_0 and a_1 be calculated from the data? Problem! There are five data points, but only two unknowns. Mathematically, the system of equations is “overdetermined”.

According to statistics, the “best” values of a_0 and a_1 are evaluated by minimizing the variance S defined as the sum of the squared deviations between the measured $f(x_i)_{\text{measured}}$ and the calculated $f(x_i)_{\text{calculated}} = a_0 + a_1x_i$ values.

$$S = \sum_{i=1}^N [f(x_i)_{\text{measured}} - a_0 - a_1x_i]^2$$

At the minimum in S : $(\partial S / \partial a_0)_{a_1} = 0$ and $(\partial S / \partial a_1)_{a_0} = 0$. Use these two partial derivatives to derive the linear regression equations for the slope and intercept. Calculate a_0 and a_1 for the five data points.

if reversible: $dq_{rev} = TdS$
 ($P_{ext} = P$) $dw = -pdV$

1. a) $S(T, V)$ for an ideal gas:

$dU = dq + dw$ (First Law) $\rightarrow dU = C_v dT$
 (U depends only on T)

$C_v dT = TdS - pdV$ (ideal gas, reversible process)

$TdS = C_v dT + pdV$

$\frac{P}{T} = \frac{nR}{V}$

$dS = \frac{C_v}{T} dT + \frac{P}{T} dV = \boxed{\frac{C_v}{T} dT + \frac{nR}{V} dV}$

b) $S(T, P)$ for an ideal gas:

start:

$dU = dq + dw$

$dU = C_v dT$

$C_p = C_v + nR$

$C_v dT = TdS - pdV$

add $nRdT$ to both sides

(why? there is $C_p dT$ in the equation we are asked to derive)

$(C_v + nR)dT = TdS - pdV + nRdT$

$C_p dT = TdS - pdV + nRdT$
 $+ vdp$

$C_p dT = TdS + vdp$

$dS = \frac{C_p}{T} dT - \frac{v}{T} dp$

ideal gas:
 $pV = nRT$
 $d(pV) = d(nRT)$
 $pdV + Vdp = nRdT$
 $Vdp = -pdV + nRdT$

$\frac{v}{T} = \frac{nR}{P}$

$dS = \boxed{\frac{C_p}{T} dT - \frac{nR}{P} dp}$

(1 b cont.)

$$\begin{aligned} \text{or // Use } d(\overbrace{U + pV}^{\equiv H}) &= dU + pdV + Vdp \\ &= TdS - pdV + pdV + Vdp \\ &= TdS + Vdp \end{aligned}$$

$$dH = C_p dT \text{ (ideal gas)}$$

$$C_p dT = TdS + Vdp \text{ (ideal gas)}$$

$$dS = \frac{C_p}{T} dT - \frac{V}{T} dp = \boxed{\frac{C_p}{T} dT - \frac{nR}{P} dp}$$

(2) S is a state function: $\Delta S = S_f - S_i$ (path independent)

$$dS = \frac{C_v}{T} dT + \frac{nR}{V} dV = \frac{C_p}{T} dT - \frac{nR}{P} dp \quad \text{derived for a convenient reversible path}$$

can be used to calculate ΔS for any process involving ideal gases, reversible or irreversible path

(3) 1 mol He(g) $\xrightarrow{\text{rev. adiabatic}}$ 1 mol He(g)
400K, 1.15 L (T_i, V_i) $T_f?, 4.65 \text{ L}$ (V_f) He: $C_{m} = \frac{3}{2} R$

$$\boxed{q_r = 0} \text{ (adiabatic)} \quad \Delta S = \int \frac{dq_{rev}}{T} \quad \boxed{\Delta S = 0}$$

$$dS = 0 = \frac{C_v}{T} dT + \frac{nR}{V} dV \Rightarrow \int_{T_i}^{T_f} \frac{C_v}{T} dT = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\frac{3}{2} nR \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V} \Rightarrow \frac{3}{2} \ln \left(\frac{T_f}{T_i} \right) = - \ln \left(\frac{V_f}{V_i} \right)$$

$$\ln \left(\frac{T_f}{T_i} \right) = -\frac{2}{3} \ln \left(\frac{V_f}{V_i} \right) = -\frac{2}{3} \ln \left(\frac{4.65 \text{ L}}{1.15 \text{ L}} \right) = -0.931$$

(3 cont.)

$$\frac{T_f}{T_i} = e^{-0.931} = 0.394 \quad T_f = 0.394(400\text{K}) = 157.6\text{ K}$$

$$\Delta U = \int C_v dT = \int n C_{vm} dT = n \frac{3}{2} R (T_f - T_i)$$

$$\Delta U = (1.00 \text{ mol}) 1.5 (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (157.6 - 400) \text{ K}$$

$$\Delta U = -3023 \text{ J} = q + w = 0 + w$$

$$w = -3023 \text{ J}$$

$$\Delta H = \int n C_{pm} dT = n (C_{vm} + R) dT = n \frac{5}{2} R (T_f - T_i)$$

$$\Delta H = -5038 \text{ J}$$

4. 1 mol He (g) $\xrightarrow{\text{adiabatic}}$ 1 mol He (g) (Reversible?
If so, then
 $\Delta S = 0$)
400 K, 1.15 L $T_f?$, 0.5 L

$$\Delta U = w + q \xrightarrow{0} = w = \int n C_{vm} dT = n \frac{3}{2} R \int dT$$

$$w = -1000 \text{ J} = n \frac{3}{2} R (T_f - T_i)$$

$$T_f = \frac{2}{3nR} w + T_i = \frac{2(-1000 \text{ J})}{3(1 \text{ mol}) 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} + 400 \text{ K}$$

$$T_f = -80.2 \text{ K} + 400 \text{ K} = 319.8 \text{ K} \quad C_v = n C_{vm} = n \frac{3}{2} R$$

$$dS = \frac{C_v dT}{T} + \frac{nR}{V} dV \quad \Delta S = \int \frac{C_v dT}{T} + \int \frac{nR}{V} dV = n \frac{3}{2} R \left(\frac{dT}{T} + \frac{dV}{V} \right)$$

$$\Delta S = nR \left[\frac{3}{2} \left(\frac{dT}{T} + \frac{dV}{V} \right) \right] = nR \left[\frac{3}{2} \ln \left(\frac{319.8}{400} \right) + \ln \left(\frac{0.5}{1.15} \right) \right] = nR [-0.336 + 1.397] \neq 0 \therefore \text{not reversible}$$

5.

molar heat capacity at constant pressure for $\text{CO}_2(\text{g})$:

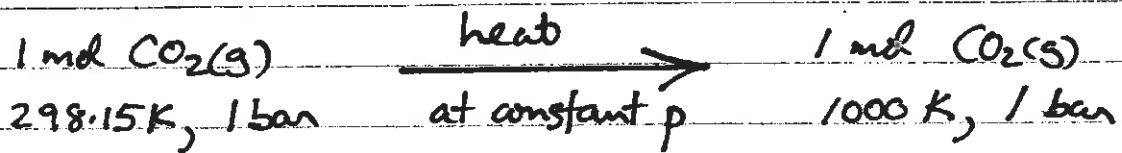
$$C_{p,m}^{\circ} / (\text{J K}^{-1} \text{mol}^{-1}) = A_0 + A_1 T + A_2 T^2$$

(quadratic in T)

$$A_0 = 26.648 \text{ J K}^{-1} \text{mol}^{-1}$$

$$A_1 = 0.042262 \text{ J K}^{-2} \text{mol}^{-1}$$

$$A_2 = -0.0001425 \text{ J K}^{-3} \text{mol}^{-1}$$

at constant pressure, recall $dq_p = dH_p$

also, $C_p = \frac{dq_p}{dT}$, leading to

$$q_p = \Delta H_p = \int_{T_i}^{T_f} dq_p = \int_{T_i}^{T_f} C_p dT = \int_{T_i}^{T_f} n C_{p,m} dT$$

$$= n \int_{T_i}^{T_f} (A_0 + A_1 T + A_2 T^2) dT$$

$$= n A_0 \int_{T_i}^{T_f} dT + n A_1 \int_{T_i}^{T_f} T dT + n A_2 \int_{T_i}^{T_f} T^2 dT$$

$$= n A_0 T \Big|_{T_i}^{T_f} + n A_1 \frac{T^2}{2} \Big|_{T_i}^{T_f} + n A_2 \frac{T^3}{3} \Big|_{T_i}^{T_f}$$

$$q_p = n \left[A_0 (T_f - T_i) + \frac{A_1}{2} (T_f^2 - T_i^2) + \frac{A_2}{3} (T_f^3 - T_i^3) \right]$$

$$= (1 \text{ mol}) \left[26.648 (1000 - 298.15) + \frac{0.042262}{2} (1000^2 - 298.15^2) - \frac{0.0001425}{3} (1000^3 - 298.15^3) \right]$$

$$q = \Delta H = (18703 + 19252 - 4624) \text{ J} = 33330 \text{ J} = 33.33 \text{ kJ}$$

important: C_p and $C_{p,m}$ are not constant here, due to increasingly active CO_2 vibrations as T increases

$A_0 + A_1 T + A_2 T^2$
here

can't take $C_{p,m}$ outside the integration
Sign - $C_{p,m}$ is not constant

(5. cont.)

$$q = \Delta H = 33330 \text{ J}$$

work w for heating 1 mol $\text{CO}_2(\text{g})$ from 298.15K to 1000K at 1 bar constant pressure: (easy!)

$$w = - \int p_{\text{ext}} dV = - p \int dV \quad (p \text{ constant}) \quad (p_f = p_i)$$

$$= -p(V_f - V_i) = -\left(\frac{pV_f}{p} - \frac{p_i V_i}{p_i}\right) = -\left(nRT_f - nRT_i\right)$$

$$= -nR(T_f - T_i) = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{K mol}}\right) (1000 - 298.15) \text{K}$$

$$w = -5835 \text{ J}$$

why negative? because the system is pushing back the surroundings, doing work on the surroundings and losing energy

$$\Delta U = q + w = (33330 - 5835) \text{ J}$$

$$\Delta U = 27495 \text{ J}$$

to calculate ΔS , take a convenient reversible path:

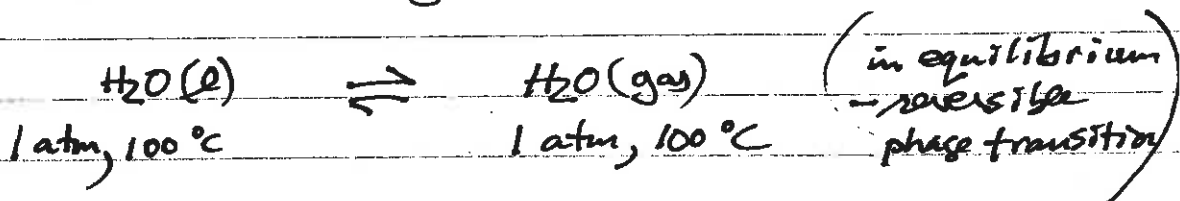
$$\begin{aligned} \Delta S &= \int_{T_i}^{T_f} \frac{dq_{\text{rev}}}{T} = \int_{T_i}^{T_f} \frac{C_p}{T} dT = n \int_{T_i}^{T_f} \frac{C_{pm}}{T} dT \\ &= n \int_{T_i}^{T_f} \left(\frac{A_0 + A_1 T + A_2 T^2}{T} \right) dT = n \left[A_0 \int \frac{dT}{T} + A_1 \int dT + A_2 \int T dT \right] \end{aligned}$$

$$\Delta S = n \left[A_0 \ln \left(\frac{T_f}{T_i} \right) + A_1 (T_f - T_i) + \frac{A_2}{2} (T_f^2 - T_i^2) \right]$$

$$= (1) \left[26.648 \ln \left(\frac{1000}{298.15} \right) + 0.042262 (1000 - 298.15) + \frac{0.0001425}{2} (1000^2 - 298.15^2) \right]$$

$$= (32.248 + 29.662 - 6.492) \text{ J K}^{-1} = 55.42 \text{ J K}^{-1}$$

6. a) liquid water and water vapor are in equilibrium at 100°C and 1.01325 bar ($= 1.00000\text{ atm}$)
 the "normal" boiling point of water at 1 atm (not 1 bar)



\therefore vaporizing liquid water at $1\text{ atm}, 100^\circ\text{C}$ is reversible - adding heat vaporizes liquid water, and removing heat condenses water vapor, forming $\text{H}_2\text{O}(l)$

because the vaporization is reversible:

$$\Delta S = \int \frac{dq}{T} = \int \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T_{\text{vap}}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}}$$

$q = \Delta H$ at constant p

$$\Delta S = \frac{n \Delta H_{\text{vap,m}}}{T_{\text{vap}}} = \frac{(1.00\text{ mol})(40.69\text{ kJ mol}^{-1})}{373.15\text{ K}}$$

$$= 109.0 \frac{\text{J}}{\text{K}}$$

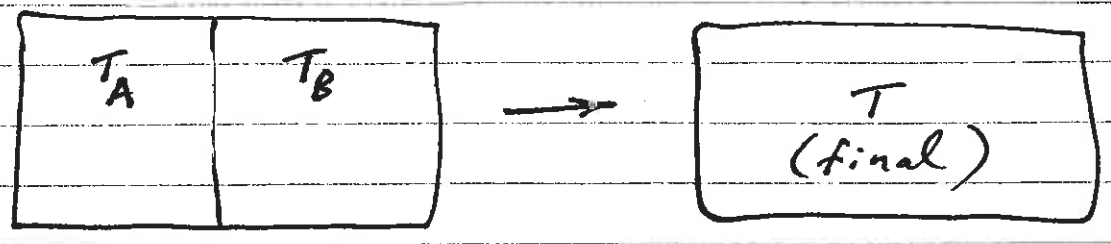
b) This is a reversible process. Vaporizing the water increases the water entropy by 109.0 J K^{-1} , but absorbs heat (40.69 kJ) from the surroundings at 373.15 K .

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}(\text{surroundings})}{T_{\text{surroundings}}} = \frac{-40690\text{ J}}{373.15\text{ K}} = -109.0 \frac{\text{J}}{\text{K}}$$

$$\boxed{(\Delta S)_{\text{isolated}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = (109.0 - 109.0) \frac{\text{J}}{\text{K}} = 0}$$

reversible process, isolated

7.



isolated system : $q = 0$
 $q = q_A + q_B$
 absorbed by block A
 absorbed by block B

$$0 = q = \int_{T_A}^T C_{VA} dT + \int_{T_B}^T C_{VB} dT = C_{VA}(T - T_A) + C_{VB}(T - T_B)$$

spontaneous process

equal size blocks : $C_{VA} = C_{VB}$

$\therefore T - T_A = T - T_B$ solve for :

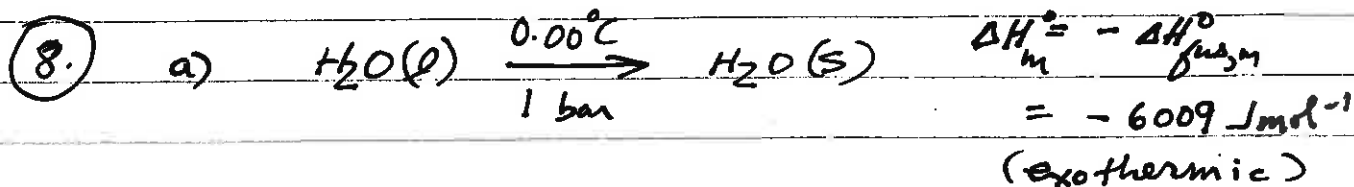
equilibrium temperature $T = \frac{T_A + T_B}{2}$

makes sense - the final temperature of the two blocks is the average of their initial temperatures

ΔS is always positive for internal heat flow in an isolated system

$$\begin{aligned} \Delta S &= \Delta S_{block A} + \Delta S_{block B} = \int_{T_A}^T \frac{dq_{rev A}}{T} + \int_{T_B}^T \frac{dq_{rev B}}{T} \\ &= \int_{T_A}^T \frac{C_{VA}}{T} dT + \int_{T_B}^T \frac{C_{VB}}{T} dT \quad (C_{VA} = C_{VB} = C_V) \\ &= C_{VA} \ln\left(\frac{T}{T_A}\right) + C_{VB} \ln\left(\frac{T}{T_B}\right) = C_V \ln\left(\frac{T_A + T_B}{2 T_A}\right) + C_V \ln\left(\frac{T_A + T_B}{2 T_B}\right) \\ &= C_V \ln\left[\frac{(T_A + T_B)}{2 T_A} \cdot \frac{(T_A + T_B)}{2 T_B}\right] = C_V \ln\left[\frac{(T_A + T_B)^2}{4 T_A T_B}\right] \end{aligned}$$

and note : $\ln a + \ln b = \ln(ab)$



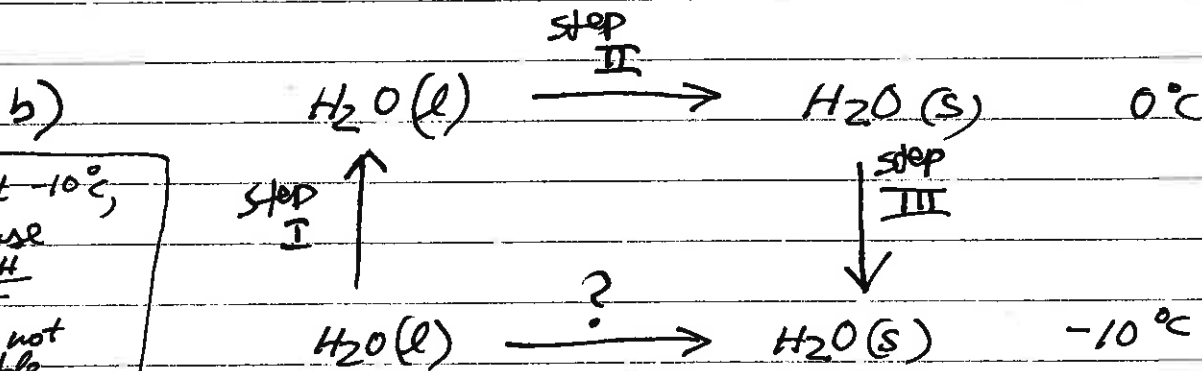
$\text{H}_2\text{O}(\ell)$ and $\text{H}_2\text{O}(\text{s})$ are in equilibrium at 0.00°C and 1 bar

freezing $\text{H}_2\text{O}(\ell)$ is reversible in this case

$$\Delta H = q = q_{\text{rev}}$$

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} \quad (T \text{ constant})$$

$$= \frac{\Delta H}{T} = \frac{-6009 \text{ J}}{273.15 \text{ K}} = -22.00 \frac{\text{J}}{\text{K}}$$



note: At -10°C ,
can't use $\Delta S = \frac{\Delta H}{T}$
freezing not reversible

$$\Delta H(-10^\circ\text{C}) = \Delta H_{\text{I}} + \Delta H_{\text{II}} + \Delta H_{\text{III}}$$

$$= \int_{-10^\circ\text{C}}^{0^\circ\text{C}} C_{p,m}(\ell) dT + \Delta H_{\text{fus},m}^\circ(0^\circ\text{C}) + \int_{0^\circ\text{C}}^{-10^\circ\text{C}} C_{p,m}(\text{s}) dT$$

$$= C_{p,m}(\ell)(10\text{K}) + \Delta H_{\text{fus},m}^\circ(0^\circ\text{C}) - C_{p,m}(\text{s})(10\text{K})$$

$$= \Delta H_{\text{freez}}^\circ(0^\circ\text{C}) + [C_{p,m}(\text{s}) - C_{p,m}(\ell)](-10\text{K})$$

$$= -6009 \frac{\text{J}}{\text{mol}} + (36.93 - 75.99)(-10) \frac{\text{J}}{\text{mol}} = -5618 \frac{\text{J}}{\text{mol}}$$

$\Delta C_p < 0$
So ΔH decreases as
 T increases:
 $\frac{d\Delta H^\circ}{dT} = \Delta C_p$

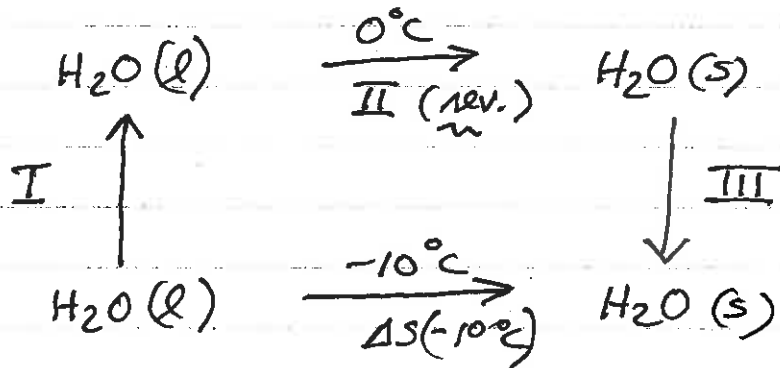
(8 b cont.)

Show that this process is spontaneous

ΔS for freezing water at -10°C ?

can't use $\Delta S(10^\circ\text{C}) = \Delta H(10^\circ\text{C}) / 263.15\text{K}$
because $q (= \Delta H)$ is not reversible

Instead, take the 3-step reversible path to calculate $\Delta S(-10^\circ\text{C})$:



$$\begin{aligned}
 \Delta S(-10^\circ\text{C}) &= \Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}} \\
 &= \int_{263.15\text{K}}^{273.15\text{K}} \frac{C_p(\text{l})}{T} dT + \frac{\Delta H(0^\circ\text{C})}{273.15\text{K}} + \int_{273.15\text{K}}^{263.15\text{K}} \frac{C_p(\text{s})}{T} dT
 \end{aligned}$$

$$= C_{p,m}(\text{l}) \ln\left(\frac{273.15}{263.15}\right) - \frac{6009\text{J}}{273.15\text{K}} + C_{p,m}(\text{s}) \ln\left(\frac{263.15}{273.15}\right)$$

$$= 75.99(0.03730) - 21.999 + 36.93(-0.03730)$$

spontaneous?

$$\Delta S(10^\circ\text{C}) = -19.20 \text{ J K}^{-1} \quad \text{HUH? A negative entropy change for a spontaneous process?}$$

Yes: the system (water) is not isolated

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -19.20 \frac{\text{J}}{\text{K}} + \frac{\Delta H_{\text{surroundings}}}{263.15\text{K}}$$

$$= -19.20 + \frac{5618\text{J}}{263.15\text{K}} = -19.20 + 21.34 = +2.15 \frac{\text{J}}{\text{K}}$$

$\Delta S > 0$ isolated system (overall)

∴ spontaneous process

system releases 5618 J heat into surroundings at 263.15K

9. Solve the equations $\partial S / \partial a_0 = 0$ and $\partial S / \partial a_1 = 0$

to evaluate a_0 (the intercept) and a_1 (the slope)

of the "line of best fit": $f(x) = a_0 + a_1 x$

$$\underline{\partial S / \partial a_0 = 0}$$

$$S \equiv \sum_{i=1}^N [f(x_i)_{\text{measured}} - f(x_i)_{\text{calculated}}]^2$$

$$S = \sum_{i=1}^N [f(x_i)_{\text{meas}} - a_0 - a_1 x_i]^2$$

$$\frac{\partial S}{\partial a_0} = \frac{\partial}{\partial a_0} \sum_{i=1}^N [f(x_i)_{\text{meas}} - a_0 - a_1 x_i]^2$$

$$= \sum_{i=1}^N 2 [f(x_i)_{\text{meas}} - a_0 - a_1 x_i] \frac{\partial}{\partial a_0} [f(x_i) - a_0 - a_1 x_i]$$

$$0 = 2 \sum_{i=1}^N [f(x_i)_{\text{meas}} - a_0 - a_1 x_i] (-1)$$

$$0 = \sum_{i=1}^N [f(x_i)_{\text{meas}} - a_0 - a_1 x_i]$$

$$\sum_{i=1}^N a_0 + \sum_{i=1}^N a_1 x_i = \sum_{i=1}^N f(x_i)_{\text{meas}}$$

$$N a_0 + \left(\sum_{i=1}^N x_i \right) a_1 = \sum_{i=1}^N f(x_i)_{\text{meas}} \quad (\text{eq. 1})$$

(9 cont.)

$$\underline{\partial S / \partial a_1 = 0}$$

$$\begin{aligned} \frac{\partial S}{\partial a_1} &= \frac{\partial}{\partial a_1} \sum_{i=1}^N [f(x_i)_{\text{meas}} - a_0 - a_1 x_i]^2 \\ &= \sum_{i=1}^N 2 [f(x_i)_{\text{meas}} - a_0 - a_1 x_i] \frac{\partial}{\partial a_1} [f(x_i)_{\text{meas}} - a_0 - a_1 x_i] \end{aligned}$$

$$0 = \sum_{i=1}^N 2 [f(x_i)_{\text{meas}} - a_0 - a_1 x_i] (-x_i)$$

$$0 = \sum_{i=1}^N [x_i f(x_i)_{\text{meas}} - a_0 x_i - a_1 x_i^2]$$

$$\sum_{i=1}^N (a_0 x_i) + \sum_{i=1}^N (a_1 x_i^2) = \sum_{i=1}^N x_i f(x_i)_{\text{meas}}$$

$$\boxed{a_0 \left(\sum_{i=1}^N x_i \right) + a_1 \left(\sum_{i=1}^N x_i^2 \right) = \sum_{i=1}^N x_i f(x_i)_{\text{meas}} \quad (\text{eq. 2})}$$

Two equations, two unknowns (a_0 and a_1):

$$\begin{pmatrix} N & \sum_{i=1}^N x_i \\ \sum_{i=1}^N x_i & \sum_{i=1}^N x_i^2 \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \end{pmatrix} = \begin{pmatrix} \sum_{i=1}^N f(x_i)_{\text{meas}} \\ \sum_{i=1}^N x_i f(x_i)_{\text{meas}} \end{pmatrix}$$

solve for a_0 and a_1 :

(9 cont.)

$$a_0 = \frac{\left(\sum_{i=1}^N f(x_i)_{\text{meas}}\right) \left(\sum_{i=1}^N x_i^2\right) - \left(\sum_{i=1}^N x_i f(x_i)_{\text{meas}}\right) \left(\sum_{i=1}^N x_i\right)}{N \sum_{i=1}^N x_i^2 - \left(\sum_{i=1}^N x_i\right)^2}$$

$$a_1 = \frac{N \left(\sum_{i=1}^N x_i f(x_i)_{\text{meas}}\right) - \left(\sum_{i=1}^N x_i\right) \left(\sum_{i=1}^N f(x_i)_{\text{meas}}\right)}{N \sum_{i=1}^N x_i^2 - \left(\sum_{i=1}^N x_i\right)^2}$$

data:

x_i	$f(x_i)_{\text{meas}}$
0.0	0.11
0.9	0.79
1.7	1.79
2.5	2.62
3.9	3.85

$$N = 5 \quad \sum_{i=1}^5 x_i = 9 \quad \sum_{i=1}^5 x_i^2 = 25.16$$

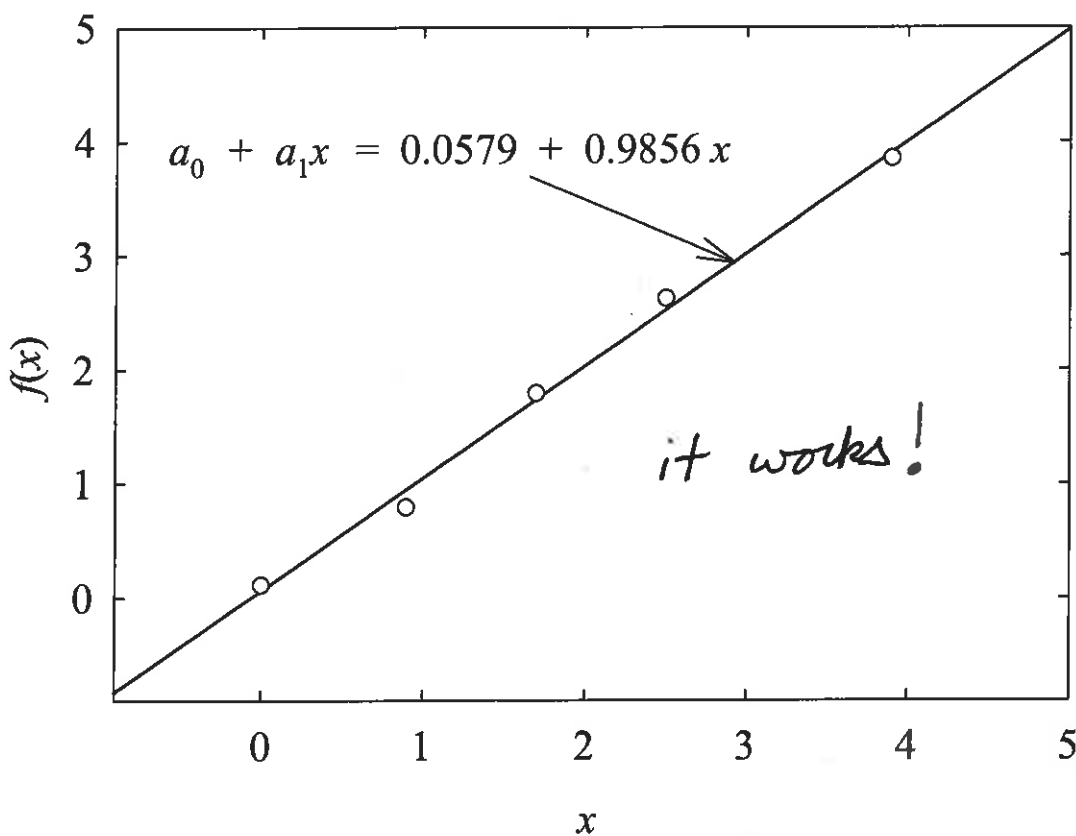
$$\sum_{i=1}^5 f(x_i)_{\text{meas}} = 9.16 \quad \sum_{i=1}^5 x_i f(x_i)_{\text{meas}} = 25.319$$

$$a_0 = \frac{9.16(25.16) - 25.319(9)}{5(25.16) - 9^2} = \frac{2.5946}{44.8} = \boxed{a_0 = 0.0579}$$

$$a_1 = \frac{5(25.319) - 9(9.16)}{5(25.16) - 9^2} = \frac{44.155}{44.8} = \boxed{a_1 = 0.9856}$$

always plot the data

- is the assumed linear behavior $a_0 + a_1 x$ a good approximation?
- any "bad points"?
- any curvature?



* least-squares calculations for lines $a_0 + a_1 x$ are easily extended to more complicated curves (e.g., $a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots$) and to nonlinear fitting equations