ChemE 2200 – Physical Chemistry II – Spring 2025

Solution to Homework Assignment 7

1. To determine if a process is spontaneous, we have two options. One approach is to calculate the total change in entropy, system plus surroundings. Another approach is to calculate ΔG for the system.

   1st Approach: Calculate the total change in entropy, system plus surroundings. Begin with the system - consider one mole of water at −10.°C and 1 atm. We need three paths to use the data at hand. First warm the water to 0°C, then freeze the water at 0°C, then cool the ice to −10.°C.

   Heat the water to 0°C.

$$\Delta S_1 = n\overline{C}_{\text{P,water}} \ln\frac{T_2}{T_1} = (1\text{ mol})(76\text{ J/(K}\cdot\text{mol)})\ln\frac{273\text{ K}}{263\text{ K}} = +2.84\text{ J/K}$$

   Freeze the water at 0°C.

$$\Delta S_2 = \frac{-n\Delta H_{\text{fusion}}}{T_{\text{fusion}}} = \frac{-(1\text{ mol})6.0\times10^3\text{ J/mol}}{273\text{ K}} = -21.98\text{ J/K}$$

   Cool the ice to −10°C.

$$\Delta S_3 = n\overline{C}_{\text{P,ice}} \ln\frac{T_2}{T_1} = (1\text{ mol})(37\text{ J/(K}\cdot\text{mol)})\ln\frac{263\text{ K}}{273\text{ K}} = -1.38\text{ J/K}$$

   The total entropy change of the H_2O is therefore

$$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = +2.84\text{ J/K} - 21.98\text{ J/K} - 1.38\text{ J/K} = -20.5\text{ J/K}$$

   Now calculate the change in the surroundings. First calculate the total reversible heat the system absorbs from the surroundings. Recall that q (and ΔH) are positive for heat transferred from the surroundings to the system.

   Heat the 1 mole of water to 0°C which transfers heat from the surroundings to the system.

$$\Delta H_{\text{system,1}} = n\overline{C}_{\text{P,water}}(T_2 - T_1) = (1\text{ mol})(76\text{ J/(K}\cdot\text{mol)})(273 - 263\text{ K}) = +760\text{ J}$$

   Freeze the water at 0°C, which releases heat from the system into the surroundings.

$$\Delta H_{\text{system,2}} = -n\Delta H_{\text{fusion}} = -(1\text{ mol})6.0\times10^3\text{ J/mol} = -6000\text{ J}$$

   Cool the ice to −10.°C, which transfers heat from the system to the surroundings.

$$\Delta H_{\text{system,3}} = n\overline{C}_{\text{P,ice}}(T_2 - T_1) = (1\text{ mol})(37\text{ J/(K}\cdot\text{mol)})(263 - 273\text{ K}) = -370\text{ J}$$

   The total enthalpy change is therefore

$$\Delta H_{\text{surroundings}} = -\Delta H_{\text{system}} = -(\Delta H_{\text{system,1}} + \Delta H_{\text{system,2}} + \Delta H_{\text{system,3}}) = -(760\text{ J} - 6000\text{ J} - 370\text{ J}) = +5610\text{ J}$$

   Thus when one mole of water freezes at −10.°C, the system delivers 5610 J to the surroundings. The entropy change of the surroundings is therefore

$$\Delta S_{\text{surroundings}} = \frac{\Delta H_{\text{surroundings}}}{T_{\text{fusion}}} = \frac{5610\text{ J}}{263\text{ K}} = +21.3\text{ J/K}$$

   The entropy of the H_2O decreases and the entropy of the surroundings increase. The total entropy change is

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -20.5\text{ J/K} + 21.3\text{ J/K} = +0.8\text{ J/K}$$

   Because the net entropy change (system plus surroundings) is positive, the process is spontaneous.

2nd Approach: Calculate ΔG for the system. As calculated above for 1 mole of water at −10°C, $\Delta H = -5610$ J and $\Delta S = -20.5$ J/K. Use the fundamental equation for ΔG.

$$\Delta G \;=\; \Delta H - T\Delta S \;=\; -5610\text{ J} - (263\text{ K})(-20.5\text{ J/K}) \;=\; -219\text{ J}$$

Because ΔG is negative, the process is spontaneous.

Adapted from J. H. Noggle, *Physical Chemistry*, 3rd edition, 1996.

2.(A) First a general note. The nomenclature for the pressures, volumes, and temperatures is potentially confusing. Subscript "1" does not necessary mean "initial" and subscript "2" does not necessarily mean "final." For example, in part (C), $P_{\text{initial}} = P_2$ and $P_{\text{final}} = P_1$.

Use the expression for ΔS in terms of T and P for an ideal gas derived in Calculation Session 6.

$$\Delta\overline{S}_{\text{A}} \;=\; \overline{C}_{\text{P}} \ln\frac{T_{\text{final}}}{T_{\text{initial}}} \;-\; R\ln\frac{P_{\text{final}}}{P_{\text{initial}}} \qquad (1)$$

For an isobaric compression, $P_{\text{initial}} = P_{\text{final}}$. In this case, $T_{\text{initial}} = T_1$ and $T_{\text{final}} = T_2$. The equation is therefore

$$\Delta\overline{S}_{\text{A}} \;=\; \overline{C}_{\text{P}} \ln\frac{T_2}{T_1}$$

Or start with the definition $d\overline{S} \;=\; \delta\overline{q}_{\text{rev}}/T$ for a reversible process. The heat transferred during cooling at constant pressure is

$$d\overline{H} \;=\; \delta\overline{q}_{\text{rev}} \;=\; \overline{C}_{\text{P}}dT$$

$$d\overline{S} \;=\; \frac{\delta\overline{q}_{\text{rev}}}{T} \;=\; \frac{\overline{C}_{\text{P}}dT}{T}$$

$$\Delta\overline{S} \;=\; \int_{T_1}^{T_2}\frac{\overline{C}_{\text{P}}dT}{T} \;=\; \overline{C}_{\text{P}}(\ln T_2 - \ln T_1) \;=\; \overline{C}_{\text{P}} \ln\frac{T_2}{T_1}$$

(B) Use the expression for ΔS in terms of T and V for an ideal gas derived in thermodynamics lecture 7.

$$\Delta\overline{S}_{\text{B}} \;=\; \overline{C}_{\text{V}} \ln\frac{T_{\text{final}}}{T_{\text{initial}}} \;+\; R\ln\frac{V_{\text{final}}}{V_{\text{initial}}} \qquad (2)$$

For an isochoric compression, $V_{\text{initial}} = V_{\text{final}}$. Again, $T_{\text{initial}} = T_1$ and $T_{\text{final}} = T_2$. The equation is therefore

$$\Delta\overline{S}_{\text{B}} \;=\; \overline{C}_{\text{V}} \ln\frac{T_2}{T_1}$$

Or again start with the definition $d\overline{S} \;=\; \delta\overline{q}_{\text{rev}}/T$ for a reversible process. The heat transferred during cooling at constant volume is

$$d\overline{U} \;=\; \delta\overline{q}_{\text{rev}} \;=\; \overline{C}_{\text{V}}dT$$

$$d\overline{S} \;=\; \frac{\delta\overline{q}_{\text{rev}}}{T} \;=\; \frac{\overline{C}_{\text{V}}dT}{T}$$

$$\Delta\overline{S} \;=\; \int_{T_1}^{T_2}\frac{\overline{C}_{\text{V}}dT}{T} \;=\; \overline{C}_{\text{V}}(\ln T_2 - \ln T_1) \;=\; \overline{C}_{\text{V}} \ln\frac{T_2}{T_1}$$

(C) Because entropy is a state function, we may take any reversible path from the initial state to the final state. Rather than follow path C, take the opposite of path B, then take path A.

$$\Delta S_{\text{C}} \;=\; \Delta S_{\text{A}} \;-\; \Delta S_{\text{B}}$$

Substitute the results from parts (A) and (B) above, and recall that $\overline{C}_{\text{P}} - \overline{C}_{\text{V}} = R$ for an ideal gas.

$$\begin{aligned}\Delta S_C &= \Delta S_A - \Delta S_B \\ &= \overline{C}_P \ln\frac{T_2}{T_1} - \overline{C}_V \ln\frac{T_2}{T_1} \\ &= \left(\overline{C}_P - \overline{C}_V\right)\ln\frac{T_2}{T_1} \\ &= R\ln\frac{T_2}{T_1}\end{aligned}$$

Another approach is to start with equation (1) and note that for an isothermal process $T_{\text{initial}} = T_{\text{final}}$. In this case, $P_{\text{initial}} = P_2$ and $P_{\text{final}} = P_1$.

$$\Delta\overline{S}_C = \overline{C}_P \ln\frac{T_{\text{final}}}{T_{\text{initial}}} - R\ln\frac{P_{\text{final}}}{P_{\text{initial}}} \qquad (1)$$

$$\Delta\overline{S}_C = -R\ln\frac{P_1}{P_2}$$

We need to express P_1/P_2 in terms of T_1 and T_2. Because this is a closed system, an analysis of path B yields:

$$\begin{aligned}n_{\text{initial}} &= n_{\text{final}} \\ \frac{P_1V_1}{RT_1} &= \frac{P_2V_1}{RT_2} \\ \frac{P_1}{P_2} &= \frac{T_1}{T_2}\end{aligned}$$

Thus,

$$\Delta\overline{S}_C = -R\ln\frac{P_1}{P_2} = -R\ln\frac{T_1}{T_2} = R\ln\frac{T_2}{T_1}$$

3.(A) The heat capacity tells us how the volume and pressure change along a path. Start with the definition of arbitrary heat capacity and substitute the ideal gas law and $\overline{C}_V = 1.5R$ for a monatomic ideal gas.

$$\begin{aligned}\overline{C} &= \overline{C}_V + P\frac{d\overline{V}}{dT} \\ \frac{7}{2}R &= \frac{3}{2}R + \frac{RT}{\overline{V}}\frac{d\overline{V}}{dT} \\ 2 &= \frac{T}{\overline{V}}\frac{d\overline{V}}{dT}\end{aligned}$$

Separate and integrate.

$$\begin{aligned}2\frac{dT}{T} &= \frac{d\overline{V}}{\overline{V}} \\ 2\int_{T_1}^{T_2}\frac{dT}{T} &= \int_{V_1}^{V_2}\frac{d\overline{V}}{\overline{V}} \\ 2\ln\frac{T_2}{T_1} &= \ln\frac{V_2}{V_1} \\ \left(\frac{T_2}{T_1}\right)^2 &= \frac{V_2}{V_1}\end{aligned}$$

Solve for V_2 and plug in the particulars.

$$V_2 = V_1\left(\frac{T_2}{T_1}\right)^2 = 20\text{ L}\left(\frac{500\text{ K}}{300\text{ K}}\right)^2 = 55.6\text{ L}$$

(B) Presented here are two different approaches to calculating ΔS. Because the process is reversible, we can start with the definition of entropy.

$$dS = \frac{\delta q_{\text{rev}}}{T} = \frac{CdT}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{CdT}{T} = C\ln\frac{T_2}{T_1} = 3.5R\ln\frac{T_2}{T_1} = 3.5(8.314\ \text{J/(K}\cdot\text{mol))}\ln\frac{500\ \text{K}}{300\ \text{K}}$$

$$\Delta S = 14.9\ \text{J/(K}\cdot\text{mol)}$$

Another approach is to devise two reversible paths to the same final state. For example, path 1 can be the isothermal expansion from 20 L to 55.6 L and path 2 is then isochoric heating from 300 K to 500 K. Calculate ΔS for the isothermal expansion.

$$\Delta S_1 = nR\ln\frac{V_2}{V_1} = (1\ \text{mol})(8.314\ \text{J/(K}\cdot\text{mol))}\ln\frac{55.6\ \text{L}}{20.\ \text{L}} = 8.50\ \text{J/(K}\cdot\text{mol)}$$

Calculate ΔS for the isochoric heating.

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{n\overline{C}_{\text{V}}dT}{T} = n\overline{C}_{\text{V}}\ln\frac{T_2}{T_1} = n\frac{3}{2}R\ln\frac{T_2}{T_1} = (1\ \text{mol})\frac{3}{2}(8.314\ \text{J/(K}\cdot\text{mol))}\ln\frac{500\ \text{K}}{300\ \text{K}}$$

$$= 6.37\ \text{J/(K}\cdot\text{mol)}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 8.50\ \text{J/(K}\cdot\text{mol)} + 6.37\ \text{J/(K}\cdot\text{mol)} = 14.9\ \text{J/(K}\cdot\text{mol)}$$

The same result obtains.

Adapted from L. M. Raff, *Principles of Physical Chemistry*, Prentice Hall, 2001.

4.(A) Heat is added to the gas during the isothermal expansion, step 1. Because the gas is ideal, U depends on temperature only, so $\Delta U = 0$ for the isothermal expansion. (Note: $n = 1$ mol)

$$\Delta U_{\text{step 1}} = 0 = q_{\text{step 1}} + w_{\text{step 1}}$$

$$q_{\text{step 1}} = -w_{\text{step 1}} = \int_{V_1}^{V_2} PdV = nRT_1\int_{V_1}^{V_2}\frac{dV}{V} = RT_1\ln\frac{V_2}{V_1}$$

Note that because $V_2 > V_1$, $q_{\text{step 1}}$ is positive, as expected.

(B) The gas discharges heat during the isochoric cooling, step 2. Because there is no change in volume, no work is done during step 2. (Again, $n = 1$ mol).

$$q_{\text{step 2}} = \Delta U_{\text{step 2}} = \int_{T_1}^{T_2} n\overline{C}_{\text{V}}dT = \overline{C}_{\text{V}}(T_2 - T_1) = \frac{3}{2}R(T_2 - T_1)$$

Note that because $T_2 < T_1$, $q_{\text{step 2}}$ is negative, as expected.

(C) The total work for the cycle is

$$w_{\text{cycle}} = w_{\text{step 1}} + w_{\text{step 2}} + w_{\text{step 3}} = -RT_1\ln\frac{V_2}{V_1} + 0 + \int_{T_2}^{T_1} n\overline{C}_{\text{V}}dT$$

$$w_{\text{cycle}} = -RT_1\ln\frac{V_2}{V_1} + \frac{3}{2}R(T_1 - T_2)$$

Because $V_2 > V_1$, the first term is negative - the system does work on the surroundings. Because $T_1 > T_2$, the second term is positive - the surroundings do work on the system.

(D) The efficiency is thus

$$\varepsilon = \frac{-w_{\text{cycle}}}{q_{\text{step 1}}} = \frac{RT_1 \ln\dfrac{V_2}{V_1} - \dfrac{3}{2}R(T_1 - T_2)}{RT_1 \ln\dfrac{V_2}{V_1}} = 1 - \frac{3(T_1 - T_2)}{2T_1 \ln\dfrac{V_2}{V_1}}$$

We need to express the ratio V_2/V_1 in terms of T_1/T_2. Recall for an adiabatic expansion of an ideal monatomic gas,

$$\left(\frac{T_1}{T_2}\right)^{3/2} = \frac{V_2}{V_1}$$

$$\ln\left(\frac{T_1}{T_2}\right)^{3/2} = \ln\frac{V_2}{V_1}$$

$$\frac{3}{2}\ln\left(\frac{T_1}{T_2}\right) = \ln\frac{V_2}{V_1}$$

Substitute this expression into the expression for the efficiency.

$$\varepsilon = 1 - \frac{3(T_1 - T_2)}{2T_1 \ln\dfrac{V_2}{V_1}} = 1 - \frac{3(T_1 - T_2)}{2T_1 \dfrac{3}{2}\ln\left(\dfrac{T_1}{T_2}\right)} = 1 - \frac{(T_1 - T_2)}{T_1 \ln\left(\dfrac{T_1}{T_2}\right)}$$

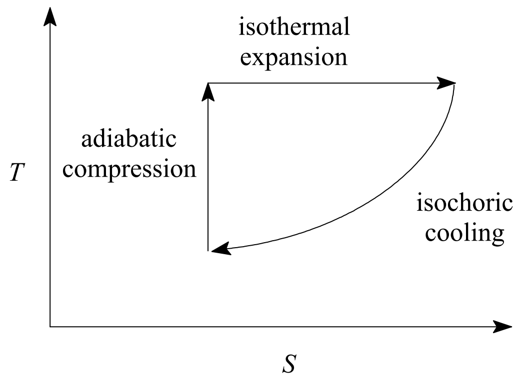
(E) Step 1 is isothermal. So the path on a plot of T vs. S will be a horizontal line. The volume increases, so S increases. Step 1 is a horizontal path to the right. Step 3 is adiabatic and reversible, so $\Delta S = 0$; the path is vertical. The temperature increases, so the path is upward. Step 2 just connects the two paths, but the line is curved. From a Useful Relationship we have

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Or in terms of the slope on the S-T plot,

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

Because C_V is constant for an ideal gas, the slope increases with temperature and the path is curved, as shown below.



5.(A) Because

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

is an exact differential, Euler's relation provides that

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T \qquad (1)$$

Apply Euler's relation to the results from Example 21-1 of McQuarrie and Simon.

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right] = \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} \qquad (2)$$

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial T}\left[\frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\right] = -\frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] + \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \frac{\partial^2 U}{\partial T \partial V}\right] \qquad (3)$$

Substitute the results of equations (2) and (3) into equation (1).

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] + \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \frac{\partial^2 U}{\partial T \partial V}\right]$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{P}{T^2} - \frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V}$$

$$-\frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{P}{T^2} - \frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

Note that the two terms on the left side of the equation cancel because *U*(*T*, *V*) is an exact differential. That is,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T$$

Solve for $(\partial U/\partial V)_T$.

$$0 = -\frac{P}{T^2} - \frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{1}{T^2}\left(\frac{\partial U}{\partial V}\right)_T = -\frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \qquad (4)$$

Use the ideal gas law, $P = nRT/V$, to substitute for P in equation (4).

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{nRT}{V} + T\left(\frac{\partial}{\partial T}\frac{nRT}{V}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{nRT}{V} + T\frac{nR}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

(B) Use the form of the gas law, $P = f(V)T$, to substitute for P in equation (4).

$$\left(\frac{\partial U}{\partial V}\right)_T = -f(V)T + T\left(\frac{\partial}{\partial T}f(V)T\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -f(V)T + f(V)T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

6. To find the minimum temperature, we need to continue to satisfy the both the 1st and 2nd laws of thermodynamics. To satisfy the 1st law, the temperature decrease must equal the temperature increase for equal flow rates of the hot and cold streams, assume the heat capacity is independent of temperature in the range T_cold. to T_hot.

$$T_\text{hot} - T_1 = T_1 - T_\text{cold}$$

$$T_\text{hot} = 2T_1 - T_\text{cold}$$

Substitute for T_hot into the expression for $\Delta\overline{S}_\text{total}$. Calculate the entropy change for expanding the gas to P_2 from P_1, cool half the gas to T_cold from T_1, and warm half the gas to T_hot from T_1.

$$\Delta\overline{S}_\text{total} = R\ln\frac{P_1}{P_2} + C_\text{P}\left[\ln\frac{T_\text{cold}}{T_1}\right] + C_\text{P}\left[\ln\frac{T_\text{hot}}{T_1}\right]$$

$$\Delta\overline{S}_\text{total} = R\ln\frac{P_1}{P_2} + C_\text{P}\left[\ln\frac{T_\text{cold}T_\text{hot}}{T_1^2}\right]$$

$$0 = R\ln\frac{P_1}{P_2} + C_\text{P}\left[\ln\frac{T_\text{cold}(2T_1 - T_\text{cold})}{T_1^2}\right]$$

$$-C_\text{P}\left[\ln\frac{T_\text{cold}(2T_1 - T_\text{cold})}{T_1^2}\right] = R\ln\frac{P_1}{P_2}$$

$$\ln\frac{T_\text{cold}(2T_1 - T_\text{cold})}{T_1^2} = -\frac{R}{C_\text{P}}\ln\frac{P_1}{P_2}$$

$$\ln\frac{T_\text{cold}(2T_1 - T_\text{cold})}{T_1^2} = \ln\left(\frac{P_1}{P_2}\right)^{-R/C_\text{P}}$$

$$\frac{T_\text{cold}(2T_1 - T_\text{cold})}{T_1^2} = \left(\frac{P_1}{P_2}\right)^{-R/C_\text{P}}$$

$$2T_1T_\text{cold} - T_\text{cold}^2 = T_1^2\left(\frac{P_1}{P_2}\right)^{-R/C_\text{P}}$$

$$T_\text{cold}^2 - 2T_1T_\text{cold} + T_1^2\left(\frac{P_1}{P_2}\right)^{-R/C_\text{P}} = 0$$

We need to solve a quadratic equation for T_cold. Although it would be nice to have a general equation for T_cold in terms of the pressures, that will have to wait. For now substitute the particulars and solve for T_cold.

$$T_{\text{cold}}^2 - 2T_1T_{\text{cold}} + T_1^2\left(\frac{P_1}{P_2}\right)^{-R/C_\text{P}} = 0$$

$$T_{\text{cold}}^2 - 2(293\text{ K})T_{\text{cold}} + (293\text{ K})^2\left(\frac{4\text{ atm}}{1\text{ atm}}\right)^{-(8.314)/29} = 0$$

$$T_{\text{cold}}^2 - 586\,T_{\text{cold}} + 57{,}694 = 0$$

$$T_{\text{cold}} = \frac{586 \pm \sqrt{586^2 - 4\times 57{,}694}}{2} = 293 \pm 168$$

$$T_{\text{cold}} = 125\text{ K}$$

The theoretical low temperature limit for a reversible process is 125 K. Of course, this temperature cannot be obtained for an irreversible process. Also, we have assumed the heat capacity is constant, which is likely inaccurate for cooling to 125 K.