Heating or *cooling* of a substance $T_1 \to T_2$

(can be done slowly, reversibly):

$$\text{constant } V: \quad \Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_V dT = \int_{T_1}^{T_2} \frac{\bar{d}q_{rev}}{T} dT = \int_{T_1}^{T_2} \frac{n\bar{C}_V}{T} dT$$

$$\text{constant } P: \quad \Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_P dT = \int_{T_1}^{T_2} \frac{\bar{d}q_{rev}}{T} dT = \int_{T_1}^{T_2} \frac{n\bar{C}_P}{T} dT$$

if $\bar{C}_V, \bar{C}_P$ independent of T $\Delta S = ...$

$$dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad or \quad dS(T,P) = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dS(T,V) = \frac{n\overline{C}_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad or \quad dS(T,P) = \frac{n\overline{C}_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

ΔS for ideal gas Lecture/Handout #29, slides ~13,14

$$\Delta S = n\overline{C}_v \, ln\left(\frac{T_{final}}{T_{initial}}\right) + nR \, ln\left(\frac{V_{final}}{V_{initial}}\right) \quad \textit{E\&R eqn 5.18}$$

$$\Delta S = n\overline{C}_P \, ln\left(\frac{T_{final}}{T_{initial}}\right) - nR \, ln\left(\frac{P_{final}}{P_{initial}}\right) \quad \textit{E\&R eqn 5.19}$$

2

25. E&R 5.16

   3.75 moles of an ideal gas with $\bar{C}_V = 3/2\,R$ undergoes the transformations described in the following list from an initial state described by T = 298K and P = 4.50 bar. Calculate $q, w, \Delta U, \Delta H, \text{and}\; \Delta S$ for each process.
   a. The gas undergoes a reversible adiabatic expansion until   **reversible**
       the final pressure is one third its initial value.
   b. The gas undergoes an adiabatic expansion against a constant external   **irrev** **ΔS=10.6 J K⁻¹**
       pressure of 1.50 bar until the final pressure is one third its initial value.
   c. The gas undergoes an expansion against a constant external pressure of zero
       bar until the final pressure is equal to one third of its initial value.   **irrev**

   (*part c is ambiguous as written*. It should have been stated: "…undergoes an adiabatic *(and also???)* expansion against a constant external pressure of zero bar until the final pressure is equal to one third of its initial value".)

   problem 26 leave answers in terms of $\bar{C}_V$ and $\bar{C}_P$
   [do not assume numerical values]

3

28. E&R P5.33

A refrigerator is operated by a 0.25-hp (1 hp =746 watts) motor. If the interior is to be maintained at 4.50°C and the room temperature on a hot day is 38°C, what is the maximum heat leak (in watts) that can be tolerated? Assume that the coefficient of performance is 50% of the maximum theoretical value. What happens if the leak is greater than your calculated maximum value?

Heat leak is maximum possible power (watts=J s^{-1}) that refrigerator with above efficiency could provide.
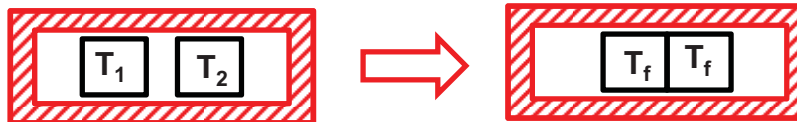*[no heat leak and the 4.5° C → 38° C temperature difference could be maintained without input power]*

**Coefficient of performance
of refrigerator:**

$$\eta_r \equiv C_R = \frac{-q_{surr\_III}}{w_{total}} = \frac{q_{III}}{w_{total}} = \frac{T_L}{T_U - T_L}$$

E&R eqn 5.45

29. Suppose two blocks of iron, each having 1 mol of iron atoms, are at differing temperatures and are then brought together in an otherwise isolated system. One of the blocks is at 273.15K and the other is at 373.15K and the process is carried out at 1 bar pressure..

   a. Would you expect $\Delta S_{sys} < 0$, $\Delta S_{sys} = 0$, $\Delta S_{sys} > 0$?

   b. Using common sense and high school physics (and perhaps the First Law), what is the common final temperature of the two blocks?

   c. Calculate ΔS_{sys} for the process (use Table 4.1 for any needed molar heat capacities needed, and assume that the molar heat capacities are independent of T).

   $\Delta S_{sys}=0.607$ J K^{-1}

   d. What is q for the isolated system? How does this value of q and the result of

   part C relate to the Clausius inequality: $\Delta S \geq \int_{initial}^{final} \dfrac{dq}{T}$?

   e. Interpret this change in entropy in terms of the ordering-disordering effects involved in the transfer of given amount of heat from a block at higher temperature to one at a lower temperature (i.e. the disordering effect of adding a given q to the cooler block vs the ordering effect of removing the same q from the hotter block).
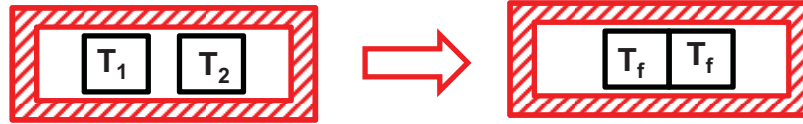
1. Is process in #29 reversible or irreversible ?

2. What are ΔS_{sys}, ΔS_{surr} and ΔS_{total} ?

3. If the heat transfer was carried out reversibly, what would be ΔS_{sys} ?

4. If the heat transfer was carried out reversibly, what would be ΔS_{total} ?

5. If the heat transfer was carried out reversibly, what would be ΔS_{surr} ?

6. How might one carry out the heat transfer in problem #29 reversibly and how could one directly show that $\Delta S_{surr} = \Delta S_{sys}$ for this process?

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30. [Adapted from Raff #4.30] Using the data in E&R Appendix A, calculate ΔS° for the following readtions:

a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

b. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

c. $C_4H_{10}(g)$ *[n-butane]* $+ \dfrac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$ $\boxed{\Delta S = 155.2 \text{ J K}^{-1}}$

d. Discuss the results of each reaction in terms of order-disorder in regard to both the sign of ΔS° for each reaction and the relative magnitudes of ΔS° for the three reactions.

31.

a. Prove, in general (but $\bar{d}\,w_{other} = 0;\quad dn = 0$), the relationship in equation 3.19 E&R)

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

b. Evaluate $\left(\dfrac{\partial U}{\partial V}\right)_T$ for an ideal gas.

c. Evaluate $\left(\dfrac{\partial \bar{U}}{\partial \bar{V}}\right)_T$ for a Van der Waals gas $\left(P + \dfrac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$

d. Interpret your (correct!) results for parts (b) and (c).

e. Prove, in general (but $\bar{d}\,w_{other} = 0;\quad dn = 0$), the relationship in equation 3.44 E&R:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

33. (*Adapted from Tinoco, Sauer, Wang, and Puglisi; Physical Chemistry; Prentice-Hall, publishers*) The denaturation of a globular protein from state $\alpha \rightarrow$ state β occurs reversibly at $T_m = 70°C$ and $P=1$ atm . At this temperature 638kJ mol^{-1} are absorbed for the transition. For this denaturation

$$\left(\overline{C}_p\right)_\beta - \left(\overline{C}_p\right)_\alpha = -8.37 \ kJ \ mol^{-1} K^{-1} \quad \text{and} \quad \Delta \overline{V} = 3 \ mL \ mol^{-1}.$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P , \left(\frac{\partial \Delta S}{\partial T}\right)_P , \left(\frac{\partial \Delta H}{\partial P}\right)_T \quad and \quad \left(\frac{\partial \Delta S}{\partial P}\right)_T$$

1st law, HO#28 (sl17), prob 31e, HO#28 (sl17)

a. What is $\Delta \overline{S}$ for this transition at 70°C and 1 atm?

$$\Delta S(P_2) = \Delta S(P_1) + \int_{P_1}^{P_2} \left(\frac{\partial \Delta S}{\partial P}\right)_T dP$$

b. What are $\Delta \overline{H}$ and $\Delta \overline{S}$ for this transition at 37°C and 1 atm?

c. Assuming that the α and β forms have identical coefficients of thermal expansion $(\Delta \overline{V} = constant, independent \ of \ T)$, calculate ΔH for the denaturation at 70°C and 1000 atm?

d. From thermodynamic arguments, which form is more disordered, α or β ? Why?

[don't expect much change in ΔH with P (~0.1%)]

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34. A 3 L container is partitioned into two sections, 2L and 1L. The 2L section contains N_2 at T= 300K, 1 atm, and the 1L contains O_2 at T= 300K, 1 atm. If the temperature of the container is maintained at T=300K, what is the change of entropy when the partition is removed (assume ideal gasses)? [Express the result in J K^{-1}]

$$\Delta S_{mixing}$$
[HO#32 (sl18)]

35. The molar enthalpy of fusion of water is 6.03 kJ mol^{-1} at 273K and the molar heat capacities of liquid water and ice are 75.3 J K^{-1} mol^{-1} and 37.9 J K^{-1} mol^{-1} respectively.

For the process 1 mole H_2O (ℓ) → H_2O (s)

a. Will this be a spontaneous process at 263K?

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P , \left(\frac{\partial \Delta S}{\partial T}\right)_P$$

b. What is ΔH at 263K?

$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2}\left(\frac{\partial \Delta S}{\partial T}\right)_P dT$$

c. What is ΔS at 263K?   -20.694 J K^{-1}

d. Is $\left(\dfrac{\Delta H}{T}\right)_{263K} = \Delta S_{263K}$? Why or why not?

e. (quickly) Repeat the calculations of parts b and c for ΔH and ΔS at T=283K.

f. From the results of b,c,d calculate the quantities:

   i. $[\Delta H - T\Delta S]_{263}$
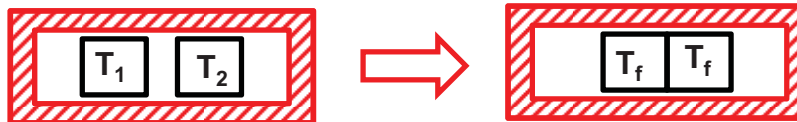   ii. $[\Delta H - T\Delta S]_{273}$ *(you should have obtained ΔS_{273} in part c)*
   iii. $[\Delta H - T\Delta S]_{283}$

how do signs of i, ii, iii compare?
what does it mean ??

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1. Is process in #29 reversible or irreversible ?

   irrev

2. What are ΔS_{sys} , ΔS_{surr} and ΔS_{total} ?

   $(\Delta S_{sys})_{irrev}$= 0.607 J K^{-1}
   $(\Delta S_{surr})_{irrev}$= 0.0 J K^{-1}

3. If the heat transfer was carried out reversibly, what would be ΔS_{sys} ?

   $(\Delta S_{sys})_{rev}$= 0.607 J K^{-1}

4. If the heat transfer was carried out reversibly, what would be ΔS_{total} ?

   $(\Delta S_{total})_{rev}$= 0.0 J K^{-1}

5. If the heat transfer was carried out reversibly, what would be ΔS_{surr} ?

   $(\Delta S_{surr})_{rev}$= -0.607 J K^{-1}

6. How might one carry out the heat transfer in problem #29 reversibly and how could one directly show that $\Delta S_{surr} = \Delta S_{sys}$ for this process?

   [Handout #36]

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