

1. Problem 20-14 in McQuarrie & Simon:

Show that

$$\Delta \bar{S} = \bar{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

if one mole of an ideal gas is taken from T_1 , V_1 to T_2 , V_2 , assuming that $\bar{C}_V$ is independent of temperature. Calculate the value of $\Delta \bar{S}$ if one mole of $N_2(g)$ is expanded from 20.0 dm³ at 273 K to 300 dm³ at 400 K. Take $\bar{C}_p = 29.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

2. Problem 20-17 in McQuarrie & Simon:

Show that

$$\Delta S \geq \frac{q}{T}$$

for an isothermal process. What does this equation say about the sign of ΔS ? Can ΔS decrease in a reversible isothermal process? Calculate the entropy change when one mole of an ideal gas is compressed reversibly and isothermally from a volume of 100 dm³ to 50.0 dm³ at 300 K.

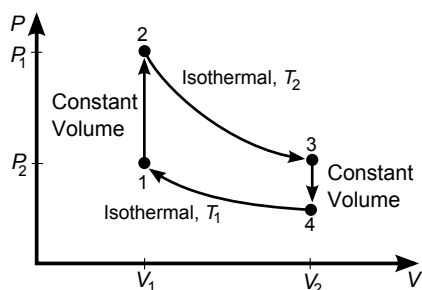
3. Problem 20-18 in McQuarrie & Simon:

Vaporization at the normal boiling point (T_{vap}) of a substance (the boiling point at one atm) can be regarded as a reversible process because if the temperature is decreased infinitesimally below T_{vap} , all the vapor will condense to liquid, whereas if it is increased infinitesimally above T_{vap} , all the liquid will vaporize. Calculate the entropy change when two moles of water vaporize at 100.0°C. The value of $\Delta_{\text{vap}} \bar{H}$ is 40.65 kJ mol⁻¹. Comment on the sign of $\Delta_{\text{vap}} S$.

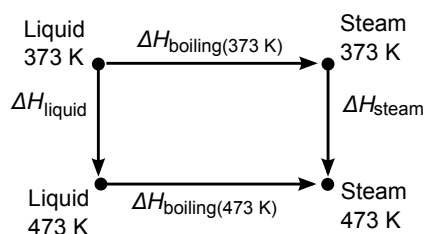
4. Problem 20-19 in McQuarrie & Simon:

Melting at the normal boiling point (T_{fus}) of a substance (the melting point at one atm) can be regarded as a reversible process because if the temperature is changed infinitesimally from exactly T_{fus} , then the substance will either melt or freeze. Calculate the change in entropy when two moles of water melt at 0°C. The value of $\Delta_{\text{fus}} \bar{H}$ is 6.01 kJ mol⁻¹. Compare your answer with the one you obtained in Problem 3. Why is $\Delta_{\text{vap}} S$ much larger than $\Delta_{\text{fus}} S$?

5. A Stirling engine has the PV cycle shown in the figure below and uses an ideal gas working fluid. The steps are quasi static.



- (a) How much work is done in the constant-volume segments w_{12} and w_{34} ?
- (b) What is the energy change around the cycle, $\Delta U_{\text{tot}} = \Delta U_{12} + \Delta U_{23} + \Delta U_{34} + \Delta U_{41}$?
- (c) What is the total work performed around the cycle, $w_{\text{tot}} = w_{12} + w_{23} + w_{34} + w_{41}$?
- (d) If $T_2 = 2000\text{ K}$, $T_1 = 300\text{ K}$, $V_2 = 1\text{ L}$, $V_1 = 0.01\text{ L}$, and $n = 0.1\text{ mol}$ of ideal gas, compute w_{tot} .
6. Suppose the compression ratio in your car engine is $V_2/V_1 = 8$. For a diatomic gas, $C_V = (5/2)Nk$ and for ethane, $C_V \approx 5Nk$.
- (a) What is the efficiency of your engine if the working fluid is a diatomic gas?
- (b) Which is more efficient: a diatomic gas or ethane?
- (c) Would your engine be more or less efficient with a higher compression ratio?
7. Suppose you want to know how much heat it would take to boil water at 473 K , rather than 373 K . At $T = 373\text{ K}$, $\Delta H_{\text{boiling}(100^\circ\text{C})} = 40.7\text{ kJ mol}^{-1}$ is the enthalpy of vaporization. Assuming that the heat capacities of the liquid ($C_{p,\text{liquid}} = 75\text{ J K}^{-1}\text{ mol}^{-1}$) and the vapor ($C_{p,\text{vapor}} = 3.5\text{ J K}^{-1}\text{ mol}^{-1}$) are constant over this temperature range, calculate the enthalpy of vaporization at 473 K using the thermodynamic cycle shown below.



8. 10 points extra credit: Maximum Entropy in Las Vegas

You play a slot machine in Las Vegas. For every \$1 coin you insert there are three outcomes:

- (a) you lose \$1.
- (b) you win \$1, so your profit is \$0.
- (c) you win \$5, so your profit is \$4.

Suppose you find that your average expected profit over many trials is \$0 (i.e. you play slots at a casino owned by someone exceedingly generous or stupid). Find the maximum entropy distribution for the probabilities p_1 , p_2 and p_3 of observing each of these three outcomes.