Thermodynamics of Materials 3.00 Fall 2001
Example Problems for Week 5

Example Problem 5.1

One mole of an ideal gas, in an initial state (T_0, P_0, V_0) *undergoes an expansion from* V_0 *to* V_1 *by three different processes:*

a. *isothermal reversible expansion*

b. *isothermal irreversible expansion against* $P_{ex} = 0$ *(free expansion)*

c. *adiabatic reversible expansion*

Calculate ΔS_{system}*,* $\Delta S_{surroundings}$*, and* $\Delta S_{universe}$ *for each.*

Solution 5.1

Before beginning the problem we can make some general statements. The entropy of a system is a state function so is path independent. Therefore ΔS_{system} should be equal for processes a and b. Also, the entropy change for a reversible process in an isolated system is zero. This means that $\Delta S_{universe}$ for processes a and c should be zero.

a. For an ideal gas the internal energy is a function of temperature only so $\Delta U = 0$. This leads to:

$$q = -w = \int PdV = RT \ln\left(\frac{V_1}{V_0}\right)$$

We know that:

$$\Delta S_{system} = \frac{q_{rev}}{T}$$

So for this reversible process:

$$\Delta S_{system} = R \ln\left(\frac{V_1}{V_0}\right)$$

For $\Delta S_{surroundings}$ we use the actual heat that flows during the process which in this case yields:

$$\Delta S_{surroundings} = -R \ln\left(\frac{V_1}{V_0}\right)$$

And:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

b. For a free expansion the system does no work on the surroundings so $w = 0$. As this is isothermal $\Delta U = 0$ as above. Therefore, $q = 0$ from the First Law. However, as the entropy of a system is a state function and the initial and final conditions here are the same as for above:

$$\Delta S_{system} = \frac{q_{rev}}{T} = R\ln\left(\frac{V_1}{V_0}\right)$$

For the surroundings there is no actual heat flow so:

$$\Delta S_{surroundings} = 0$$

And the entropy change for the universe is given by:

$$\Delta S_{surroundings} = \Delta S_{system} + \Delta S_{surroundings} = R\ln\left(\frac{V_1}{V_0}\right)$$

c. In an adiabatic process $q = 0$ and since this is a reversible process $q_{rev} = 0$. This leads to:

$$\Delta S_{system} = 0 \Delta S_{surroundings} = 0 \Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

In summary:

Process	ΔS_{system}	$\Delta S_{surroundings}$	$\Delta S_{universe}$
a	$R\ln\left(\frac{V_1}{V_0}\right)$	$-R\ln\left(\frac{V_1}{V_0}\right)$	0
b	$R\ln\left(\frac{V_1}{V_0}\right)$	0	$R\ln\left(\frac{V_1}{V_0}\right)$
c	0	0	0

Example Problem 5.2

One mole of a diatomic ideal gas initially at $1atm$ and $298K$ undergoes the following cycle:

a. a constant volume heating to twice the initial temperature

b. an adiabatic reversible expansion back to $298K$

c. an isothermal, reversible compression back to $1atm$

Calculate Q, W ΔU and ΔS for each process and the entire cycle

Solution 5.2

First we construct the P-V diagram and calculate (T, P, V) for the gas at each stage. Using the ideal gas law for one mole:

$$V_1 = \frac{RT_1}{P_1} = 24.4\text{L}$$
$$P_2 = \frac{P_1 T_2}{T_1} = 2\text{atm}$$

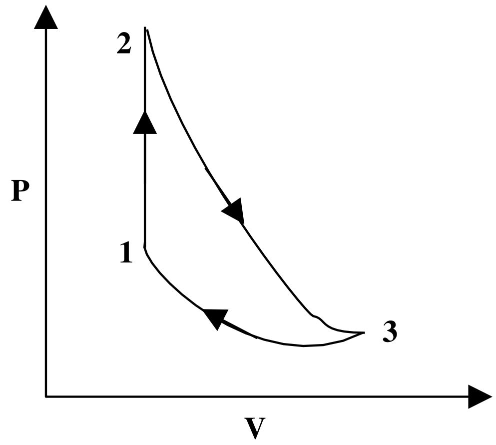

Figure 1: P-V diagram cycle

Calculating the volume and pressure for state 3 is a little more tricky. We must employ the equation for the adiabats of an ideal gas to first find the volume. The general derivation for the equation of an adiabat is shown in Example Problem 4.2. The result for an ideal gas is just stated here.

$$V_3 = V_2 \left(\frac{T_2}{T_3}\right)_\gamma$$
$$\text{with } \gamma = \frac{\overline{C}_v}{R} = \frac{5}{2}$$

$$V_3 = V_2 \left(\frac{T_2}{T_3}\right)_{\frac{5}{2}} = 138\text{L}$$
$$P_3 = \frac{RT_3}{V_3} = 0.177\text{atm}$$

In summary:

state	P (atm)	T (K)	V (L)
1	1	298	24.4
2	2	596	24.4
3	0.177	298	138

$(1 \rightarrow 2)$

$$W = -\int PdV = 0$$
$$\Delta U = Q = C_V \Delta T = \frac{5}{2}R(596 - 298) = 745R$$
$$\Delta S = \int_{298}^{596} \frac{C_V}{T} dT = \frac{5}{2} R \ln \frac{596}{298} = 1.7R$$

$(2 \rightarrow 3)$

$$Q = 0$$
$$\Delta U = W = C_V \Delta T = \frac{5}{2}R(298 - 596) = -745R$$
$$\Delta S = 0 \text{ as } (Q = Q_{rev} = 0)$$

$(2 \rightarrow 3)$

$$\Delta U = 0 \text{ as } (\Delta T = 0)$$
$$W = -Q = -\int_{V_3}^{V_1} RT \frac{dV}{V} = -RT \ln \frac{V_1}{V_3}$$
$$W = 516R$$
$$\Delta S = \frac{Q_{rev}}{T} = -1.7R$$

In summary:

Process	Q	W	ΔU	ΔS
$1 \rightarrow 2$	$745R$K	0	$745R$K	$1.7R$
$2 \rightarrow 3$	0	$-745R$K	$-745R$K	0
$3 \rightarrow 1$	$516R$K	$-516R$K	0	$-1.7R$
cycle	$1261R$K	$-1261R$K	0	0