

## Thermodynamics of Materials 3.00 Example Problems for Week 3

### Example Problem 3.1

One mole of an ideal gas, in an initial state  $P = 10\text{atm}$ ,  $V = 5\text{L}$ , is taken, reversibly, in a clockwise direction, around a circular path given by  $(V - 10)^2 + (P - 10)^2 = 25$ . Calculate the amount of work done by the gas as a result of this process, the change in internal energy of the gas, and the maximum and minimum temperatures attained by the gas during the cycle. How do these answers change if the number of moles of gas double for the same  $P$ - $V$  cycle?

### Solution 3.1

The internal energy is a state function and only depends on the initial and final states of the system. This is a closed integral so the change in internal energy is zero.  $\oint dU = 0$ .

There are two ways to calculate the work done by the system during the cycle. The first is to analytically integrate  $\int P dV$ , the second is to assess the area under the curve graphically.  $(P - 10)^2 + (V - 10)^2 = 25$  is the equation of a circle in the  $P$ - $V$  plane with center at  $(10, 10)$  and radius 5. The initial state is at the lowest allowed volume for the system,  $(V_0, P_0)$ .

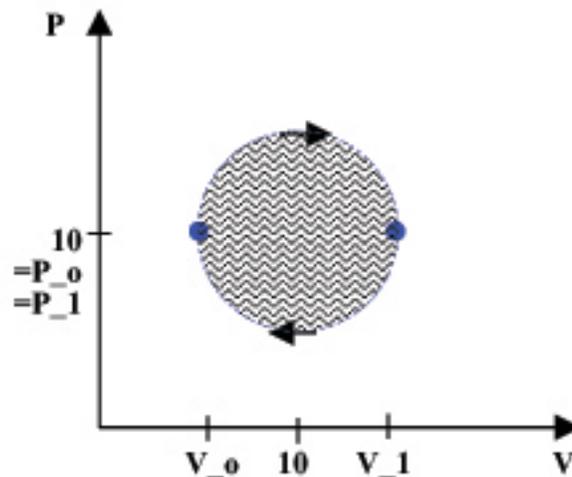


Figure 1:  $P$ - $V$  diagram for the work cycle.

First we must find  $P = P(V)$  in order to perform the integration.  $P = 10 \pm \sqrt{25 - (V - 10)^2}$  where the plus sign corresponds to the upper half of the circle ( $P_+(V)$ ) and the minus sign corresponds to the lower half ( $P_-(V)$ ). Now let  $V' = V - 10$  in the following.

$$\begin{aligned}
 W_s &= \int P dV \\
 W_s &= \int_{V_0=5}^{V_1=15} P_+(V) dV + \int_{V_1=15}^{V_0=5} P_-(V) dV \\
 W_s &= \int_{V'_0=-5}^{V'_1=5} 10 + \sqrt{25 - V'^2} dV' + \int_{V'_1=5}^{V'_0=-5} 10 - \sqrt{25 - V'^2} dV'
 \end{aligned}$$

$$W_s = \frac{25}{2}(\pi + 8) + \frac{25}{2}(\pi - 8) = 25\pi L \cdot atm$$

By this method the work done by the system is  $25\pi * 101.3J = 7956J$ . The second method involves examining the area under the curve, a circle with radius 5. So the area is  $25\pi L \cdot atm$ . This again is the work done by the system equal to  $7956J$ .

The maximum and minimum temperatures can be found from the ideal gas law for one mole of gas,  $PV = RT$ .  $T_{max}$  attains when  $(PV)$  is a maximum and  $T_{min}$  attains when  $(PV)$  is a minimum. Let  $P' = P - 10$  and  $V' = V - 10$  so  $PV$  is an extremal when  $P'V'$  is extremal.

$$P'V' = f(P'(V'), V') = \pm\sqrt{25 - V'^2}V'$$

$$\frac{df}{dV'} = 0 = \pm\sqrt{25 - V'^2} \pm V' \frac{1}{2} \frac{-2V'}{\sqrt{25 - V'^2}}$$

$$0 = \pm \left[ \frac{25 - V'^2 - V'^2}{\sqrt{25 - V'^2}} \right]$$

The extrema are for  $V' = \pm\sqrt{\frac{25}{2}}$ . Examination or checking the sign of the second derivative,  $\frac{d^2F}{dV'^2} > 0$  for a minimum and  $\frac{d^2F}{dV'^2} < 0$  for a maximum, gives the following.

[h]	$V'$	$P'$	$V$	$P$
max	$\sqrt{\frac{25}{2}}$	$\sqrt{\frac{25}{2}}$	$10 + \sqrt{\frac{25}{2}}$	$10 + \sqrt{\frac{25}{2}}$
min	$-\sqrt{\frac{25}{2}}$	$-\sqrt{\frac{25}{2}}$	$10 - \sqrt{\frac{25}{2}}$	$10 - \sqrt{\frac{25}{2}}$

This leads to  $T_{max} = (PV)_{max}/R = 2203K$  and  $T_{min} = (PV)_{min}/R = 502K$ .

If the number of moles are doubled the work done by the system is still  $W = 7956J$  but the maximum and minimum temperatures are decreased by a factor of two from  $T = PV/(nR)$  and  $T_{max} = 1102K$  and  $T_{min} = 251K$ .

### Example Problem 3.2

*One mole of ideal gas at 25° C and 1atm undergoes the following reversible process:*

1. *Isothermal expansion to 0.5atm, followed by*
2. *Isobaric expansion to 100° C, followed by*
3. *Isothermal compression to 1atm, followed by*
4. *Isobaric compression to 25° C*

*The system then undergoes the following cyclic process:*

1. *Isobaric expansion to 100° C, followed by*
2. *A decrease in pressure at constant volume to Patm, followed by*
3. *An isobaric compression at Patm to 24.5L, followed by*
4. *An increase in pressure at constant volume to 1atm.*

Calculate the value of  $P$  which makes the work done on the gas in the first cycle equal to the work done by the gas in the second cycle.

### Solution 3.2

For one mole of an ideal gas  $PV = RT$  and  $W = \int PdV$ .  $W$  is the work done by the gas. There are 3 kinds of processes here and the work must be calculated accordingly.

1. For an isothermal process ( $T$  is constant):  $P = RT/V$  so  $W = RT \ln \frac{V_1}{V_0} = RT \ln \frac{P_0}{P_1}$ .
2. For an isobaric process ( $P$  is constant):  $W = P(V_1 - V_0) = R(T_1 - T_0)$
3. For a constant volume process (one of the isochoric processes)  $W = 0$  but the pressure and temperature will change.

Let's begin by summarizing the transformations of the gas by recording the  $T, P, V$  before and after each process in liters, atmospheres and Kelvin and also the form of the work done by the system.

$T_0$	$P_0$	$V_0$	$T_1$	$P_1$	$V_1$	$W_i$
298	1	.	298	0.5	.	$W_1 = RT \ln \frac{P_0}{P_1}$
298	0.5	.	373	0.5	.	$W_2 = R(T_1 - T_0)$
373	0.5	.	373	1	.	$W_3 = RT \ln \frac{P_0}{P_1}$
373	1	.	298	1	.	$W_4 = R(T_1 - T_0)$
298	1	.	373	1	$V_u$	$W'_1 = R(T_1 - T_0)$
373	1	$V_u$	$T_3$	$P_u$	$V_u$	$W'_2 = 0$
$T_3$	$P_u$	$V_u$	$T_4$	$P_u$	24.5	$W'_3 = R(T_1 - T_0)$
.	$P_u$	24.5	.	1	24.5	$W'_4 = 0$

For the first reversible process the work done by the system is  $W = \sum_{i=1}^4 W_i$ .

$$W = \sum_{i=1}^4 W_i = 298R \ln 2 + R(373 - 298) + 373R \ln 0.5 + R(298 - 373)$$

$$W = (298 - 373)R \ln 2 = -75R \ln 2$$

For the second cyclic process the work done by the system is  $W' = \sum_{i=1}^4 W'_i$ .

$$W' = \sum_{i=1}^4 W'_i = R(373 - 298) + 0 + R(T_4 - T_3) + 0$$

$$W' = 75R + R(T_4 - T_3)$$

So we must find the unknown temperatures using  $T = PV/R$  and  $V = RT/P$ .

$$T_3 = \frac{P_u}{R} V_u = \frac{P_u}{R} \frac{373R}{1} = 373P_u$$

$$T_4 = \frac{P_u 24.5}{R}$$

Now  $W' = 75R + R\left(\frac{P_u 24.5}{R} - 373P_u\right) = 75R + RP_u\left(\frac{24.5}{R} - 373\right)$ .

The restriction that the work done on the gas in the first cycle equals the work done by the gas in the second cycle is equivalent to  $-W = W'$ .

$$W + W' = 0 = -75R \ln 2 + 75R + RP_u \left( \frac{24.5}{R} - 373 \right)$$
$$P_u = \frac{75(\ln 2 - 1)}{\frac{24.5}{R} - 373}$$

In the above  $R = 8.314 \frac{\text{J}}{\text{moleK}} \cdot \frac{1\text{atm}}{1.01310^5\text{Pa}} \cdot \frac{10^3\text{L}}{\text{m}^3} = 0.08207 \frac{\text{L}\cdot\text{atm}}{\text{moleK}}$ . So  $P_u = 0.3\text{atm}$ .