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PART I: TRUE-FALSE QUESTIONS

1. TRUE

The ideal gas law states that $PV = NkT$. For a monatomic ideal gas, $E = \frac{3}{2}NkT$. Dividing this equation by the ideal gas law yields:

$$\frac{E}{PV} = \frac{3}{2}$$

or

$$P = \frac{2}{3} \frac{E}{V}$$

2. TRUE

For an ideal gas at pressure P and volume V ,

(i) an isothermal process satisfies $PV = \text{constant}$

(ii) an adiabatic process satisfies $PV^\gamma = \text{constant}$

with $\gamma \equiv \frac{C_p}{C_v} > 1$.

For process (i),

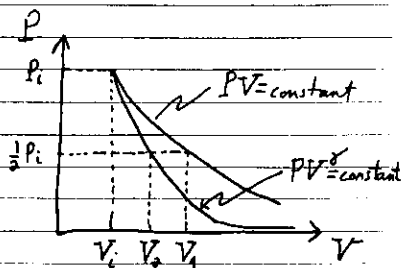
$$P_i V_i = \frac{1}{2} P_i V_1 \Rightarrow V_2 = 2V$$

For process (ii),

$$P_i V_i^\gamma = \frac{1}{2} P_i V_2^\gamma \Rightarrow V_2 = 2^{1/\gamma} V$$

Since $\gamma > 1$, $2^{1/\gamma} < 2$ which implies that $V_2 < V_1$.

THE PICTURE



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3. FALSE

An adiabatic process is one in which there is no heat exchange. For reversible processes, $q = T\Delta S$, so $q=0$ implies that $\Delta S=0$. However, for irreversible processes, $q \neq T\Delta S$. So $q=0$ does not imply that $\Delta S=0$. If the system is thermally isolated, then $q=0$ but the second law of thermodynamics implies that for irreversible processes in isolated systems, $\Delta S > 0$.

4. FALSE

For free expansion into a vacuum, we have $q=w=0$. Thus, by the first law of thermodynamics, $q = \Delta E + w$ implies that $\Delta E=0$. However, for a classical ideal gas, E is a function of the temperature alone (assuming N is fixed). Thus, $\Delta E=0$ implies that $\Delta T=0$. The temperature does not change during the free expansion of an ideal (classical) gas into a vacuum.

5. FALSE

The second law of thermodynamics states that the entropy of a system can never decrease, only if the system is isolated. In general, a system can lose entropy if the surroundings gain at least (if not more) entropy that was lost by the system. A trivial example: any object whose temperature decreases (in a reversible manner) has lost entropy.

6. TRUE

By the first law of thermodynamics, $q = dE + w$. For a reversible process, $q = TdS$ and $w = PdV$. Thus,

$$dE = TdS - PdV$$

for a reversible process. But this result is valid for any change, reversible or irreversible, which connects the same initial and final equilibrium states, since the energy depends only on the values of the parameters that describe the equilibrium macrostate.

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7. FALSE

The entropy depends only on the values of the parameters that describe the equilibrium macrostate. Thus, ΔS between two equilibrium states is independent of the path. Both reversible and irreversible paths yield the same value for ΔS .

8. FALSE

The thermal efficiency of a Carnot engine is

$$\eta = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} = 1 - \frac{Q_c}{Q_h}$$

A refrigerator works best if it removes as much heat Q_c as possible at the expense of as little work $W = Q_h - Q_c$ as possible. That is, the larger the value of

$$\frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}$$

the better the refrigerator. But we can rewrite this as

$$\begin{aligned} \frac{Q_c}{W} &= \left(\frac{Q_h - Q_c}{Q_c} \right)^{-1} = \left(\frac{Q_h}{Q_c} - 1 \right)^{-1} \\ &= \left(\frac{1}{1-\eta} - 1 \right)^{-1} \\ &= \frac{1-\eta}{\eta} \end{aligned}$$

If η is very high (i.e. η close to 1, since $\eta < 1$), then $\frac{Q_c}{W}$ is small. This is not a good refrigerator.

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PART II: Problems.

① (a) Given 500 moles of a substance,

$$\begin{aligned} N &= 500 N_A \\ &= (500) (6.022 \times 10^{23}) \\ &= 3.011 \times 10^{26} \end{aligned}$$

(b) Using $P_i V_i = N k T_i$

$$P_i = \frac{(3.011 \times 10^{26}) (1.381 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})}{1 \text{ m}^3}$$

$$= 1.247 \times 10^6 \text{ N m}^{-2}$$

$$= 12.31 \text{ atm}$$

(c) The final pressure is obtained by noting that the system is in mechanical equilibrium, so that the pressure is equal to the weight of the piston divided by its cross-sectional area.

$$\begin{aligned} P_f &= \frac{M_{\text{piston}} g}{A} = \frac{(50 \text{ kg}) (9.8 \text{ m s}^{-2})}{0.01 \text{ m}^2} \\ &= 4.9 \times 10^4 \text{ N m}^{-2} \\ &= 0.48 \text{ atm} \end{aligned}$$

(d) The system is thermally isolated, so there is no heat exchange, i.e. $q=0$. By the 1st law of thermodynamics, $q = \Delta E + w$. Hence,

$$\Delta E = -w$$

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where w is the work done by the system as the gas expands.
In this case,

$$w = P_f \Delta V \\ = P_f (V_f - V_i)$$

The relevant pressure is P_f , since the gas is pushing against the full weight of the piston. This is not a quasi-static reversible process!

(e) For an ideal monatomic ideal gas, $E = \frac{3}{2} NkT$, so

$$\Delta E = \frac{3}{2} Nk\Delta T$$

Using the ideal gas law, $Nk\Delta T = P_f V_f - P_i V_i$. So,

$$\Delta E = \frac{3}{2} (P_f V_f - P_i V_i)$$

Finally, using the results of part (d),

$$\Delta E = -w = -P_f (V_f - V_i)$$

we end up with

$$\frac{3}{2} (P_f V_f - P_i V_i) = -P_f (V_f - V_i)$$

Solving for V_f ,

$$V_f = \frac{2}{5} V_i \left(1 + \frac{3}{2} \frac{P_i}{P_f} \right) \\ = \frac{2}{5} (1 \text{ m}^3) \left(1 + \frac{3}{2} \frac{12.31 \text{ atm}}{0.48 \text{ atm}} \right) \\ = 15.8 \text{ m}^3$$

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(f) Now that we have V_f and P_f , we can use the ideal gas law to obtain T_f :

$$T_f = \frac{P_f V_f}{Nk} = \frac{(4.9 \times 10^4 \text{ N m}^{-2})(15.8 \text{ m}^3)}{(3.011 \times 10^{26})(1.381 \times 10^{-23} \text{ J K}^{-1})} \\ = 186 \text{ K}$$

Note: Alternatively, I can express V_f in terms of V_i and the initial and final pressures. Then, use the ideal gas law to eliminate V_i . The result is:

$$T_f = \frac{3}{5} T_i \left(1 + \frac{3}{2} \frac{P_f}{P_i} \right)$$

which yields the same numerical result for T_f .

- (2) (a) Consider $n = n_1 + n_2 + \dots + n_w$, where the n_j are non-negative integers. The number of possible arrangements of n_j is equal to the number of ways of distributing n indistinguishable balls in N boxes. In class, we showed how to do the counting. Let $*$ represent a ball and a vertical line represent the wall of one of the boxes. Then, a typical configuration might be

|*|**||*|***|**|

Different arrangements correspond to the number of ways of choosing n stars out of $n+N-1$ symbols (either $*$'s or $|$'s). Note that the two vertical lines at either end remain fixed, so we have $N-1$ vertical lines to move around. Thus,

$$g(N, n) = C(n+N-1, n) \\ = \frac{(n+N-1)!}{n!(N-1)!}$$

- (b) The entropy is given by

$$S = k \ln g(N, n) \\ = k [\ln(n+N-1)! - \ln n! - \ln(N-1)!]$$

Since $E = k_w n$, we can write this as:

$$S = k \left[\ln \left(N + \frac{E}{k_w} - 1 \right)! - \ln \left(\frac{E}{k_w} \right)! - \ln(N-1)! \right]$$

For $N \gg 1$ and $E \gg k_w$, we can use Stirling's approximation: $\ln N! \approx N \ln N - N$ to write:

$$S = k \left[\left(N + \frac{E}{k_w} - 1 \right) \ln \left(N + \frac{E}{k_w} - 1 \right) - \left(N + \frac{E}{k_w} - 1 \right) \right. \\ \left. - \frac{E}{k_w} \ln \frac{E}{k_w} + \frac{E}{k_w} - (N-1) \ln(N-1) + N-1 \right]$$

or

$$S = k \left[\left(N + \frac{E}{k_w} - 1 \right) \ln \left(N + \frac{E}{k_w} - 1 \right) - \frac{E}{k_w} \ln \frac{E}{k_w} \right. \\ \left. - (N-1) \ln(N-1) \right]$$

Finally, since $N \gg 1$, we can approximate $N-1 \approx N$. Thus,

$$S = k \left[\left(N + \frac{E}{k_w} \right) \ln \left(N + \frac{E}{k_w} \right) - \frac{E}{k_w} \ln \frac{E}{k_w} - N \ln N \right]$$

(c) $\frac{1}{T} = \frac{\partial S}{\partial E}$

Using the result of part (b),

$$\frac{1}{T} = k \left[\frac{1}{k_w} \ln \left(N + \frac{E}{k_w} \right) - \frac{1}{k_w} - \frac{1}{k_w} \ln \frac{E}{k_w} + \frac{1}{k_w} \right] \\ = \frac{k}{k_w} \left[\ln \left(N + \frac{E}{k_w} \right) - \ln \left(\frac{E}{k_w} \right) \right] \\ = \frac{k}{k_w} \ln \left(\frac{k_w N}{E} + 1 \right)$$

Thus,

$$kT = \frac{k_w}{\ln \left(\frac{k_w N}{E} + 1 \right)}$$

(9)

(d) Defining $\varepsilon \equiv \frac{E}{N}$, we can rewrite the result of part (c) as

$$\frac{kW}{RT} = \ln\left(\frac{kW}{\varepsilon} + 1\right)$$

or

$$\frac{kW}{\varepsilon} + 1 = e^{kW/RT}$$

Solving for ε ,

$$\varepsilon = \frac{kW}{e^{kW/RT} - 1}$$

(e) In the limit of $T \rightarrow \infty$, $\frac{kW}{RT} \rightarrow 0$. Thus,

$$e^{kW/RT} \approx 1 + \frac{kW}{RT}$$

Thus, in this approximation,

$$\varepsilon \approx \frac{kW}{\left(1 + \frac{kW}{RT}\right) - 1} = \frac{kW}{\left(\frac{kW}{RT}\right)}$$

That is,

$$\varepsilon = kT$$

or equivalently, $\lim_{T \rightarrow \infty} \frac{\varepsilon}{RT} = 1$.