Tuesday & Wednesday Oct 1 & 2  

F19 110A LECTURE #3 & 4 

LECTURE #3

LAST TIME (#2) WE CONSIDERED A PARTICULAR SYSTEM (n moles of gas at temperature T) UNDERGOING A GIVEN CHANGE OF STATE (n, T, pi, Vi → n, T, ½pi, 2Vi). WE FOUND THAT THE WORK PERFORMED ON THE SYSTEM DEPENDED ON THE PATH USED TO CARRY OUT THIS CHANGE OF STATE, e.g.,

\[ w = w_{1-step} \neq w' = w_{2-step}. \]

WHAT IS ΔU FOR THESE TWO PROCESSES?

IT DOES NOT DEPEND ON PATH!

BUT, RATHER, ΔU DEPENDS ONLY ON INITIAL AND FINAL STATES, because – unlike w, and q – U is a state function, i.e., it is uniquely (well-) defined for each state of the system.

It follows (from ΔU = q + w) that the heat absorbed, q, must also – like w – depend on path (and in a way that “cancels” the path-dependence of w).

Further, in this particular case, involving an ideal gas whose energy depends only on temperature, ΔU = 0 (because T is constant) and q(>0) = -w for each path.

NOTE: The 1-step and 2-step paths are irreversible in the sense that these processes – unlike a reversible one – cannot be reversed at any point by an infinitesimal change in the surroundings (external pressure ↔ mass on piston, in this instance).

\[ \rightarrow \text{Any m-step process (even for m large) is still irreversible, and (see # 4 in Problem Set 1)} \]

\[ \rightarrow |w_{1-step}| < |w_{2-step}| < |w_{3-step}| < \ldots \ldots < |w_{\infty-step}| \]

i.e.,

\[ |w_{irreversible}| < |w_{reversible}|, \text{for expansion} \]

(with the opposite holding for compression)

\[ \rightarrow \text{Further, ΔU is the same (ΔU = 0 in this case) for all paths.} \]

HOW DO WE CALCULATE THE WORK PERFORMED, FOR THE ∞-step (REVERSIBLE!) PATH FOLLOWED BY THIS CONFINED GAS?

The way to think about it is in terms of decreasing the mass on the piston by an infinitesimal amount in each of the infinite number of expansion steps, as we carry out the doubling of the volume.

Throughout this process, p_{ext} never differs more than infinitesimally from

\[ p_{system} = p = p_{gas} = \frac{nRT}{V} \]

so that we can evaluate the work as follows:
\[ w_{\infty-\text{step}} = -\int_{i}^{f} p_{\text{ext}} \, dV = -\int_{i}^{f} \frac{nRT}{V} \, dV = -nRT \int_{V_{i}}^{V_{f}} \frac{1}{V} \, dV = -nRT \ln \frac{V_{f}}{V_{i}} = -nRT \ln 2 \]

\[ = -0.693nRT, \]

confirming that, indeed,

\[ |w_{1-\text{step}}| = \left(\frac{1}{2} = 0.50\right)nRT \quad < \quad |w_{2-\text{step}}| = \left(\frac{7}{12} = 0.58\right)nRT \quad < \quad |w_{\infty-\text{step}}| = 0.69nRT. \]

NOTE: The mechanical work is always defined and calculated the same way, namely, by evaluating \( w_{\text{mech}} = -\int_{V_{i}}^{V_{f}} p_{\text{ext}}(V) \, dV \), regardless of whether the process involved is reversible or not. Further, \( p_{\text{ext}}(V) \equiv p(V) \) if and only if the process is reversible.

\[ \rightarrow \text{Clearly, for any process is which the volume } V \text{ remains constant throughout, } w_{\text{mech}} \text{ is identically zero.} \]

In this (constant-volume) case, \( \Delta U = q + w = q = q_{V} \), and measurement of the heat absorbed (in a constant-\( V \)) process implies directly \( \Delta U \) for that change of state—as long as no other kind of work is involved.

BUT WHAT ABOUT OTHER KINDS OF WORK (e.g., electrical work, \( w_{\text{elec}} \))?

\[ \rightarrow w_{\text{elec}} = \text{work done in moving charge } Q \text{ through a potential difference (voltage) } \phi \]
\[ = Q \phi. \]

For a steady current \( I \) flowing for a time \( t \), \( Q = I \, t \) and \( w_{\text{elec}} = I \, t \, \phi \) with \( I \) in amps (A), \( t \) in sec (s) and \( \phi \) in volts (v). (Further, 1 A s J = 1 J [Joule].)

(Chapter 2 figure in textbook)

\( \rightarrow \) Lowering of mass generates current \( I \) for time \( t \) through aqueous solution, across voltage \( \phi \). The transfer of electrons drives the hydrolysis reaction

\[ H_{2}O(l) \rightarrow H_{2}(g) + \frac{1}{2}O_{2}(g), \]

with associated electrical work

\[ w_{\text{elec}} = I \, t \, \phi, >0, \]

done by surroundings on system.

\[ \rightarrow \text{As a consequence, liquid is transformed to gas, and the resulting expansion leads to the system doing work on the surroundings:} \]

\[ w_{\text{mech}} = -p_{\text{ext}}(V_{f} - V_{i}), < 0. \]
Lecture #4

Let’s consider again the reversible expansion/compression of an ideal gas.

→ Again start with the gas in thermal equilibrium at temperature $T_i$, confined by a movable piston in a cylinder.

But instead of keeping the temperature constant, we make the walls adiabatic, implying $q = 0$ and $\Delta U = w$ (dU = d\bar{w}) for the expansion/compression change of state.

Here $dU = d\bar{w}$ is the differential/infinitesimal statement of $\Delta U = w$.

Note: The overbar on $d$ in $d\bar{w}$ calls attention to the fact that the $w$ is not a difference between state functions evaluated at initial and final state.

We do not put an overbar on the $d$ in $dU$ because $U$ is a state function and the infinitesimal quantity (exact differential) $dU$ can be integrated (from initial to final state along any path) to give $\Delta U$, which depends on the initial and final states. By contrast, the integral of $d\bar{w}$ over a given path is intended to give $w$, the path-dependent work performed in carrying out the change from initial to final state. Similarly, $q$ is the integral of $d\bar{q}$.

→ $dU = C_V dT$ for an ideal gas, where $C_V$ is the constant-volume heat capacity.

“Proof”: Start with the 1st Law written in its differential form, $dU = \bar{d}q + d\bar{w}$. Writing $d\bar{w} = -P_{\text{ext}} dV$ and imposing the condition of constant volume, we have $dU = \bar{d}q$ (constant $V$), or $dU = \bar{d} q_V$. But then from the definition of the constant-volume heat capacity, $C_V \equiv \frac{\bar{d}q_V}{dT}$, we have $dU = \bar{d} q_V$.

Thus we can write $C_V dT = \bar{d}w = -P_{\text{ext}} dV$.

It follows that, if the change of state is carried out reversibly, we can write $P_{\text{ext}} = p = \frac{nRT}{V}$ and hence $C_V dT = -\frac{nRT}{V} dV$, or $C_V \frac{dT}{T} = -nR \frac{dV}{V}$.

Integrating from the initial $(T_i, V_i)$ to final $(T_f, V_f)$ state, and neglecting the weak dependence of $C_V$ on temperature, we obtain

$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$.

→ Using $nR = C_p - C_V$ for an ideal gas, which we’ll show in a later lecture (here $C_p$ is the constant-pressure heat capacity), the above equation becomes

$\ln \frac{T_f}{T_i} = -(\gamma - 1) \ln \frac{V_f}{V_i}$ with $\gamma \equiv \frac{C_p}{C_V}$,

⇒’ing $T_f = \left(\frac{V_i}{V_f}\right)^{\gamma-1} T_i$. 

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More explicitly, if we carry out a reversible, adiabatic, expansion/compression (of an ideal gas) from an initial volume $V_i$ to a final volume $V_f$, the temperature will change from to $T_i$ to $T_f = \left(\frac{V_i}{V_f}\right)^{\gamma - 1}T_i$.

Further, because $\gamma(\equiv \frac{C_p}{C_v}) > 1 \iff (\gamma - 1) > 0$, it follows that

$$\left(\frac{V_i}{V_f}\right) < 1 \text{ (i.e., expansion)} \implies T_f < T_i \text{ (i.e., gas cools)}$$

and

$$\left(\frac{V_i}{V_f}\right) > 1 \text{ (i.e., compression)} \implies T_f > T_i \text{ (i.e., gas warms up)}$$

→ How does the gas pressure change?

Substituting $\frac{P_fV_f}{P_iV_i} = \frac{T_f}{T_i}$ into the preceding equation ($T_f = \left(\frac{V_i}{V_f}\right)^{\gamma - 1}T_i$), gives

$$P_f = \left(\frac{V_i}{V_f}\right)^{\gamma}P_i.$$  

NOTE: The fact that $\gamma > 1$ implies that $P_f < P_i$ for expansion, whereas $P_f > P_i$ for compression.

What if we compare “isotherms” and “adiabats”? That is, we compare $P$ vs $V$ curves for isothermal/reversible and adiabatic/reversible changes of state (for an ideal gas).

→ Consider 1 mole of gas at a pressure of 1 atm and a volume of 25L, \(\Rightarrow\) ing $T_i = \frac{P_iV_i}{(1 \text{ mole})R} = \frac{(1 \text{ atm})(25L)}{(0.082L \cdot \text{atm} / K)} = 305K$

FIRST we have this system undergo a reversible isothermal compression from 25L to 10L:

$$P_{iso}^f = \frac{nRT_f}{V_f} = \frac{nRT_i}{V_f} \quad \text{(why?)} = \frac{P_iV_i}{V_f} = \frac{(1 \text{ atm})(25L)}{10L} = 2.5 \text{ atm.}$$

SECOND, we have the system undergo a reversible adiabatic compression, again from 25 to 10L.

$$P_{ad}^f = \left(\frac{V_i}{V_f}\right)^\gamma P_i = \left(\frac{25L}{10L}\right)^{7/5} (1 \text{ atm}) = 3.5 \text{ atm.}$$

[Here we have used the value (7/5) of $\gamma$ appropriate to a diatomic gas.]

Comparing the $P$ vs $V$ curves corresponding to the above results, we have
(for 1 mole of diatomic, ideal, gas)

(CAN YOU REPRODUCE (CALCULATE) THESE PLOTS?)