Reversible and irreversible work

In chemical reactions we cannot often control the pressure. This is why we say that the pressure is constant and we write w = -P∆V. However, when we design a process to extract work from heat (i.e. in an engine) we want the pressure to change gradually. In the ideal case the pressure change is infinitely slow and we have a reversible process. Let's compare the energy we can extract from a reversible and irreversible process.

$$w_{irr} = -P_{ext}(V_2 - V_1) \qquad w_{rev} = -nRTln\left(\frac{V_2}{V_1}\right)$$

What is the maximum pressure you can have as the final pressure (P_{ext})? Note that V_1 is the initial volume and V_2 is the final volume, so the pressure must correspond to the final condition. The number of moles is n and the temperature is T in both cases (i.e. it is the same).

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Using the final condition we have

$$P_{ext} = \frac{nRT}{V_2}$$

Therefore,

$$w_{irr} = -\frac{nRT}{V_2}(V_2 - V_1)$$

Finally, we can write an expression only in terms of n, T and the two volumes, precisely as we did for the reversible case.

$$w_{irr} = -nRT\left(1 - \frac{V_1}{V_2}\right)$$