Now, fix *T* (isothermic) $p_1, V_1, T_0 \rightarrow p_2, V_2, T_0$

add heat quasi-statically

$p_{ext} = p_{\text{int}}$, but not constant

$$w = -\int_{V_1}^{V_2} p_{ext}\, dV = -\int_{V_1}^{V_2} p_{\text{int}}\, dV$$

$$w = -\int_{V_1}^{V_2} \frac{NkT_0}{V}\, dV = -NkT_0 \ell n\left(\frac{V_2}{V_1}\right) = -NkT_0 \ell n\left(\frac{p_1}{p_2}\right)$$

$$\left[\text{Ideal gas } C_V = \frac{3R}{2} \text{ or } U = \frac{3RT}{2}\right]$$

for const. *T* process, energy of an ideal gas does not change

$$q = -w = NkT_0 \ell n\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = q / T_0$$

or

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

$$dS = \frac{NkT}{T}\frac{dV}{V}$$

$$\Delta S = Nk \ell n\left(\frac{V_2}{V_1}\right) = \frac{q}{T_0}$$

Const. *T* process

quasi-static

rev

a quasi-static process can be irreversible if heat flows in or out of system or if entropy is created

$$dU = TdS - pdV$$

Fourth case: adiabatic: no heat flow

$$dU = \delta w$$

if you change one of *T, p, V*, the other two variables change

$$(p_1, V_1, T_1) \rightarrow (p_2, V_2, T_2)$$

$$dU = C_V dT = -pdV$$

$$C_V dT = \frac{-NkT}{V} dV \quad \Big| \quad p = \frac{NkT}{V}, \quad \text{ideal gas}$$

p appears rather than p_{ext} since we are assuming a reversible process

$$\frac{C_V dT}{T} = -\frac{Nk}{V} dV$$

$$C_V \ell n \frac{T_2}{T_1} = -Nk \ell n \left(\frac{V_2}{V_1} \right)$$

$$\rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{NK/C_V}$$

Pathways

None of the 4 processes just considered allows one to reach an arbitrary (p_2, V_2, T_2) from a starting (p_1, V_1, T_1)

You can achieve this through a sequence of steps (a pathway)

w, q are path dependent
S, U are state functions

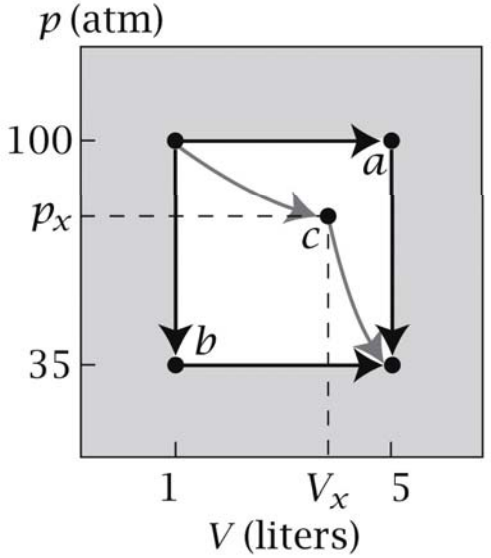


Figure 7.3 Molecular Driving Forces 2/e (© Garland Science 2011)

Path *a*

1 mol of gas (ideal) with *V* = 1 L, *p* = 100 atm, evolves to *V* = 5L, *p* = 35 atm,

(1) fixed applied p_1
expand to V_2

$$w = -p_1(V_2 - V_1) = -400 liter \cdot atm$$

(2) now decrease pressure to p_2 at fixed V_2

$$w = 0$$

So for the complete path a: w = -400 liter•atm

Path ***b***

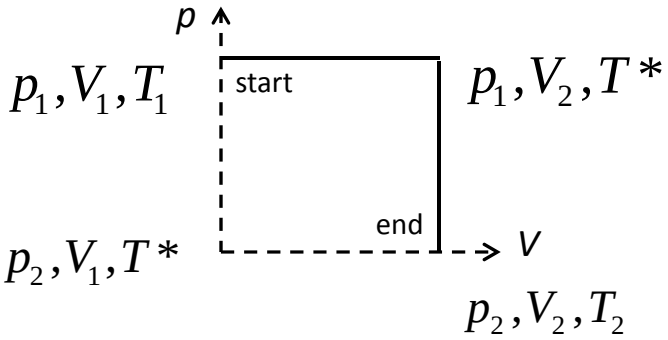
Along path b:

change vol. from V_1 to V_2 at fixed p_2

Then change p_2 to p_1 at fixed V_2

$$w_{tot} = 0 - p_2\left(V_2 - V_1\right) = -140\ell atm$$

For the two pathways, considered above the energy charge is the same



$$T_1 = p_1V_1 / R = \frac{100(1)}{.0820} = 1200K$$

$$R = 0.0820\frac{L \bullet atm}{K \bullet mol}$$

$$T_2 = \frac{p_2 V_2}{R} = \frac{(35)(5)}{0.0820} = 2100K$$

$$\Delta U = C_V \Delta T = 3/2R\left(T_2 - T_1\right) = 111\ell \bullet atm$$ independent of path

For any pathway $q + w = \Delta U$

Route a const. *p* $q = C_V\left(T_2 - T_x\right) + p_1\left(V_2 - V_1\right)$

const. *V* $q = C_V\left(T_x - T_1\right)$

$$q_{tot} = C_V\left(T_2 - T_1\right) + p_1\left(V_2 - V_1\right)$$

$$\Delta U = q_a + w_a = C_V\left(T_2 - T_1\right)$$

corrected Eq. 7.14

quasi-static

Eq. 7.14 $$q = \left(\frac{C_V}{Nk} + 1\right) p_1\left(V_2 - V_1\right)$$

$$= \frac{C_V}{Nk} p_1\left(V_2 - V_1\right) + p_1\left(V_2 - V_1\right)$$

$$= C_V\left(T_2 - T_1\right) + p_1\left(V_2 - V_1\right)$$

If you cannot measure ΔU or ΔS directly, can measure heat + work along some convenient quasi-static pathway to get ΔU , ΔS

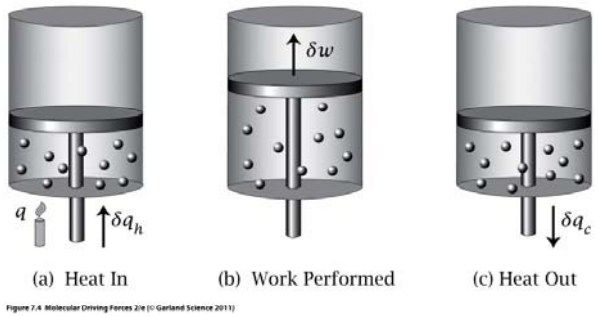
Can use reversible path to get $\Delta S = \frac{q_{rev}}{T}$

$$TdS = dU + pdV = \delta q - \delta w + pdV$$
$$= \delta q - p_{ext}dV + pdV$$
$$= \delta q_{rev}$$

Cycle – starting state → intermediate states → starting state

Examples are engines, refrigerators

For a cycle $\Delta U = 0$



heat in (T_h)

work performed (δw)

heat out (T_c)

Carnot cycle (1824): gives us a handle on efficiency

$A \to B$ isothermal expansion

$$q_h = -w = NkT_h \ell n\left(\frac{V_B}{V_A}\right)$$

$B \to C$ adiabatic expansion

$$q = 0$$

$C \to D$ isothermal compression

$$q_C = -w = NkT_c \ell n\left(\frac{V_D}{V_C}\right)$$

$D \to A$ adiabatic compression

$$q = 0$$

work depends on

T_h, T_c

V_B / V_A = compression ratio

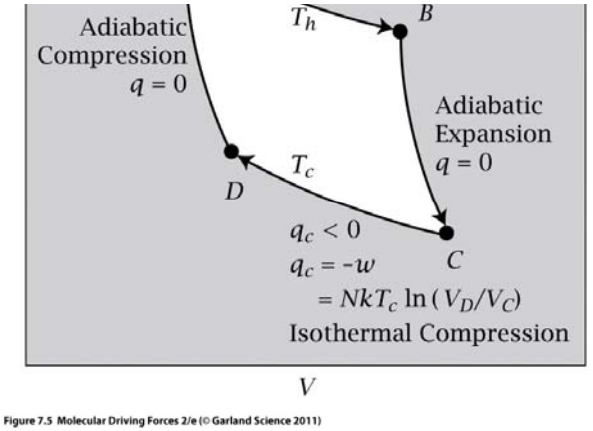


Figure 7.5 Molecular Driving Forces 2/e (© Garland Science 2011)

$$q_{tot} = kT_h \ell n\left(\frac{V_B}{V_A}\right) + NkT_C \ell n\left(\frac{V_D}{V_C}\right)$$

$$w_{tot} = -q_{tot} = -Nk\left(T_h - T_c\right) \ell n\left(\frac{V_B}{V_A}\right)$$

using Eq. 7.21

$p_A V_A T_A$ $\quad T_A = T_{hot}$

$\downarrow$

$p_B V_B T_B,$ $\quad T_B = T_{hot}$

$\downarrow$

$p_A V_C T_C$ $\quad \left(T_C = T_{cold}\right)$

$\downarrow$

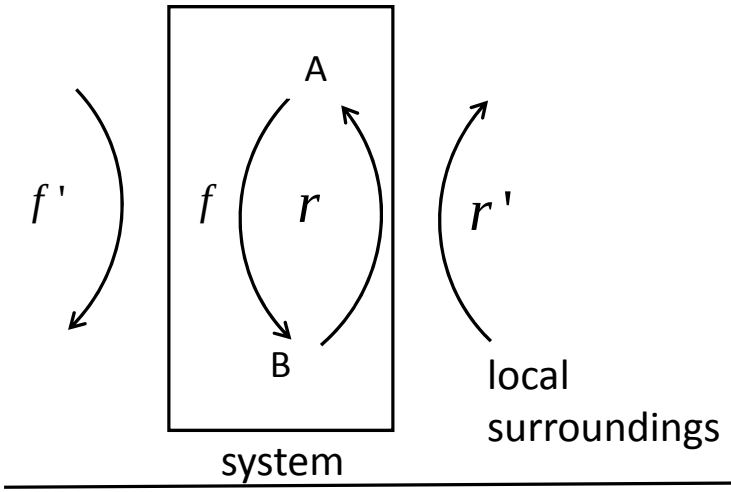
$p_D V_D T_D,$ $\quad T_D = T_{cold}$

$\downarrow$

$p_A V_A T_A$

Maximum possible work requires reversible processes

$$\Delta S_f + \Delta S_r = 0$$
system closed cycle



$$\Delta S_{tot} = \Delta S_f + \Delta S_{f'} \geq 0$$
$$\Delta S_r + \Delta S_{r'} \geq 0$$

= 0 at equilibrium

If reversible $\rightarrow$ both system + surroundings are restored to initial state

$$\Delta S = \Delta S_f + \Delta S_r + \Delta S_{f'} + \Delta S_{r'} = 0$$

$\Delta S_{f'} + \Delta S_{r'} = 0$ for rev. process

Carnot cycle each step assumed to be reversible

two steps are adiabatic $\Rightarrow \Delta S = q/T = 0$

two steps are isothermal $\Delta S_{AB} = \dfrac{q_h}{T_h} = Nk\ell n \dfrac{V_B}{V_A}$ $\Bigg|$ $\dfrac{V_B}{V_A} = \dfrac{V_C}{V_D}$ $\Rightarrow \Delta S_{cycle} = 0$

$$\Delta S_{CD} = \frac{q_c}{T_c} = Nk\ell n \frac{V_A}{V_B}$$

Efficiency of an engine: Ratio of work done to heat transferred

1. take in heat q_h at T_h
2. perform work w adiabatically
3. expel heat q_c at T_c

efficiency = $\eta = \dfrac{-w}{q_h} = 1 + \dfrac{q_c}{q_h}$ $\Bigg|$ $\Delta U_{cycle} = 0$, $w = q_h + q_c$

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

Free expansion of a gas is irreversible

free expansion of gas against 0 applied pressure $\left(p_{ext}=0\right)$

work = 0

If done adiabatically $q=0$

$\Delta U=0$

$\Delta U = C_V \Delta T = 0 \Rightarrow$ process is isothermal

What is the entropy change for free expansion at fixed *T*?

$$\Delta S_{system} = Nk\ell n\left(\frac{V_2}{V_1}\right) > 0$$

$$\Delta S_{surr} = 0 \qquad \left| \; q=0, \text{ so } \Delta S = q_{rev}/T = 0 \right.$$

$$\Delta S_{tot} > 0$$

Other irreversible processes:

- diffusion/mixing
- heat flow from hot to cold object
- friction

$$\eta = 1 - \frac{q_c}{q_h}$$

$$\Delta S = \Delta S_h + \Delta S_a + \Delta S_c$$

$$\Delta S_h = \frac{q_h}{T_h},\ \Delta S_c = \frac{q_c}{T_c} \quad \text{or} \quad \frac{q_c}{q_h} = -\frac{T_c}{T_h}$$

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

want as large a temperature differential as possible

Can only get 100% efficiency if $T_c = 0$ or $T_h = \infty$

NOTE This has assumed no friction

Internal combustion engine

$(b)\ \ w_3 = 0$

$$q_b = \Delta U_b = C_V \left(T_2 - T_1\right)$$

$(c)\ \ q_c = 0$

$$w_c = \Delta U_c = C_V \left(T_3 - T_2\right)$$

$(d+e)\ \ w = 0$

$$q_{de} = C_V \left(T_4 - T_3\right)$$

$(f)\ \ q_f = 0$

$$w_f = C_V \left(T_1 - T_4\right)$$

a) ignition	V_1, p_1	
b) explosion	V_1, p_2	
c) exp work	V_2, p_3	adiabatic
d) exhaust	V_1, p_4	
e) intake	V_2, p_4	
f) compression	V_1, p_1	adiabatic

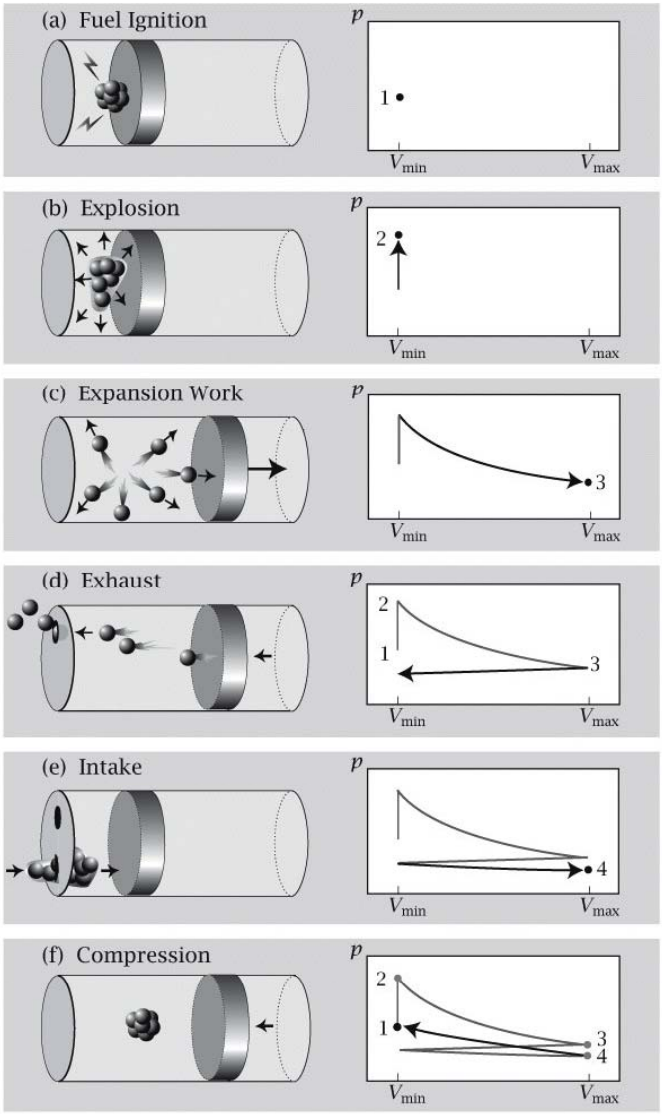


Figure 7.7 Molecular Driving Forces 2/e (© Garland Science 2011)

$$\eta = \frac{-\left(w_f + w_c\right)}{q_b} = \frac{-C_V\left(T_1 - T_4\right) - C_V\left(T_3 - T_2\right)}{C_V\left(T_2 - T_1\right)} = 1 - \frac{T_3 - T_4}{T_2 - T_1}$$

$$\frac{T_3}{T_2} = \left(\frac{V_1}{V_2}\right)^{Nk/C_V} ; \frac{T_4}{T_1} = \left(\frac{V_1}{V_2}\right)^{Nk/C_V}$$

$$\eta = 1 - \left(\frac{V_1}{V_2}\right)^{Nk/C_V}$$

compression ratios 4-10

$$\eta = 1 - \left(0.4\right)^{2/3} = 0.46$$

$$\eta = 1 - \left(0.1\right)^{2/3} = 0.78$$

Actually using the C_V value for octane (a major component of gasoline) shows that it is hard to get above ~25 % efficiency for the internal combustion engine.

Many cars are doing much more poorly than this.