So far we have written a large number of equations. Working a problem would be a terrible task if it were done by searching through such a bewildering array of equations in the hope of quickly finding the right one. Only the fundamental equations should be used in application to any problem. The conditions set in the problem immediately limit these fundamental equations to simple forms from which it should be clear how to calculate the unknowns in the problem. So far we have only seven fundamental equations:

1. Expansion or compression work	$\delta W = -p_{op} dV$
2. The statement of the first law	$\mathrm{d}U = \partial q + \partial W$
3. The definition of enthalpy	$H \equiv U + pV$

4. The definition of the heat capacities:

$$C_{V} \equiv (\partial q_{V} / dT) = (\partial U / \partial T)_{V}$$

$$C_{p} \equiv (\partial q_{p} / dT) = (\partial H / \partial T)_{p}$$

5. Two purely mathematical consequences:

$$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T dV$$
$$d\boldsymbol{H} = C_p dT + (\partial \boldsymbol{H}/\partial p)_T dp$$

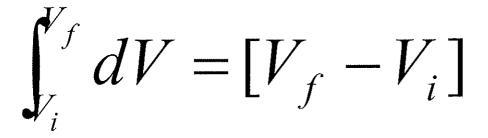
Of course it is essential to understand the meaning of these equations and the meaning of such terms as isothermal, adiabatic, reversible, etc. These terms have definite mathematical consequences to the equations.

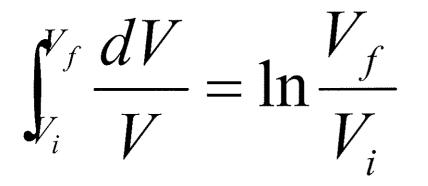
In addition, for problems involving the ideal gas,

- the equation of state should be known, pV = nRT
- the mathematical consequences of Joule's law, $(\partial U/\partial V)_T = 0$
- the relation between the heat capacities $C_p C_V = R$ which can be derived from the above equations

The equations which solve each problem must be <u>derived</u> from these few fundamental equations.

Integration:





 $\int_{V_{i}}^{V_{f}} \frac{dV}{V^{2}} = -2[V_{f}^{-1} - V_{i}^{-1}]$

 $\int_{V_{i}}^{f} V dV = \mathbb{1}[V_{f}^{2} - V_{i}^{2}]$

 $\int_{V_{\cdot}}^{V_{f}} F(V) dV \neq F(V) \int_{V_{\cdot}}^{V_{f}} dV$

Common	
misconceptions	INSTEAD, USE:
DO NOT USE:	
$\Delta H = C_p \Delta T$	$\Delta H = \int C_{\rho} \mathrm{d}T$
	+∫(∂ <i>H/∂p)</i> _T dp
$\Delta U = C_v \Delta T$ or	$\Delta U = \int C_V \mathrm{d}T$
(3/2)RAT	+∫(∂ <i>U/</i> ∂ <i>V</i>) ₇ d <i>V</i>
$q = C_p \Delta T$	$q_p = \int C_p \mathrm{d}T$
	or $q_p = \Delta H$
	$q_V = \int C_V dT$
	or $q_V = \Delta U$
q = 0 for	q=0 for an
isothermal	adiabatic process.
process	dT = 0 for an
	isothermal process.
	isothermal process
	can have q≠0,
	examples are
	changes in phase
	or structure

Common misconceptions	INSTEAD, USE:
DO NOT USE:	
$W = -p_{op} \int dV$ or	$W = - \int p_{op} dV$
W = -∫pdV or	
$W = -p\Delta V$ or	
$W = -RTln(V_f/V_i)$	
U = q + W or	$\Delta U = q + W$
$U = \Delta q + \Delta W$ or	
$q_1/w_1 = q_2/W_2$	
$p_1T_1=P_2T_2$ ideal	pV =nRT, ideal gas
gas	
$\Delta H = -0.1 \text{ Lmol}^{-1}$	check dimensions
	are correct
dU = 80 J	dU is an arbitrarily
	infinitesimally small
	increment in U and
	an exact differential
	so that
	$\int dU = U_f - U_i \equiv \Delta U$

Common misconceptions DO NOT USE:	INSTEAD, USE:
wrong signs of q and W	∆U =q + W consider system bank account of internal energy use sign according to what goes in or out
-b∫dp = - b ∫[nRT/(V-nb)]dV	no need to change variables unless necessary - b∫dp = -b[p _f - p _i]
$\Delta H = \Delta U + W \text{ or}$ $\Delta H = \Delta U + nRT$	$H \equiv U + pV$ dH = dU+pdV+Vdp
$\Delta H = q$	Only in a constant pressure process we can find ΔH by measuring q_p

Common misconceptions DO NOT USE:	INSTEAD, USE:
reverse the signs of q and	reversing the sign of ΔU or ΔH when
W for reverse	the process in the
process	opposite direction is being considered
	is based on
	switching the final and initial states
	since $U_f - U_i \equiv \Delta U$.
	q and Ŵ are <u>not</u>
	state functions so
	this can not be
	applied.

 $dU = 0 + (\partial U / \partial V)_T dV = C_V$???? (from a student paper)

Question: How do you keep yourself from doing something like this?

Answer. THINK about what you are writing down.

In calculus, the symbol d means an infinitesimal quantity, that means, the left hand side d*U* is an INFINITESIMALLY SMALL number with units of energy.

On the other hand, the far right hand side, C_V , is a finite number, something like (3/2)R, and therefore should not appear in an equation as equal to an infinitesimal. Moreover, C_V has units, according to the definition, of energy divided by temperature, whereas the left hand side has units of energy!

Whenever you have an equal sign, check to see that the dimensions are the same for both sides.

van der Waals gas: $\{p + n^2 a/V^2\} \bullet (V-nb) = nRT$

or a more intuitively obvious form:

$$p = \{nRT/(V-nb)\} - n^2a/V^2$$

which shows that "sticky, associative" encounters lead to smaller pressure than ideal

NOT $\{(p + n^2 a)/V^2\} \bullet \{V - nb\} = nRT$ because if so, the dimensions of the larger term $\{p/V^2\} \bullet \{V\}$ don't make units of energy, as dictated by the right hand side!! NOT $p = \{nRT/(V - nb)\} \bullet V^2 - n^2 a$ because if so, the dimensions of the larger term $p = \{nRT\} \bullet \{V\} + ... L^2$ atm makes no sense, since p should be atm, not L² atm! fractions:

