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 $đW = -p_{op}\mathrm{d}V$
2. The statement of the first law $\mathrm{d}U = đq + đW$
3. The definition of enthalpy $H \equiv U + pV$

4. The definition of the heat capacities:

$$\boldsymbol{C_V} \equiv (đ\boldsymbol{q_V}/\mathrm{d}T) = (\partial \boldsymbol{U}/\partial T)_V$$
$$\boldsymbol{C_p} \equiv (đ\boldsymbol{q_p}/\mathrm{d}T) = (\partial \boldsymbol{H}/\partial T)_p$$

5. Two purely mathematical consequences:

$$\mathrm{d}\boldsymbol{U} = C_V\mathrm{d}T + (\partial \boldsymbol{U}/\partial V)_T\mathrm{d}V$$
$$\mathrm{d}\boldsymbol{H} = C_p\mathrm{d}T + (\partial \boldsymbol{H}/\partial p)_T\mathrm{d}p$$

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, $(\partial \boldsymbol{U}/\partial V)_T = 0$
- 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 derived from these few fundamental equations.

Integration:

$$\int_{V_i}^{V_f} dV = [V_f - V_i]$$

$$\int_{V_i}^{V_f} \frac{dV}{V} = \ln \frac{V_f}{V_i}$$

$$\int_{V_i}^{V_f} \frac{dV}{V^2} = -2[V_f{}^{-1} - V_i{}^{-1}]$$

$$\int_{V_i}^{V_f} V dV = 1[V_f{}^2 - V_i{}^2]$$

$$\int_{V_i}^{V_f} F(V) dV \neq F(V) \int_{V_i}^{V_f} dV$$

Common misconceptions DO NOT USE:	INSTEAD, USE:
$\Delta H = C_p \Delta T$	$\Delta H = \int C_p \, dT$ $+ \int (\partial H/\partial p)_T dp$
$\Delta U = C_V \Delta T$ or $(3/2) R \Delta T$	$\Delta U = \int C_V \, dT$ $+ \int (\partial U/\partial V)_T dV$
$q = C_p \Delta T$	$q_p = \int C_p \, dT$ or $q_p = \Delta H$ $q_V = \int C_V \, dT$ or $q_V = \Delta U$
q = 0 for isothermal process	*$q=0$ for an adiabatic process. $dT = 0$ for an isothermal process.*
	isothermal process can have $q \neq 0$, examples are changes in phase or structure

Common misconceptions DO NOT USE:	INSTEAD, USE:
$W = -p_{op}\int dV$ or $W = -\int p dV$ or $W = -p\Delta V$ or $W = -RT\ln(V_f/V_i)$	$W = -\int p_{op} dV$
$U = q + W$ or $U = \Delta q + \Delta W$ or $q_1/w_1 = q_2/W_2$	$\Delta U = q + W$
$p_1T_1=P_2T_2$ ideal gas	$pV = nRT$, *ideal gas*
$\Delta H = -0.1 \text{ L mol}^{-1}$	*check dimensions are correct*
$dU = 80 \text{ J}$	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	$\Delta U = q + W$ *consider system bank account of internal energy use sign according to what goes in or out*
$-b\int dp = -b\int[nRT/(V-nb)]dV$	*no need to change variables unless necessary* $-b\int dp = -b[p_f - p_i]$
$\Delta H = \Delta U + W$ or $\Delta H = \Delta U + nRT$	$H \equiv U + pV$ $dH = dU + p\,dV + V\,dp$
$\Delta H = q$	*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 W for reverse process`	*reversing the sign of ΔU or ΔH when the process in the opposite direction is being considered is based on switching the final and initial states since $U_f - U_i \equiv \Delta U$. q and W 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 dU 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:

$\{p + \mathrm{n}^2\mathrm{a}/V^2\}\bullet (V-\mathrm{nb}) = \mathrm{nR}T$

or a more intuitively obvious form:

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

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

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

fractions:

$$if \quad \ldots \quad p = \frac{B}{V} + \frac{C}{V^2}$$

$$then \quad \ldots \quad \frac{1}{p} \neq \frac{V}{B} + \frac{V^2}{C}$$