5.60: Recitation 1 Problems Solutions:

1) In a given change in state, 44J of work is obtained from a system and the internal energy increases by 170J. If the temperature of the system rises by 10K, what is the heat capacity of the system?

According to the first law (discrete form), $\Delta U = q + w$. (*)

The problem indicates that 44J of work is obtained from the system, i.e. work is done by the system on the surroundings: therefore $w < 0$.

$w = -44J$.

Using (*):
$$\Delta U = q + w$$
$$+170\,J = q + (-44J)$$
$$\downarrow$$
$$\boxed{q = +214\,J}$$

The heat capacity is defined as $C = \frac{q}{\Delta T}$, i.e. the ratio of heat exchange to the change in temperature.

$$\boxed{C = \frac{+214J}{10K} = 21.4\,J/K.}$$

Is this C the constant volume (C_v) or constant heat (C_p) heat capacity? We do not have enough information. But, considering the nonzero work, one might make the claim that the work indicates PV expansion (change in volume of the system) and that our C above cannot be C_v. However, this assumes that we are dealing with only PV work. If other forms of work are possible (for example expansion of surface area, electrical work, etc. - you'll find this in PS #1) then it is possible that the above C represents C_v.

As for the C_p case, we simply do not know anything about the pressure of the system

---

2) Three moles of an ideal gas expand isothermally against a constant external pressure of 100kPa from 20dm^3 to 60dm^3. Compute q, w, ΔU.

First: we are dealing with an ideal gas for which the internal energy U is a function of only T. (Mathematically, $U = U(T)$.)

The initial and final temperatures are the same, since the process is isothermal. Hence there is no ΔU associated with this process.

$$\boxed{\Delta U = 0.}$$

Second: we find w from the definition $dw = -P_{ext} \cdot dV$.
$$\int dw = w = -\int P_{ext} \cdot dV$$

But since P_{ext} is constant along the process:

$$w = -P_{ext} \cdot \int_{V_1}^{V_2} dV = -P_{ext} \cdot (V_2 - V_1)$$
$$= -(100\,kPa)\left[60\,dm^3 - 20\,dm^3\right] = -(100\,kPa)\cdot(40\,dm^3)$$
$$= -4000\ kPa \cdot dm^3 .$$

Believe it or not, $kPa \cdot dm^3$ ([pressure][volume]) has the dimensions of energy.

A neat trick for conversions of quantities like $kPa \cdot dm^3$ to more familiar forms of energy is to use the gas constant. For example, consider the two values of R, below:

$$\underbrace{R = 8.315\ \frac{J}{mol \cdot K} = 8.315\ \frac{L \cdot kPa}{mol \cdot K}}_{} \qquad (\text{Recall that } 1L = 1\,dm^3)$$

So we see that the ratio $\dfrac{8.315\ J/mol \cdot K}{8.315\ \frac{L \cdot kPa}{mol \cdot K}} = 1$.

Multiplying our quantity of work by this factor, we find:

$$w = -4000\,kPa \cdot dm^3 \cdot \left(\frac{8.315\ J/mol \cdot K}{8.315\ \frac{L \cdot kPa}{mol \cdot K}} \right) = -4000\,J$$ after the unit cancellations.

$$\boxed{w = -4000\ J}$$

Lastly, to find q, we return to the first law.

$\Delta U = q + w$ We also know now that $\Delta U = 0$.
$w = -4000\,J$.

therefore $\boxed{q = +4000\,J}$

Hence, as the gas expands against external pressure, it is doing work on the surroundings at the expense of its internal energy. However, as this occurs, an equivalent amount of heat flows into the system from the surroundings. Because of these two interactions, the system is able to maintain constant energy (and since it is an I.G. maintain the same temperature.)

3) Three moles of an ideal gas expand isothermally and reversibly from $60\,dm^3$ to $20\,dm^3$ at 298K. Compute q, w, ΔT.

Again, since we are dealing with an I.G. and the process is isothermal, $\Delta U = 0$.

We start with the definition of work: $\text{đ}w = -P_{ext} \cdot dV$ (*)

For a reversible process, we are modifying the external pressure P_{ext} such that it equals the gas's pressure p throughout the process. (i.e. we proceed with the process "slowly" that the intermediate states are in equilibrium.) : $P_{ext} = p$.

So for the reversible work we may write: $\text{đ}w_{rev} = -P_{ext}\,dV = -P \cdot dV$ where p is the pressure of the system.

Since the intermediate steps are equilibrium states as well, and our system is the ideal gas, the pressure p is described by the ideal gas law.

$$p = p(V) = \frac{nRT}{V}$$

Now our $\text{đ}w_{rev}$ expression is:

$$\text{đ}w = \frac{-nRT}{V} \cdot dV$$

Now we integrate the above differential relation:

$$\int \text{đ}w = w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Using the given values, we find:

$$w = -(3\,\text{mol})(8.315\,\text{J}/\text{mol}\cdot\text{K})(298\,\text{K}) \ln\left(\frac{20\,\text{dm}^3}{60\,\text{dm}^3}\right)$$

$$\boxed{\approx +8200\,\text{J}.}$$ (Positive work in compression. Work is done on system.)

Again, to compute q, we rearrange the first law to obtain:

$$\Delta U = q + w \quad \text{(First law)}$$

$$q = \Delta U - w = 0\,\text{J} - 8200\,\text{J}. \boxed{= -8200\,\text{J}.}$$

4. For a more thorough discussion of exact and inexact differentials, consult:
   - § Lecture notes #2 (pg 8-9)
   - § SAB 2.3 Exact and inexact differentials.

Given $df = M(x,y)\,dx + N(x,y)\,dy$, df is said to be "exact" and f is a state function (path-independent) iff:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This is known as Euler's criterion for exactness.

In the case $df = dx - \frac{x}{y}dy$, $M(x,y) = 1$
$N(x,y) = \frac{x}{y}$

hence $\left(\frac{\partial M}{\partial y}\right)_x = 0$ and $\left(\frac{\partial N}{\partial x}\right)_y = \frac{-1}{y}$

Clearly, $\left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y$: df does not satisfy Euler's criterion for exactness and is not a state function.

If $dg = \frac{1}{y} \cdot df = \frac{1}{y} \cdot \left(dx - \frac{x}{y} \cdot dy\right) = \frac{1}{y} \cdot dx - \frac{x}{y^2} \cdot dy$. For dg, then:

$$M(x,y) = \frac{1}{y} \rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \frac{-1}{y^2}$$

$$N(x,y) = \frac{-x}{y^2} \rightarrow \left(\frac{\partial N}{\partial x}\right)_y = \frac{-1}{y^2}$$

Since $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = -\frac{1}{y^2}$, Euler's criterion is satisfied by dg and g is a state variable. (path-independent function).

Remark: the factor $\frac{1}{y}$ is referred to as an "integrating factor" for f.