

1. Prove  $(\partial C_V/\partial V)_T = 0$  and  $(\partial C_p/\partial p)_T = 0$  for an ideal gas. (*Hint: The order of differentiation “doesn’t matter”.*)  
[4]

2. a) For an ideal gas undergoing a reversible process, show:

i)  $dq_{\text{rev}} = C_V dT + p dV$   
[7]

ii)  $dq_{\text{rev}}$  is not an exact differential.

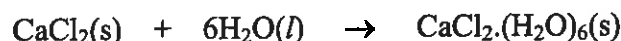
iii)  $dS$  defined by  $dS = \frac{dq_{\text{rev}}}{T}$  is an exact differential

b) Explain why part a) illustrates the important result that the change in  $S$  (the entropy) depends only on the initial and final states of a system, but  $q_{\text{rev}}$  also depends on the path taken.

3. a) Why are the compressibilities of liquids much lower than the compressibilities of gases?  
[2]

b) Explain why hydraulic machinery (*e.g.*, power steering and power brakes on a car) essential for the operation of motor vehicles, aircraft, industrial equipment, and many other devices depends on the fact that liquids are nearly incompressible. (*Suggestion: Wiki has a nice article on hydraulic machinery.*)

4. Suppose you are on a design team developing commercial “hand-warmer” products for cold Canadian winters. A proposal is made to use the reaction of calcium chloride (a cheap non-toxic salt) and water to form hydrated calcium chloride:  
[3]



Estimate the maximum (adiabatic) temperature that can be reached by this reaction. Assume 25 °C for the temperature of the reactants. Data:  $\Delta H_{\text{fm}}^\circ(\text{CaCl}_2, \text{s}) = -795.4 \text{ kJ mol}^{-1}$ ;  $\Delta H_{\text{fm}}^\circ(\text{CaCl}_2 \cdot (\text{H}_2\text{O})_6, \text{s}) = -2608.0 \text{ kJ mol}^{-1}$ ;  $C_{\text{pm}}^\circ(\text{CaCl}_2 \cdot (\text{H}_2\text{O})_6, \text{s}) = 300.7 \text{ J K}^{-1} \text{ mol}^{-1}$

5. Table 3.3 in your textbook gives  $-0.62 \text{ K MPa}^{-1}$  for the Joule-Thomson coefficient ( $\mu_{\text{JT}}$ ) of He and  $10.9 \text{ K MPa}^{-1}$  for  $\text{CO}_2$  at 273 K and 1 bar.  
[3]

a) Why is  $\mu_{\text{JT}}$  for  $\text{CO}_2$  much larger than  $\mu_{\text{JT}}$  for He?

b) He initially at 273 K and 1 bar undergoes a JT expansion into a vacuum ( $p = 0$ ). Estimate the final temperature. Estimate the final temperature of  $\text{CO}_2$  undergoing the same process.

6. Your instructor carelessly typed  $(\partial T/\partial p)_H = -V(1 - \beta T)/C_{\text{pm}}$  on version 1 of your Chem 231 equation sheet. Show that this equation is wrong. (*Hint: LHS and RHS units must match for a valid equation. Also, an intensive property and an extensive property cannot be equal.*)  
[1]

1. Show  $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$  for an ideal gas

for any system:  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

Why? A constant volume  $dU = dq - p_{\text{ext}} dV$   
 $dU = C_V dT$   
 $(\partial U / \partial T)_V = C_V$

This means  $\left(\frac{\partial C_V}{\partial V}\right)_T$  is a second derivative:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right]_V$$

(any system)

the order of differentiation can be reversed for 2nd derivatives

Similarly, recalling that  $C_p = (\partial H / \partial T)_p$   
 (why?  $dq_p = dH$  at constant pressure)

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial T}\right)_p\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial p}\right)_T\right]_p$$

(any system)

specializing to an ideal gas:

$U$  and  $H$  depend only on  $T$   
 $(dU = C_V dT \text{ and } dH = C_p dT)$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right]_V = \left(\frac{\partial(0)}{\partial T}\right)_V = 0$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial p}\right)_T\right]_p = \left(\frac{\partial(0)}{\partial T}\right)_p = 0$$

2. a) i) ideal gas ( $dU = C_V dT$ ), reversible process ( $p = p_{ext}$ )  
 ( $dw = -pdV$ )

$$dU = dq + dw \text{ (First Law)} \Rightarrow C_V dT = dq_{rev} - pdV$$

$$dq_{rev} = C_V dT + pdV$$

ii) if  $dq_{rev} = C_V dT + pdV$  is exact,

then 
$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$LS = \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \text{ (from Q1)}$$

$$RS = \left(\frac{\partial p}{\partial T}\right)_V = \left[\frac{\partial}{\partial T} \left(\frac{nRT}{V}\right)\right]_V = \frac{nR}{V} \left(\frac{\partial T}{\partial T}\right)_V = \frac{nR}{V}$$

$LS \neq RS$

$dq_{rev}$  is not exact (fails "the test")

iii)  $dS = \frac{dq_{rev}}{T} = \frac{C_V}{T} dT + \frac{p}{T} dV$

$dS$  is exact if  $\left[\frac{\partial \left(\frac{C_V}{T}\right)}{\partial V}\right]_T = \left[\frac{\partial \left(\frac{p}{T}\right)}{\partial T}\right]_V$

$$\frac{p}{T} = \frac{nR}{V}$$

depends only on T  
 $LS = \left[\frac{\partial \left(\frac{C_V}{T}\right)}{\partial V}\right]_T = 0$

$RS = \left[\frac{\partial}{\partial T} \left(\frac{nR}{V}\right)\right]_V = 0$   
 const

$LS = RS$   
 $\checkmark$  exact  $dS$

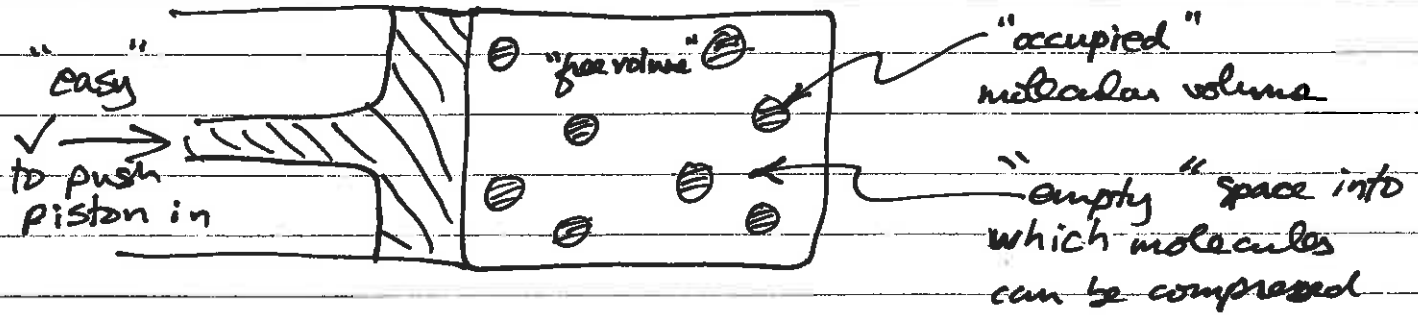
b)  $dq_{rev}$  is not exact  $\Rightarrow q_{rev}(T, V)$  function does not exist

$q_{rev} \neq q_{rev f} - q_{rev i}$  path must be specified

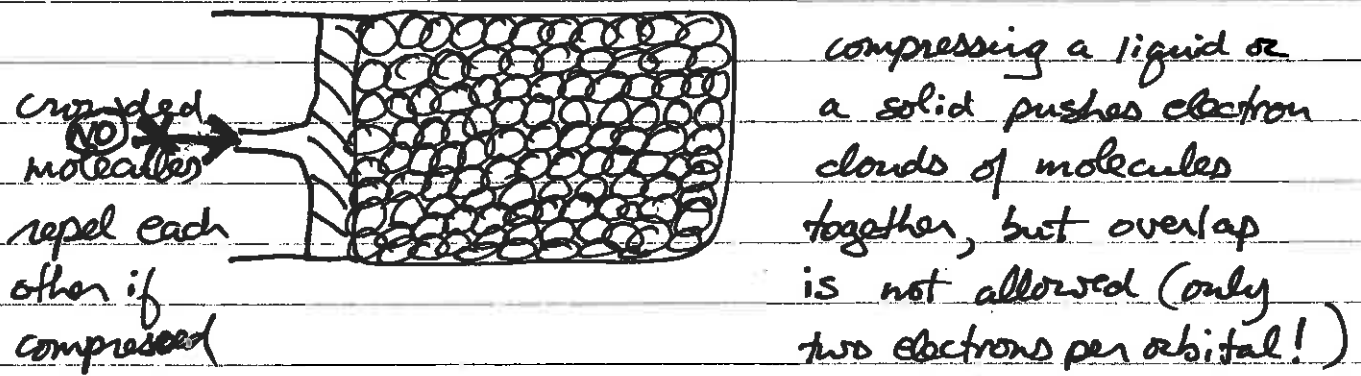
$\Delta S$  is path independent

$dS$  is exact  $\Rightarrow$  the state function  $S(T, V)$  exists,  $\Delta S = S(T_2, V_2) - S(T_1, V_1)$

3. a) In gases, the molecules are relatively far apart (compared to the molecular sizes), resulting in "lots of free volume" that gas molecules can occupy if compressed



In liquids and solids, the molecules are in close contact, with little or no "free volume".



b) Because liquid hydraulic fluid is almost incompressible, a small cylinder and piston of area  $A_1$  and applied force  $F_1$  can generate a much larger force  $F_2$  on a cylinder and piston of area  $A_2$  (larger)  $A_1$

If a gas is used, work would be wasted compressing the gas

$$A_1 F_1 = A_2 F_2$$

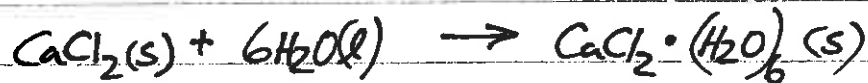


Large Mechanical forces can be generated and transmitted through fluid circuits without gears, levers, or cables (very reliable, low weight)

4. The maximum temperature reached by the hydration of  $\text{CaCl}_2$  looks like a complicated calculation, but just use

$$T_f = T_i - \frac{\Delta H^\circ}{C_p(\text{products})}$$

for the adiabatic (no heat lost) temperature of the products



$$\begin{aligned} \Delta H^\circ &= \Delta H_{\text{fm}}^\circ(\text{CaCl}_2 \cdot (\text{H}_2\text{O})_6, \text{s}) - \Delta H_{\text{fm}}^\circ(\text{CaCl}_2, \text{s}) - 6\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, \text{l}) \\ &= -2608.0 - (-795.4) - 6(-285.8) \quad \text{kJ} \end{aligned}$$

$$\Delta H^\circ = -97.8 \text{ kJ}$$

If the reaction is run adiabatically ( $q=0$ ),

then 97.8 kJ is fed back in to heat up

the  $\text{CaCl}_2 \cdot (\text{H}_2\text{O})_6$  reaction product

just use (from equation sheet):

$$\begin{aligned} T_f &= T_i - \frac{\Delta H^\circ}{C_p(\text{products})} = 298 \text{ K} - \frac{-97800 \text{ J mol}^{-1}}{300.7 \text{ J K}^{-1} \text{ mol}^{-1}} \\ &= 298 \text{ K} + 325 \text{ K} = \boxed{623 \text{ K}} \\ &\quad T_f \end{aligned}$$

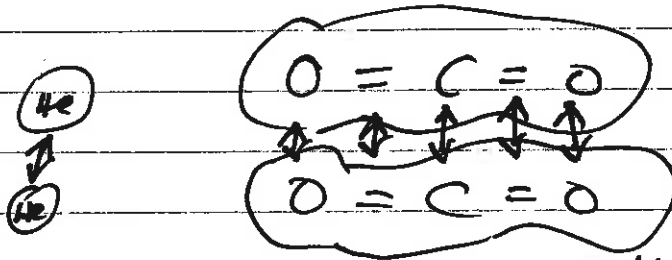
yikes  
going to burn  
their hands off!

5. a) at 273 K and 1 bar:

$$\text{He } \mu_{JT} = -0.62 \text{ K MPa}^{-1}$$

$$\text{CO}_2 \mu_{JT} = 10.9 \text{ K MPa}^{-1}$$

≈ 20 times larger and positive — why?



He-He interactions involve <sup>only</sup> 4 electrons on small atoms

CO<sub>2</sub>-CO<sub>2</sub> interactions involve 28 electrons on significantly larger molecules

$\mu_{JT}$  is zero for ideal gases (no intermolecular interactions) but increases as a gas becomes more ideal, so qualitatively, at least,

$$\text{expect } \mu_{JT}(\text{CO}_2) > \mu_{JT}(\text{He})$$

1 bar = 10<sup>5</sup> Pa = 0.10 MPa

b) **He:**  $\mu_{JT} = -0.62 \frac{\text{K}}{\text{MPa}} \approx \left(\frac{\partial T}{\partial P}\right)_H \approx \frac{\Delta T}{\Delta P}$

$$\Delta P = P_f - P_i = 0 - 1.00 \text{ bar} = -1.00 \text{ bar} = -0.10 \text{ MPa}$$

$$\Delta T \approx \mu_{JT} \Delta P = \left(-0.62 \frac{\text{K}}{\text{MPa}}\right) (-0.10 \text{ MPa}) = +0.062 \text{ K}$$

Slight warming

**CO<sub>2</sub>:**  $\mu_{JT} = 10.9 \text{ K MPa}^{-1}$

$$\text{Similarly } \Delta T \approx + (10.9 \text{ K MPa}^{-1}) (-0.10 \text{ MPa}) = -1.09 \text{ K}$$

Slight (but larger) cooling

6.  $\left(\frac{\partial T}{\partial p}\right)_H \stackrel{?}{=} - \frac{V(1-\beta T)}{C_{pm}}$

$LS = \left(\frac{\partial T}{\partial p}\right)_H = \frac{\text{temperature change}}{\text{pressure change}}$

intensive property  
(independent of  
the system size  
or mass)

also intensive

$\Rightarrow$  intensive

extensive  
(size dependent)

pure number, (must be intensive)

$RS = - \frac{V(1-\beta T)}{C_{pm}}$

per mole heat capacity - size independent  $\rightarrow$  intensive

$RS \Rightarrow \frac{\text{extensive property}}{\text{intensive property}} \rightarrow \text{extensive overall}$

LS intensive and RS extensive impossible!

/// 02 ///

$\rightarrow$  LS units  $\sim \left(\frac{\partial T}{\partial p}\right)_H \sim \frac{\Delta T}{\Delta p} \sim \frac{K}{\text{bar}}$

(don't match)

$\rightarrow$  RS units  $\sim \frac{V(1-\beta T)}{C_{pm}} \sim \frac{\text{no units}}{\text{J K}^{-1} \text{mol}^{-1}}$

$\sim \frac{L}{L \text{ bar K}^{-1} \text{ mol}^{-1}} \sim \frac{K \text{ mol}}{\text{bar}}$