

Chapter 2

First Law Formalism

2.1 The Special Character of State Variables

A gas can be characterized by a set of state variables. Some, such as temperature, pressure, and volume, are measured directly in the laboratory. Others, such as internal energy and enthalpy, are determined by measuring work and heat transferred or determined from changes in the experimentally observable state variables.

Changes in state variables are determined if the initial and final values of these variables are known. For example,

$$\Delta T = T_2 - T_1$$

The actual path for the change is irrelevant. If internal energy is proportional only to temperature, the initial and final temperatures alone dictate the total temperature difference needed to calculate the change in internal energy.

Gravitational potential energy is proportional to the state variable height (h). A mass m has a potential energy mgh where g is the acceleration of gravity. Ground level is $h=0$. The energy difference between the mass m at heights h_1 and h_2 ,

$$\Delta E = E_2 - E_1 = mg(h_2 - h_1)$$

depends only on the initial and final heights and not the path.

Heat and work can vary when a mass is raised from $h=0$ to h at the top of a building. A student (as the system) who wishes to go from the ground floor to the top floor of the building by elevator loses little chemical energy as work and generates little heat. The sum of heat and work is mgh . A student who elects to run up the stairs loses significant energy as work while producing considerable heat so that the sum is again mgh . q and w are path dependent, whereas E is not.

A system with initial values T_1 , V_1 , and E_1 is changed to have final values T_2 , V_2 , and E_2 . In a second step, the variables are returned to T_1 , V_1 , and E_1 , the initial values. The net change in all the state variables for this cycle is 0,

$$\Delta T = T_1 - T_1 = 0$$

$$\Delta V = V_1 - V_1 = 0$$

$$\Delta E = E_1 - E_1 = 0$$

A transition from state 1 to state 2 with an internal energy change of +100 J will require $\Delta E = -100$ J to return to the original state by any path; the total energy change for the full cycle is 0,

$$\Delta E_{\text{cycle}} = 0 = \Delta E_1 + \Delta E_2 = +100 - 100 = 0$$

Any path, not just the actual path followed in the laboratory, is used to determine a state function. Heating a gas might produce simultaneous increases in temperature and volume. The internal energy can be calculated on a two step path:

- (1) determine the change in energy with a temperature change at constant volume and
- (2) hold the final temperature constant and determine the change in energy with volume at constant T

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

2.2 Energy and Enthalpy for Chemical Reactions

An isomerization



is a rearrangement of bonds for a set of atoms. The new bonds have different energies so energy is released or absorbed on reaction. If the bonds in the B isomer require less energy than the bonds of the A isomer, some bond energy is released during the reaction and appears as system kinetic energy of the B isomers. Since this energy is proportional to the temperature, the temperature of the system increases when this energy is released.

Internal energy changes for a reaction at constant volume are listed for a constant temperature, e.g., 25°C. However, the isomer reaction above releases energy and the temperature should rise following the reaction. If 10,000 J of energy is released by the reaction, this would appear as an internal energy increase,

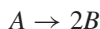
$$E = +10,000 \text{ J}$$

with the concomitant temperature increase. Many reactions release considerable energy and the resultant temperature change produced by this release would lead to an unrealistic rise in the system temperature. To alleviate this problem, the chemical reaction internal energies are defined as the heat transferred to maintain the constant system temperature. Thus, the 10,000 J of heat released when the new bonds are formed defines a negative, or exothermic, internal energy of reaction

$$\Delta E_r = q_v = -10,000 \text{ J}$$

An endothermic reaction requires extra energy transferred from the surroundings. Because the system gains energy at constant temperature, an endothermic reaction is positive.

The enthalpy of a reaction such as the isomerization is determined for constant pressure conditions. The difference between the energy and the enthalpy for the same reaction is illustrated by the dissociation reaction at constant volume,



where $\Delta E = -50,000 \text{ J}$. The same reaction occurring in a cylinder fitted with a frictionless piston is reversible when the pressure within the system is always equal to the external pressure on the piston so that the system pressure remains constant. The increase in moles by dissociation changes the gas volume and the piston must rise to accommodate the new volume. Some of the energy released by the reaction raises the piston so less is available to leave the system and maintain 25°C .

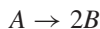
The enthalpy for the gaseous reaction is predicted using the enthalpy definition and the ideal gas law

$$\Delta H_r = \Delta E_r + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta(nRT) = \Delta E + (\Delta n)RT$$

since the temperature is constant when this energy leaves.

The dissociation



in a closed (constant volume) vessel gives an internal energy change of $-50,000 \text{ J}$ for the reaction as written. Since both A and B are gaseous, reaction produces a net increase of 1 mol of gas,

$$\Delta n = 2 - 1 = 1$$

and the predicted enthalpy for this reaction is

$$\Delta H = \Delta E + \Delta nRT = -50,000 + (+1)(8.31)(298) = -47,523 \text{ J}$$

The reaction under constant pressure conditions releases 2476 fewer joules, the energy required to raise the piston.

The enthalpy of reaction is defined for gases in a cylinder with constant pressure. Reactions of solids and liquid involve small changes in volume and internal energy and enthalpy are almost equal. By convention, the enthalpy of reaction is recorded for constant pressure.

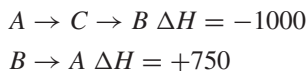
2.3 Hess's Law and Reaction Cycles

The energy and enthalpy of a chemical reaction are determined only by the initial (reactants) and final (product) states and not the path the system follows to move between these states. The internal energy change for the reaction is the difference between these product and reactant energies and is independent of the reaction path between these species. The enthalpy of reaction is also path independent.

The path independence is demonstrated with a hypothetical (and incorrect) situation where the energy of reaction does depend on path. Two different reaction pathways give different energies. Reactant (*A*) reacts to product (*B*) through an intermediate *C*



with a total enthalpy of reaction, $\Delta H = -1000$ J for the two steps. If *A* goes to *B* directly in one step, $\Delta H = -750$ J. If the one-step reaction from *A* to *B* releases 750 J of energy, the reverse (endothermic) reaction from *B* to *A* must absorb 750 J. The two reactions are combined to form a cycle that begins and ends with *A*. The forward reaction follows the two-step path, while the reverse reaction to complete the cycle is the one-step path. The reactions for the full cycle are



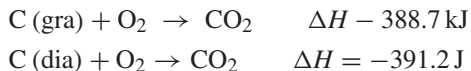
The enthalpy for the cycle (H_{cyl}) is determined by adding the enthalpies of reaction for each step in the cycle to give -250 J for this hypothetical situation. *A* is exactly the same but 250 J of energy has been created in violation of the conservation of energy. The state function, enthalpy, for the reaction depends on the final (*B*) and initial (*A*) states. Each path between reactants and product must give exactly the same result.

The total enthalpy change for the cycle is

$$\Delta H_{\text{cycle}} = -1000 + 1000 = 0$$

The path independence of reactions is the basis of Hess' law. The unknown enthalpy or energy for a reaction is determined by combining other reactions with known energies and enthalpies.

The enthalpy required to change carbon as graphite into carbon as diamond cannot be determined directly since graphite does not change into diamond at normal temperatures and pressures. However, this enthalpy can be determined by the simple, but expensive, task of burning both graphite and diamond and determining their enthalpies for combustion



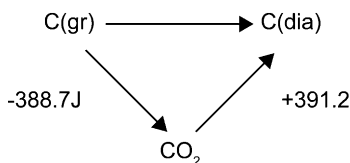
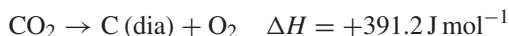


Fig. 2.1 Two paths to create graphite from diamond

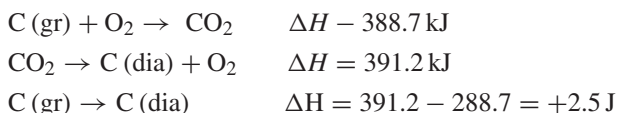
The oxidation equation for diamond is reversed



If 391.2 kJ of energy is released when diamond is burned, 391.2 kJ must be added to remake the diamond from CO_2 . The enthalpy is 2.5 J for the two-step path and also the direct path from graphite to diamond.

The enthalpy for the reaction from graphite to diamond uses the two combustion reactions to complete the path from graphite to diamond (Fig. 2.1).

The two reactions can be added and their enthalpies with proper sign added to give the final reaction and enthalpy,



The graphite to diamond enthalpy is also determined by placing each reaction on a vertical scale. CO_2 is a common energy and C(dia) is 2.5 J above C(gra) on this scale (Fig. 2.2).

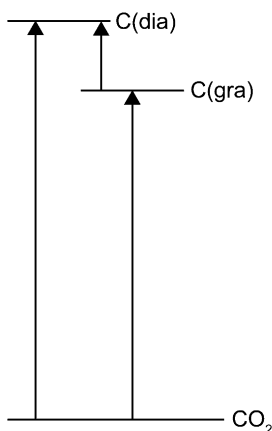


Fig. 2.2 Relative enthalpies for diamond and graphite

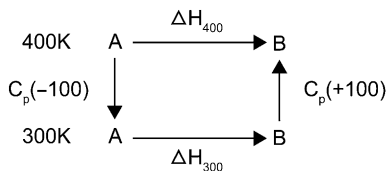


Fig. 2.3 A three-step path for reaction at 400 K when its energy at 300 K and the heat capacities are known

Any state function change can be determined using the most convenient pathway. For example, the enthalpy for the reaction,



is $-10,000$ J at 300 K. The enthalpy for the same reaction at 400 K is determined with a path that goes from reactants to products at 400 K. One such path (Fig. 2.3) uses three steps: (1) A at 400 K is cooled to 300 K, (2) A is changed to B at 300 K, and (3) B at 300 K is heated to 400 K.

The change in enthalpy for a change in temperature is determined via the heat capacities at constant pressure, C_p , for $A(C_p(A))$ and $B(C_p(B))$. The enthalpy change for A when it is cooled to 300 K is

$$\Delta H = C_p(A) \Delta T = C_p(A) (300 - 400) = C_p(A) (-100)$$

The change from A to B at 300 K is already known to be $-10,000$ J. The enthalpy change for step 3 is

$$\Delta H_3 = C_p(B) \Delta T = C_p(B) (400 - 300) = C_p(B) (+100)$$

The enthalpy change for the reaction at 400 K is the sum of these three steps,

$$\begin{aligned} \Delta H_r(400^\circ) &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= C_p(A) (300 - 400) + (-10,000) + C_p(B) (400 - 300) \\ &= -10,000 + (C_p(B) - C_p(A)) (400 - 300) \\ &= -10,000 + \Delta C_p \Delta T = -10,000 + \Delta C_p (100) \end{aligned}$$

where the ΔC_p is just the difference between the heat capacities of all the products less the heat capacities of all the reactants. The second term corrects the reaction enthalpy at 300 K for the new temperature.

In general, the enthalpy for a reaction,



at any temperature includes the net difference of heat capacities for the reactants and products,

$$\Delta C_P = cC_P(C) - aC_P(A) - bC_P(B)$$

When the product and reactant total heat capacities are similar, the enthalpy changes little with temperature and is essentially constant. This property is useful when a constant enthalpy gives a linear plot in some graphs.

2.4 Standard States

The CO₂ enthalpy served as a common energy for both graphite and diamond. When both had a common reference, their energy of reaction was the difference between their energies. Standard states use this information to select an energy that is common to all molecules as a reference or standard state. The reference is the energy of the atoms of the molecules in their most common states. Enthalpy or energy differences for the molecules are then differences of these standard state enthalpies. For the graphite–diamond example, C(gra) is selected as the standard state and assigned a standard enthalpy 0. C(dia) is then 2.5 J mol^{−1} higher so its standard enthalpy is 2.5 J mol^{−1}. The CO₂ molecule has enthalpy 388.7 kJ less than C(gr) so its standard enthalpy is −388.7 kJ. The enthalpy to convert diamond into CO₂ is just the difference of standard state enthalpies for product CO₂ (−388.7) and the reactant diamond (2.5)

$$\Delta H = H_f^\circ(\text{CO}_2) - H_f^\circ(\text{C(dia)}) = -388.7 - 2.5 = 391.2 \text{ J mol}^{-1}$$

The subscript f indicates formation from the elements, while the o indicates 25°C. Deltas are absent because the standard states are all relative to an assigned value of 0 for the elements in their standard states.

For a general reaction,



the total enthalpy of formation for products is the sum of the enthalpies of formation of all the products less the enthalpies of formation of all the reactants

$$[cH_f^\circ(C) + dH_f^\circ(D)] - [aH_f^\circ(A) + bH_f^\circ(B)]$$

For a reaction,



the enthalpy of reaction is

$$\Delta H_r = 2\Delta_f^\circ(C) - 1\Delta_f^\circ(A) - 2\Delta_f^\circ(B)$$

The negative signs for the reactants show that these reactions have been reversed to produce the proper net reaction.

2.5 More Partial Derivatives

Partial derivatives are used to establish a path involving several independent variables. Each term is a slope (partial derivative) and a differential. The power of the formalism is revealed when the partial derivatives are known.

The pressure P of an ideal gas is related to the volume and temperature as the independent variables so that

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

A differential dP is determined by the derivatives and differentials for T and V . The derivatives are evaluated from ideal gas law

$$P = RT/V$$

The change in P with T at constant V is

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial \left(\frac{RT}{V} \right)}{\partial T} \right)_V = \frac{R}{V} \left(\frac{\partial T}{\partial T} \right) = \frac{R}{V}$$

and the change in P with V at constant T is

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial \left(\frac{RT}{V} \right)}{\partial V} \right)_T = RT \left(\frac{\partial \left(\frac{1}{V} \right)}{\partial V} \right)_T = RT \left(-\frac{1}{V^2} \right)$$

to generate dP for an ideal gas

$$dP = \frac{R}{V} dT - \frac{RT}{V^2} dV$$

The ideal gas constant R is approximated as $0.08 \text{ Latm K}^{-1} \text{ mol}^{-1}$ to give an initial pressure, volume, and temperature $(P, V, T) = (1 \text{ atm}, 10 \text{ L}, 125 \text{ K})$ for 1 mol of gas. The final (P, V, T) are $(2 \text{ atm}, 20 \text{ L}, 500 \text{ K})$. The pressure change is

$$dP = \int_1^2 dP = 2 - 1 = 1$$

Using the right side of the equation, T is changed from 125 to 500 K with $V = 10 \text{ L}$. The constant temperature is 500 K during the second leg. The pressure change for the first leg

$$\Delta P = (+R/V)\Delta T = +0.08/(10 \text{ L}) [500 - 125] = +3$$

is added to the pressure change for the second leg

$$\Delta P = -RT \int_{10}^{20} \frac{dV}{V^2} = + \frac{RT}{V} \Big|_{10}^{20} = \frac{RT}{V_2} - \frac{RT}{V_1}$$

$$0.08 (500) \left(\frac{1}{20} - \frac{1}{10} \right) = 40 (0.05 - 0.1) = -2 \text{ atm}$$

The net change in pressure for the two-step path is $3-2=1$. If volume is changed first while $T=125$, the result is the same

$$\Delta P = RT \int_{10}^{20} -\frac{1}{V^2} dV + \frac{R}{V} \int_{125}^{500} dT = (0.08) (125) \frac{1}{V} \Big|_{10}^{20} + \frac{0.08}{20} T \Big|_{125}^{500}$$

$$= 10 (0.05 - 0.1) + 0.004 (375) = 1$$

Path differential equations are also used for error analysis. If the experimental errors in measuring T and V are ΔT and ΔV , respectively, each of these errors could produce an error in the value of P , ΔP . The rates of change of pressure with respect to T and V are multiplied by the errors ΔT and ΔV , respectively

$$\Delta P = \frac{R}{V} \Delta T$$

$$\Delta P = -\frac{RT}{V^2} \Delta V$$

These independent errors are combined by squaring each, adding, and then taking the square root of the sum

$$\Delta P^2 = \sqrt{\left[\left(\frac{\partial P}{\partial T} \right)_V dT \right]^2 + \left[\left(\frac{\partial P}{\partial V} \right)_T dV \right]^2}$$

The change in internal energy is expressed as the sum of T and V legs:

$$dE = C_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

The derivatives for some simple systems are 0 and this simplifies the path expressions. For example, an ideal gas has

$$\left(\frac{\partial E}{\partial V} \right)_T = 0$$

so that

$$dE = C_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV = C_v dT$$

2.6 Generalized Thermodynamic Equations

The relation between the heat capacity at constant pressure and the heat capacity at constant volume

$$C_P = C_V + R$$

is valid for an ideal gas. A more general expression works for any equation of state with P , T , and V .

The heat capacity at constant pressure is

$$\left(\frac{\partial H}{\partial T}\right)_P$$

Since

$$H = E + PV$$

the terms on the right side of the equation are differentiated with respect to T at constant pressure. The derivative of H with respect to T at constant P is

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

The partial derivative

$$\left(\frac{\partial E}{\partial T}\right)_P$$

is not a standard heat capacity and must be related to C_V .

The internal energy is expressed in terms of its standard variables, T and V , using partial derivatives:

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

These T and V differentials become partial derivatives if they are each differentiated with respect to T at constant P :

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this equation into the heat capacity expression to gives the general expression relating C_P and C_V ,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = C_V + \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$\#C_P = C_V + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P$$

for any gas with any equation of state. For an ideal gas, with

$$\left(\frac{\partial E}{\partial V} \right)_T = 0$$

and

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \frac{dT}{dT} = \frac{R}{P}$$

$$C_P = C_V + [0 + P] \frac{R}{P} = C_V + R$$

as expected.

A dependent state variable that depends on two (or more) other thermodynamic variables might be constant during a change of state so that its differential is 0 and the partial derivative terms on the right side of the equation must also equal 0. For example, if the enthalpy remains constant during an expansion, $dH = 0$ and

$$dH = 0 = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

For the independent variables, T and P , the differentials (not the partials) are differentiated with respect to temperature to give

$$\left(\frac{\partial H}{\partial T} \right)_P \frac{dT}{dP} = - \left(\frac{\partial H}{\partial P} \right)_T \left(\frac{dP}{dP} \right)$$

$$\left(\frac{\partial H}{\partial T} \right)_P \frac{dT}{dP} = - \left(\frac{\partial H}{\partial P} \right)_T$$

The standard derivative dT/dP is replaced with partial derivatives to show the process proceeds at constant enthalpy:

$$\frac{dT}{dP} = \left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P}$$

2.7 Calculating Internal Energy

The differential expansion for dE

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

has derivatives that depend on the specific system under study. For example, an ideal gas has a constant heat capacity:

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V = \text{constant}$$

and

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

ΔE is determined by integrating dT from its initial (T_i) to its final temperature (T_f). If C_V is temperature dependent,

If

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

$$\Delta E = \int_{T_i}^{T_f} C_V(T) dT$$

If $C_V = \text{constant}$,

$$\Delta E = \int_{T_i}^{T_f} C_V dT = C_V \Delta T$$

A molar heat capacity linear in temperature

$$C(T) = C_v + aT$$

gives

$$\Delta E = \int_{T_i}^{T_f} [C_v + aT] dT = C_v T \Big|_{T_i}^{T_f} + \frac{aT^2}{2} \Big|_{T_i}^{T_f} = C_v \Delta T + \frac{a}{2} [T_f^2 - T_i^2]$$

The temperature dependent term is usually small relative to the constant C_V term. For real gases, the $C_v dT$ changes are usually much larger than

$$\left(\frac{\partial E}{\partial V}\right)_T dV$$

changes. For isothermal ($dT=0$) conditions

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV$$

This energy change is larger for a small volume where the gas molecules are closer together on average so that intermolecular interaction energies are significant. This potential energy of interaction is released as the volume increases and the molecules separate.

One mole of a van der Waals gas has a partial derivative in volume that depends on the molecular interaction constant a ,

$$\left(\frac{\partial E}{\partial V}\right)_V = \frac{a}{V^2}$$

the pressure correction term in the van der Waals equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

with units of pressure.

If the van der Waals gas is expanded from V_i to V_f at constant temperature, $dT = 0$, and

$$dE = \left(\frac{dE}{dV}\right)_T dV$$

is integrated to give

$$\Delta E = \int_{u_i}^{u_f} dE = \int_{V_i}^{V_f} \left(\frac{\partial E}{\partial V}\right)_T dV = \int_{V_i}^{V_f} \frac{a}{V^2} dV = -\frac{a}{V} \Big|_{V_i}^{V_f} = -\frac{a}{V_f} + \frac{a}{V_i}$$

As volume increases, the internal energy will increase reflecting the change of potential energy of interaction to kinetic or internal energy as the molecules separate.

Problems

2.1 The heat of formation of HBr(g) from $\text{H}_2(\text{g})$ and $\text{Br}_2(\text{g})$ is -38 kJ mol^{-1} . Determine the heat of formation at 400 K.

2.2 A diatomic gas expands isothermally (constant temperature) against an external pressure $P_{\text{ex}}=1$ from $V_1=1 \text{ L}$ to $V_2=2 \text{ L}$. The gas is non-ideal and

$$\int \frac{\partial E}{\partial V} dV = -0.1 \text{ Latm}$$

Determine w , ΔE , and q .

2.3 An ideal monatomic gas expands reversibly in two steps: (1) an isothermal ($dT=0$) expansion at 400 K and (2) an adiabatic expansion ($q=0$). During the two steps, the system absorbs 5000 J of heat and its internal energy decreases by -500 J mol^{-1} .

- Determine the internal energy changes for each step.
- Determine the work for each step.

2.4 A non-ideal monatomic gas has

$$\int_{V_1}^{V_2} \frac{\partial E}{\partial V} dV = a = \text{constant}$$

Write an integrated expression for the change in internal energy when the temperature increases from T_1 to T_2 and the volume increases from V_1 to V_2 .

2.5 The standard enthalpies of formation use elements in their most stable states. For the reaction



with

$$\Delta H_f^\circ(A) = -1000 \text{ J}$$

$$\Delta H_f^\circ(B) = -2000 \text{ J}$$

Determine the "standard" enthalpy of A if B is selected as the 0 enthalpy reference state.

2.6 One mole of a non-ideal gas with $C_V = 12.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\left(\frac{\partial E}{\partial V}\right)_T = 20 \text{ J L}^{-1}$ expands against a constant pressure of 0.2 atm from 1 to 11 L while the temperature decreases from 350 to 300 K.

- Determine ΔE and w .
- Determine ΔH if

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

2.7 A non-ideal monatomic gas expands with $\Delta H = +1000 \text{ J}$.

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

- Determine the final T .
- Determine ΔE .



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