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**IDEAL GAS AND IDEAL-GAS STATE**

The equation  $PV = RT$  is now understood to define an ideal gas and to represent a model of behavior more or less approximating the behavior of real gases. It is called the ideal gas law, but is in fact valid only for pressures approaching zero and temperatures approaching infinity.

The internal energy of a real gas depends on both pressure and temperature. Pressure dependence results from intermolecular forces. If such forces did not exist, no energy would be required to alter intermolecular distances, and no energy would be required to bring about pressure and volume changes in a gas at constant temperature. Thus, in the absence of intermolecular forces, internal energy would depend on temperature only.

Two equations are fundamental to this state, namely the “ideal-gas law” and an expression showing that internal energy depends on temperature alone:

- The equation of state:

$$PV^{ig} = RT \quad (3.7)$$

- Internal energy:

$$U^{ig} = U(T) \quad (3.8)$$

The superscript *ig* denotes properties for the ideal-gas state.

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### Property Relations for the Ideal-Gas State

The definition of heat capacity at constant volume, Eq. (2.15), leads for the ideal-gas state to the conclusion that  $C_V^{ig}$  is a function of temperature only:

$$C_V^{ig} \equiv \left( \frac{\partial U^{ig}}{\partial T} \right)_V = \frac{dU^{ig}(T)}{dT} = C_V^{ig}(T) \quad (3.9)$$

The defining equation for enthalpy, Eq. (2.10), applied to the ideal-gas state, leads to the conclusion that  $H^{ig}$  is also a function only of temperature:

$$H^{ig} \equiv U^{ig} + PV^{ig} = U^{ig}(T) + RT = H^{ig}(T) \quad (3.10)$$

The heat capacity at constant pressure  $C_P^{ig}$ , defined by Eq. (2.19), like  $C_V^{ig}$ , is a function of temperature only:

$$C_P^{ig} \equiv \left( \frac{\partial H^{ig}}{\partial T} \right)_P = \frac{dH^{ig}(T)}{dT} = C_P^{ig}(T) \quad (3.11)$$

A useful relation between  $C_P^{ig}$  and  $C_V^{ig}$  for the ideal-gas state comes from differentiation of Eq. (3.10):

$$C_P^{ig} \equiv \frac{dH^{ig}}{dT} = \frac{dU^{ig}}{dT} + R = C_V^{ig} + R \quad (3.12)$$

This equation does not mean that  $C_P^{ig}$  and  $C_V^{ig}$  are themselves constant for the ideal-gas state, but only that they vary with temperature in such a way that their *difference* is equal to  $R$ . For any change in the ideal-gas state, Eqs. (3.9) and (3.11) lead to:

$dU^{ig} = C_V^{ig} dT \quad (3.13a)$	$\Delta U^{ig} = \int C_V^{ig} dT \quad (3.13b)$
$dH^{ig} = C_P^{ig} dT \quad (3.14a)$	$\Delta H^{ig} = \int C_P^{ig} dT \quad (3.14b)$

Because both  $U^{ig}$  and  $C_V^{ig}$  for the ideal-gas state are functions of temperature only,  $\Delta U^{ig}$  for the ideal-gas state is always given by Eq. (3.13b), regardless of the kind of process causing the change.

### Process Calculations for the Ideal-Gas State

Process calculations provide work and heat quantities. The work of a mechanically reversible closed-system process is given by Eq. (1.3), here written:

$$dW = -P dV^{ig} \quad (1.3)$$

For the ideal-gas state in any closed-system process, the first law as given by Eq. (2.6) written for a unit mass or a mole, may be combined with Eq. (3.13a) to give:

$$dQ + dW = C_V^{ig} dT$$

Substitution for  $dW$  by Eq. (1.3) and solution for  $dQ$  yields an equation valid for the ideal-gas state in any mechanically reversible closed-system process:

$$dQ = C_V^{ig} dT + P dV^{ig} \quad (3.15)$$

This equation contains the variables  $P$ ,  $V^{ig}$ , and  $T$ , only two of which are independent. Working equations for  $dQ$  and  $dW$  depend on which pair of these variables is selected as independent; i.e., upon which variable is eliminated by Eq. (3.7). We consider two cases, eliminating first  $P$ , and second,  $V^{ig}$ . With  $P = RT/V^{ig}$ , Eqs. (3.15) and (1.3) become:

$dQ = C_V^{ig} dT + RT \frac{dV^{ig}}{V^{ig}} \quad (3.16)$	$dW = -RT \frac{dV^{ig}}{V^{ig}} \quad (3.17)$
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For  $V^{ig} = RT/P$ ,  $dV^{ig} = \frac{R}{P}(dT - T \frac{dP}{P})$ . Substituting for  $dV^{ig}$  and for  $C_V^{ig} = C_P^{ig} - R$  transforms Eqs. (3.15) and (1.3) into:

$dQ = C_P^{ig} dT - RT \frac{dP}{P} \quad (3.18)$	$dW = -RdT + RT \frac{dP}{P} \quad (3.19)$
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**These equations apply to the Ideal-gas state for various process calculations. The assumptions implicit in their derivation are that the system is closed and the process is mechanically reversible.**

***Isothermal Process***

By Eqs. (3.13b) and (3.14b),

$$\Delta U^{ig} = \Delta H^{ig} = 0 \quad (\text{const } T)$$

By Eqs. (3.16) and (3.18),  $Q = RT \ln \frac{V_2^{ig}}{V_1^{ig}} = RT \ln \frac{P_1}{P_2}$

By Eqs. (3.17) and (3.19),  $W = RT \ln \frac{V_1^{ig}}{V_2^{ig}} = RT \ln \frac{P_2}{P_1}$

Because  $Q = -W$ , a result that also follows from Eq. (2.3), we can write in summary:

$$Q = -W = RT \ln \frac{V_2^{ig}}{V_1^{ig}} = RT \ln \frac{P_1}{P_2} \quad (\text{const } T) \quad (3.20)$$

***Isobaric Process***

By Eqs. (3.13b) and (3.19) with  $dP = 0$ ,

$$\Delta U^{ig} = \int C_V^{ig} dT \quad \text{and} \quad W = -R(T_2 - T_1)$$

By Eqs. (3.14b) and (3.18),

$$Q = \Delta H^{ig} = \int C_P^{ig} dT \quad (\text{const } P) \quad (3.21)$$

***Isochoric (Constant-V) Process***

With  $dV^{ig} = 0$ ,  $W = 0$ , and by Eqs. (3.13b) and (3.16),

$$Q = \Delta U^{ig} = \int C_V^{ig} dT \quad (\text{const } V^{ig}) \quad (3.22)$$

***Adiabatic Process; Constant Heat Capacities***

An adiabatic process is one for which there is no heat transfer between the system and its surroundings; i.e.,  $dQ = 0$ . Each of Eqs. (3.16) and (3.18) may therefore be set equal to zero. Integration with  $C_V^{ig}$  and  $C_P^{ig}$  constant then yields simple relations among the variables  $T$ ,  $P$ , and  $V^{ig}$ , valid for mechanically reversible adiabatic compression or expansion in the ideal-gas state with constant heat capacities. For example, Eq. (3.16) becomes:

$$\frac{dT}{T} = -\frac{R}{C_V^{ig}} \frac{dV^{ig}}{V^{ig}}$$

Integration with  $C_V^{ig}$  constant gives:

$$\frac{T_2}{T_1} = \left( \frac{V_1^{ig}}{V_2^{ig}} \right)^{R/C_V^{ig}}$$

Similarly, Eq. (3.18) leads to:

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{R/C_P^{ig}}$$

These equations may also be expressed as:

$T(V^{ig})^{\gamma-1} = \text{const} \quad (3.23a)$	$TP^{(1-\gamma)/\gamma} = \text{const} \quad (3.23b)$	$P(V^{ig})^\gamma = \text{const} \quad (3.23c)$
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where Eq. (3.23c) results by combining Eqs. (3.23a) and (3.23b) and where by **definition**,<sup>4</sup>

$$\gamma \equiv \frac{C_P^{ig}}{C_V^{ig}} \quad (3.24)$$

**Equations (3.23) apply for the ideal-gas state with constant heat capacities and are restricted to mechanically reversible adiabatic expansion or compression.**

The first law for an adiabatic process in a closed system combined with Eq. (3.13a) yields:

$$dW = dU = C_V^{ig} dT$$

For constant  $C_V^{ig}$ ,

$$W = \Delta U^{ig} = C_V^{ig} \Delta T \quad (3.25)$$

Alternative forms of Eq. (3.25) result if  $C_V^{ig}$  is eliminated in favor of the heat-capacity ratio  $\gamma$ :

$$\gamma \equiv \frac{C_P^{ig}}{C_V^{ig}} = \frac{C_V^{ig} + R}{C_V^{ig}} = 1 + \frac{R}{C_V^{ig}} \quad \text{or} \quad C_V^{ig} = \frac{R}{\gamma - 1}$$

and

$$W = C_V^{ig} \Delta T = \frac{R \Delta T}{\gamma - 1}$$

Because  $RT_1 = P_1V_1^{ig}$  and  $RT_2 = P_2V_2^{ig}$ , this expression may be written:

$$W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2V_2^{ig} - P_1V_1^{ig}}{\gamma - 1} \quad (3.26)$$

Equations (3.25) and (3.26) are general for adiabatic compression and expansion processes in a closed system, whether reversible or not, because  $P$ ,  $V^{ig}$ , and  $T$  are state functions, independent of path. However,  $T_2$  and  $V_2^{ig}$  are usually unknown. Elimination of  $V_2^{ig}$  from Eq. (3.26) by Eq. (3.23c), valid only for mechanically reversible processes, leads to the expression:

$$W = \frac{P_1V_1^{ig}}{\gamma - 1} \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma - 1)\gamma} - 1 \right] = \frac{RT_1}{\gamma - 1} \left[ \left( \frac{P_2}{P_1} \right)^{(\gamma - 1)\gamma} - 1 \right] \quad (3.27)$$

The same result is obtained when the relation between  $P$  and  $V^{ig}$  given by Eq. (3.23c) is used for the integration,  $W = -\int P dV^{ig}$ .

**Equation (3.27) is valid only for the ideal-gas state, for constant heat capacities, and for adiabatic, mechanically reversible, closed-system processes.**

When applied to real gases, Eqs. (3.23) through (3.27) often yield satisfactory approximations, provided the deviations from ideality are relatively small. For monatomic gases,  $\gamma = 1.67$ ; approximate values of  $\gamma$  are 1.4 for diatomic gases and 1.3 for simple polyatomic gases such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{CH}_4$ .

### Irreversible Processes

All equations developed in this section have been *derived* for mechanically reversible, closed-system processes for the ideal-gas state. However, the equations for *property changes*— $dU^{ig}$ ,  $dH^{ig}$ ,  $\Delta U^{ig}$ , and  $\Delta H^{ig}$ —are valid for the ideal-gas state *regardless of the process*. They apply equally to reversible and irreversible processes in both closed and open systems, because changes in properties depend only on initial and final states of the system. On the other hand, an equation for  $Q$  or  $W$ , unless it is equal to a property change, is subject to the restrictions of its derivation.

The work of an *irreversible* process is usually calculated by a two-step procedure. First,  $W$  is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process. Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is larger than the value for the actual irreversible process and must be multiplied by an efficiency. If the process requires work, the value for the reversible process is smaller than the value for the actual irreversible process and must be divided by an efficiency.

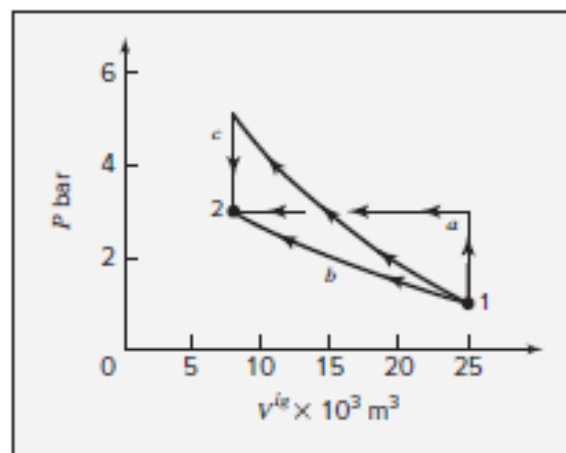
Applications of the concepts and equations of this section are illustrated in the examples that follow. In particular, the work of irreversible processes is treated in Ex. 3.5.

### Example 3.3

Air is compressed from an initial state of 1 bar and 298.15 K to a final state of 3 bar and 298.15 K by three different mechanically reversible processes in a closed system:

- Heating at constant volume followed by cooling at constant pressure.
- Isothermal compression.
- Adiabatic compression followed by cooling at constant volume.

These processes are shown in the figure. We assume air to be in its ideal-gas state, and assume constant heat capacities,  $C_V^{ig} = 20.785$  and  $C_P^{ig} = 29.100 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Calculate the work required, heat transferred, and the changes in internal energy and enthalpy of the air for each process.



### Solution 3.3

Choose the system as 1 mol of air. The initial and final states of the air are identical with those of Ex. 2.7. The molar volumes given there are

$$V_1^{ig} = 0.02479 \text{ m}^3 \quad V_2^{ig} = 0.008263 \text{ m}^3$$

Because  $T$  is the same at the beginning and end of the process, in all cases,

$$\Delta U^{ig} = \Delta H^{ig} = 0$$

(a) The process here is exactly that of Ex. 2.7(b), for which:

$$Q = -4958 \text{ J} \quad \text{and} \quad W = 4958 \text{ J}$$

(b) Equation (3.20) for isothermal compression applies. The appropriate value of  $R$  here (from Table A.2 of App. A) is  $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

$$Q = -W = RT \ln \frac{P_1}{P_2} = (8.314)(298.15) \ln \frac{1}{3} = -2723 \text{ J}$$

(c) The initial step of adiabatic compression takes the air to its final volume of  $0.008263 \text{ m}^3$ . By Eq. (3.23a), the temperature at this point is:

$$T' = T_1 \left( \frac{V_1^{ig}}{V_2^{ig}} \right)^{\gamma-1} = (298.15) \left( \frac{0.02479}{0.008263} \right)^{0.4} = 462.69 \text{ K}$$

For this step,  $Q = 0$ , and by Eq. (3.25), the work of compression is:

$$W = C_V^{ig} \Delta T = C_V^{ig} (T' - T_1) = (20.785) (462.69 - 298.15) = 3420 \text{ J}$$

For the constant-volume step, no work is done; the heat transfer is:

$$Q = \Delta U^{ig} = C_V^{ig} (T_2 - T') = 20.785 (298.15 - 462.69) = -3420 \text{ J}$$

Thus for process (c),

$$W = 3420 \text{ J} \quad \text{and} \quad Q = -3420 \text{ J}$$

Although the property changes  $\Delta U^{ig}$  and  $\Delta H^{ig}$  are zero for each process,  $Q$  and  $W$  are path-dependent, and here  $Q = -W$ . The figure shows each process on a  $PV^{ig}$  diagram. Because the work for each of these mechanically reversible processes is given by  $W = -\int P dV^{ig}$ , the work for each process is proportional to the total area below the paths on the  $PV^{ig}$  diagram from 1 to 2. The relative sizes of these areas correspond to the numerical values of  $W$ .

### Example 3.4

A gas in its Ideal-gas state undergoes the following sequence of mechanically reversible processes in a closed system:

- From an initial state of 70°C and 1 bar, it is compressed adiabatically to 150°C.
- It is then cooled from 150 to 70°C at constant pressure.
- Finally, it expands isothermally to its original state.

Calculate  $W$ ,  $Q$ ,  $\Delta U^{ig}$ , and  $\Delta H^{ig}$  for each of the three processes and for the entire cycle. Take  $C_V^{ig} = 12.471$  and  $C_P^{ig} = 20.785 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

### Solution 3.4

Take as a basis 1 mol of gas.

- (a) For adiabatic compression,  $Q = 0$ , and

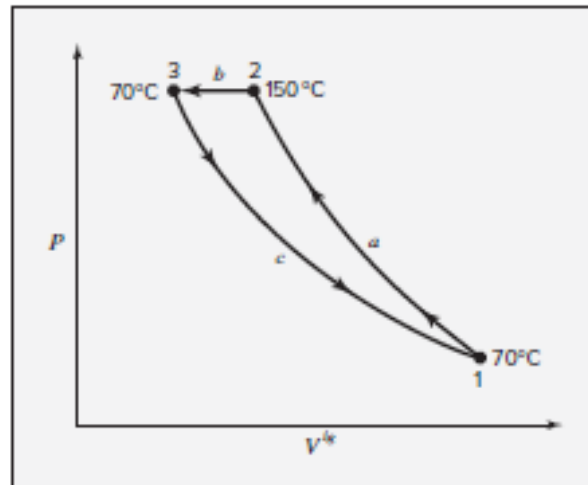
$$\Delta U^{ig} = W = C_V^{ig} \Delta T = (12.471)(150 - 70) = 998 \text{ J}$$

$$\Delta H^{ig} = C_P^{ig} \Delta T = (20.785)(150 - 70) = 1663 \text{ J}$$

Pressure  $P_2$  is found from Eq. (3.23b):

$$P_2 = P_1 \left( \frac{T_2}{T_1} \right)^{\gamma/(\gamma-1)} = (1) \left( \frac{150 + 273.15}{70 + 273.15} \right)^{2.5} = 1.689 \text{ bar}$$





(b) For this constant-pressure process,

$$Q = \Delta H^{ig} = C_p^{ig} \Delta T = (20.785)(70 - 150) = -1663 \text{ J}$$

$$\Delta U = C_v^{ig} \Delta T = (12.471)(70 - 150) = -998 \text{ J}$$

$$W = \Delta U^{ig} - Q = -998 - (-1663) = 665 \text{ J}$$

(c) For this isothermal process,  $\Delta U^{ig}$  and  $\Delta H^{ig}$  are zero; Eq. (3.20) yields:

$$Q = -W = RT \ln \frac{P_3}{P_1} = RT \ln \frac{P_2}{P_1} = (8.314)(343.15) \ln \frac{1.689}{1} = 1495 \text{ J}$$

For the entire cycle,

$$Q = 0 - 1663 + 1495 = -168 \text{ J}$$

$$W = 998 + 665 - 1495 = 168 \text{ J}$$

$$\Delta U^{ig} = 998 - 998 + 0 = 0$$

$$\Delta H^{ig} = 1663 - 1663 + 0 = 0$$

The property changes  $\Delta U^{ig}$  and  $\Delta H^{ig}$  both are zero for the entire cycle because the initial and final states are identical. Note also that  $Q = -W$  for the cycle. This follows from the first law with  $\Delta U^{ig} = 0$ .

### Example 3.5

If the processes of Ex. 3.4 are carried out *irreversibly* but so as to accomplish exactly the same *changes of state*—the same changes in  $P$ ,  $T$ ,  $U^g$ , and  $H^{ig}$ —then different values of  $Q$  and  $W$  result. Calculate  $Q$  and  $W$  if each step is carried out with a work efficiency of 80%.

### Solution 3.5

If the same changes of state as in Ex. 3.4 are carried out by irreversible processes, the property changes for the steps are identical with those of Ex. 3.4. However, the values of  $Q$  and  $W$  change.

(a) For mechanically reversible, adiabatic compression, the work is  $W_{rev} = 998 \text{ J}$ . If the process is 80% efficient compared with this, the actual work is larger, and  $W = 998/0.80 = 1248 \text{ J}$ . This step cannot here be adiabatic. By the first law,

$$Q = \Delta U^{ig} - W = 998 - 1248 = -250 \text{ J}$$

(b) The work required for the mechanically reversible cooling process is 665 J. For the irreversible process,  $W = 665/0.80 = 831 \text{ J}$ . From Ex. 3.4(b),  $\Delta U^{ig} = -998 \text{ J}$ , and

$$Q = \Delta U^{ig} - W = -998 - 831 = -1829 \text{ J}$$

(c) As work is done *by* the system in this step, the irreversible work in absolute value is less than the reversible work of  $-1495 \text{ J}$ , and the actual work done is:

$$W = (0.80)(-1495) = -1196 \text{ J}$$

$$Q = \Delta U^{ig} - W = 0 + 1196 = 1196 \text{ J}$$

For the entire cycle,  $\Delta U^{ig}$  and  $\Delta H^{ig}$  are zero, with

$$Q = -250 - 1829 + 1196 = -883 \text{ J}$$

$$W = 1248 + 831 - 1196 = 883 \text{ J}$$

A summary of these results and those for Ex. 3.4 is given in the following table; values are in joules.

	Mechanically reversible, Ex. 3.4				Irreversible, Ex. 3.5			
	$\Delta U^{ig}$	$\Delta H^{ig}$	$Q$	$W$	$\Delta U^{ig}$	$\Delta H^{ig}$	$Q$	$W$
(a)	998	1663	0	998	998	1663	-250	1248
(b)	-998	-1663	-1663	665	-998	-1663	-1829	831
(c)	0	0	1495	-1495	0	0	1196	-1196
Cycle	0	0	-168	168	0	0	-883	883

The cycle is one which requires work and produces an equal amount of heat. The striking feature of the comparison shown in the table is that the total work required when the cycle consists of three irreversible steps is more than five times the total work required when the steps are mechanically reversible, even though each irreversible step is assumed to be 80% efficient.