UNIVERSITY Of MUSTANSIRIYAH | COLLAGE OF SCIENCE
DEPARTMENT OF CHEMISTRY

Physical Chemistry for 2nd Year UGS

Chapter-2 Thermodynamic (Work done)

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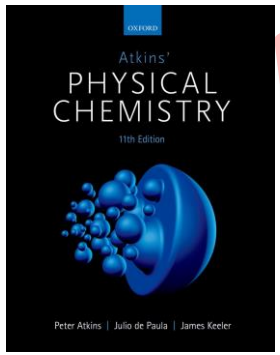

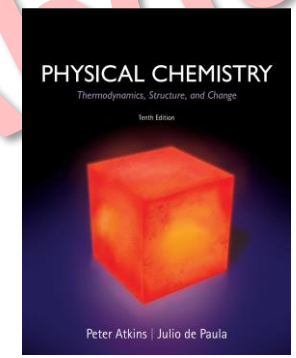

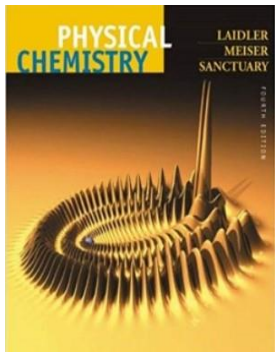

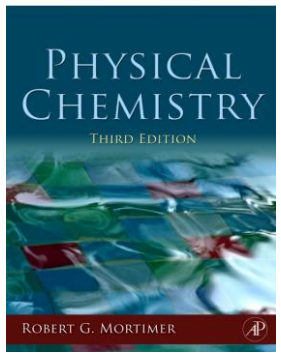

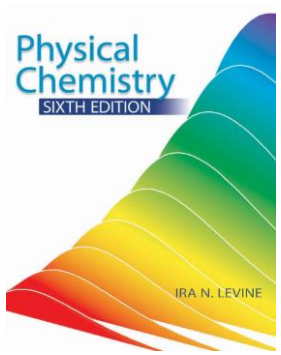

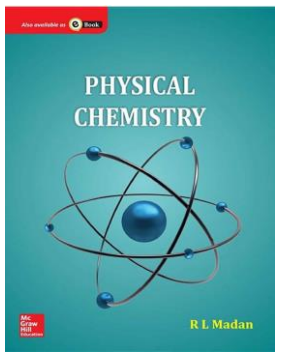

Links of how to get the lecture as a pdf file

- From academic profile:
- https://uomustansiriyah.edu.iq/e-learn/profile.php?id=3689

- From google classroom:
- https://classroom.google.com/c/NjI2NDA3NzkzMDRa

- From telegram:
- https://t.me/DrAbduljabbarIRRushdi

Types of expansion work

1- Constant volume (Isochoric process)

- في هذا النوع من العملية لا يتحرر غاز وتتم العملية عند حجمٍ ثابت أي إنَّ (ΔV = 0) وبالتالي تصبح المعادلة (2-14) للعملية العكسية وكذلك المعادلة (2-15) للعملية اللاعكسية كالتالي:

$$w_{rev} = -nRT\ (\ln\frac{V_f}{V_i} = Zero), because\ V_i = V_f \qquad (2\text{-}14)$$

$$w_{\text{irrev}} = -p_{ex}\ (\Delta V = zero),\ \text{then } w = 0, \text{ so } \Delta U = q \qquad (2\text{-}15)$$

- وعند التعويض عن قيمة الشغل في معادلة القانون الأول لحفظ الطاقة (2-6) نحصل على العلاقة التالية:

$$\Delta U = q + 0,\ \text{then } \Delta U = q \qquad (2\text{-}6)$$

- وحيث إنّ العملية في هذه الحالة تسمى بثبوت الحجم (Isochoric) وعندها يرمز للحرارة بالرمز q_v أي الحرارة المنتقلة من أو الى النظام عند ثبوت الحجم.

$$\Delta U = q_v \qquad (2\text{-}16)$$

2- Free expansion

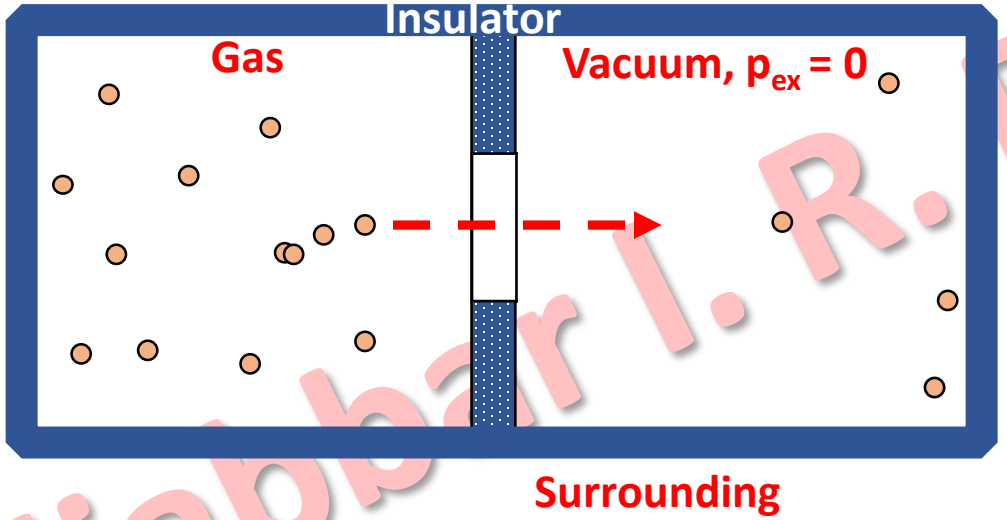

Figure 2.4: Free expansion of an ideal gas in vacuum and p_{ex} equals to zero, before and after expansion.

وعند التعويض عن قيمة (p_{ex}) في معادلة حساب الشغل للعملية اللاعكسية تصبح كالآتي:

$$w_{irr} = -(p_{ex} = zero)\,\Delta V = 0 \qquad (2\text{-}15)$$

Example of free expansion into a vacuum

Example: How much work is required to expand 2 L of an ideal gas at a pressure of 10 atm into a vacuum until its total volume is 10 L?

Solution: $P_{ex} = 0$ atm, $V_i = 2$ L, $V_f = 10$ L.

$$w_{irr} = -p_{ex}\ (V_f - V_i) \qquad (2\text{-}15)$$

$$w_{irr} = -0\ atm\ (10 - 2)\ L$$

$$w_{irr} = \text{zero}$$

3- Isothermal reversible expansion of a perfect gas

يحصل هذا النوع من التمدد العكسي للغاز المثالي بثبوت درجة الحراة أي (Isothermal, ΔT = 0) نحصل على الشغل المنجز من خلال المعادلة التالية:

$$w_{rev} = -nRT \ln \frac{V_f}{V_i} \qquad (2\text{-}14)$$

The equation (2-14) is for calculating of the work done of isothermal reversible expansion for an ideal gas.

Examples of isothermal reversible expansion of a perfect gas

Example 1: Calculate the work done by the system when 6.00 moles of an ideal gas at 25.0 °C are allowed to expand isothermally and reversibly from an initial volume of 5.00 dm^3 to a final volume of 15.00 dm^3.

Solution: n = 6.00 mol, V_i = 5.00 dm^3, V_f = 15.00 dm^3 and T = 25.0 °C + 273 = 298 K.

$$w_{rev} = -nRT \ln \frac{V_f}{V_i} \qquad \text{(2-14)}$$

$$w_{rev} = -6.00 \ \cancel{mol} \ x \ 298 \ \cancel{K} \ x \ 8.314 \ J \ \cancel{mol^{-1} K^{-1}} \ \ln \frac{15.00 \ \cancel{dm^3}}{5.00 \ \cancel{dm^3}}$$

$$w_{rev} = -6.00 \ \cancel{mol} \ x \ 298 \ \cancel{K} \ x \ 8.314 \ J (ln \ 3)$$

$$w_{rev} = -16331 \ J = -16.3 \ kJ$$

Example 2: How much work is required to compress 7.5 moles of an ideal gas to get 127.0 °C from 5.2 L to 2.1 L? What is the change in the internal energy of the gas? How much heat will be transferred during this process?

Solution: n = 7.5 mol, V_i = 5.2 L, V_f = 2.1 L and T = 127.0 °C + 273 = 400 K. *Compress means $V_f < V_i$*

$$w_{rev} = -nRT \ln \frac{V_f}{V_i} \qquad (2\text{-}14)$$

$$w_{rev} = -7.5 \ \cancel{mol} \ x \ 400 \ \cancel{K} \ x \ 8.314 \ J \ \cancel{mol^{-1}K^{-1}} \ \ln \frac{2.1 \ \cancel{dm^3}}{5.2 \ \cancel{dm^3}}$$

$$w_{rev} = -24942 \ x \ (-0.907) = 22615 = 22.615 \ kJ$$

ومن خلال السؤال يمكن ملاحظة أنَّ درجة الحرارة المعطاة لها قيمة واحدة (T = 400 K)، وهذا يعني عدم تغير درجة الحرارة خلال هذه العملية، أي أنَّ العملية تمت بثبوت درجة الحرارة (Isothermal, ΔT = 0).

وبما إنَّ ΔT = 0، عليه لا يحصل تغير بالطلقة الداخلية، (ΔU = 0) وبالتالي تصبح المعادلة (2-6) بالشكل التالي:

$$\Delta U = q + w, 0 = q + w, then \ q = -W = -22.615 kJ \qquad (2\text{-}6)$$

من المثال أعلاه نلاحظ أن قيمة الحرارة سالبة (q = – 22.615 kJ) وهذا يعني أنَّ الحرارة قد إنتقلت من النظام الى المحيط عند انضغاط غاز النظام (أي النقصان في حجم الغاز)، وإنَّ القيمة الموجبة للشغل (w = + 22.615 kJ) تدل على إنَّ الشغل قد أنجز من قبل المحيط.

Homework 1: From the last two examples (1 & 2), how it can be knew that the two processes are reversible?

Homework 2: If the process is compressed, how it can be knew that the heat is transferred into or out of the system?

Note: The homework have to be sent to our group (google classroom) which is stated above in the 2nd slid

حسب قانون بويل المعادلة (1-1) فإنَّ العلاقة بين الحجم والضغط هي علاقة عكسية ($p\ \alpha\ \frac{1}{V}$) وبثبوت درجة الحرارة.

$$pV = T\ (proportionality\ constant) \qquad (1\text{-}1)$$

$$p_i V_i = p_f V_f\ or\ \frac{p_i}{p_f} = \frac{V_f}{V_i} \qquad (1\text{-}2)$$

وعند تعويض المعادلة (1-2) بالمعادلة (2-14) نحصل على المعادلة التالية:

$$w_{rev} = -nRT \ln \frac{p_i}{p_f} \qquad (2\text{-}17)$$

نستخدم المعادلة (2-17) عندما لا تكون لدينا معلومات تخص التغير في الحجم للغاز المتمدد او المتقلص وبالمقابل لدينا معلومات تخص التغير بالضغط الداخلي للغاز.

Example of isothermal reversible by changing the internal pressure

Example: 3.2 moles of an ideal gas expands from a pressure of 5.0 atm to 1.4 atm at a constant temperature of 127.0 °C. (a) Is the work done by the gas or on the gas (b) How much energy was transferred by work and heat?

Solution: n = 3.2 mol p_i = 5.0 atm, p_f = 1.4 L and T = 127.0 °C + 273 = 400 K.

$$w_{rev} = -nRT \ln \frac{p_i}{p_f} \qquad (2\text{-}17)$$

$$w_{rev} = -3.2 \ \cancel{mol} \ x \ 400 \ \cancel{K} \ x \ 8.314 \ J \ \cancel{mol^{-1}K^{-1}} \ \ln \frac{5.0 \ \cancel{atm}}{1.4 \ \cancel{atm}}$$

$$w_{rev} = -13548 \ J = -13.548 \ kJ$$

Because of the temperature is constant, ΔT = 0, therefore ΔU = 0, then q = – w, and then q = – (– 13.548 kJ) = + 13.548 kJ. So, this means that the work is done by the gas on the surrounding and the heat is transferred from the surrounding to the system.

Homework

Homework-1: A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU.

Answer (a) 1.633 kJ (b) 1.38 kJ (c) 0

Homework-2: A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w and ΔU.