Assessment of Refrigerant Loss Rates from Hoses and Components

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Annual Refrigerant Emissions

Current calculation methods:

- 1) Measure emission rate at one or two temperatures
  - Extrapolate rate against known temperatures in vehicle or simply apply rate to annual basis
- 2) Proposed: Build system and put in chamber to measure permeation at different conditions
  - Either simulate annual drive cycle or apply data to known vehicle conditions to calculate annual rate

Calculation Problems

Extrapolating

- Tested temperatures 80°C or 90°C represent less than 5% of vehicle life
- The pressures tested are static saturated pressure for the temperature

Chamber method

- Costly and tedious
- Difficult to separate emission contributions from individual components

Theory

Refrigerant Emissions from hoses and components consist of two terms:

- Leakage
  - the escape of refrigerant *between* sealing components (tube to hose, o-ring to tube, etc)
  - Leakage is related to quality, design, assembly and durability
- Permeation
  - The diffusion of refrigerant *through* [thermoplastic or elastomeric] components
  - Permeation is a construction / materials issue
- “Emissions” addresses only permeation

Permeation variables

Emission (permeation) rate can be expressed as an equation with the following variables:

- Temperature
- Pressure
- Hose internal surface area (or seal surface)
- Baseline permeation rate
- Arrhenius-T factor

The equation can be established by testing at least three temperatures and then calculating the Arrhenius-T factor to fit the data.

Diffusion – Fick's Law

- Since diffusion is a thermally activated process the temperature dependence of diffusion appears in the diffusivity as an "Arrhenius-type" equation:

$$D = D_0 e^{-\frac{E_a}{RT}}$$

- Where:
  - E_a = activation energy
  - R = Gas constant
  - T = Temperature (Kelvin)

Assumptions

The following assumptions apply:

- For a given material (hose construction or seal material), absorption, diffusion and desorption all respond to pressure and temperature in a similar way and can be combined into a single factor together with layer thicknesses
- Emission rate has a linear relationship to the partial pressure differential of refrigerant across the layer

Pressure differential

The effect of different pressures on emission rate can be expressed as:

$$E_{(P_1,T)} = \frac{\rho_1 - \rho_{atm}}{\rho_0 - \rho_{atm}} \cdot E_{(P_0,T)}$$

Assuming:

- Internal refrigerant partial pressure = internal pressure
- Atmospheric refrigerant partial pressure = 0

$$E_{(P_1,T)} = \frac{P_1}{P_0} \cdot E_{(P_0,T)} \qquad \text{(Eq 1.1)}$$

Emission Equation

- Substitute E (emission rate) for D, and Arrhenius-T factor:

$$G = \frac{X \cdot E_a}{R}$$

  - Where X = Adjustment factor for material properties
  - Gives: $E_1 = E_0 e^{-\frac{G}{T_1}}$ Or: $E_1 = E_2 e^{G\frac{T_1 - T_2}{T_1 T_2}}$ (Eq 1.2)
  - Where: $G = \left[\frac{T_1 T_2 \cdot \ln\left(E_1 / E_2 \right)}{(T_1 - T_2)} \right]$

Theory Confirmation

- We expect that the value for the Arrhenius-T factor (G) should have little variation for similar construction of hoses
- To confirm the theory, we tested:
  - 4 different hose constructions with as many as 4 different diameters:
    - All-Rubber (GY-4842) - 16 & 19mm
    - Veneer (GY-4870) – 11mm
    - Low permeation (SLE) barrier (GY-4890) - 8, 10, 16 & 19mm
    - Extremely low permeation (ZE) barrier (GY-XX) – 10 & 16mm
  - 4 temperatures
    - 32.2°C (90°F)
    - 50°C (122°F)
    - 80°C (176°F)
    - 90°C (194°F)

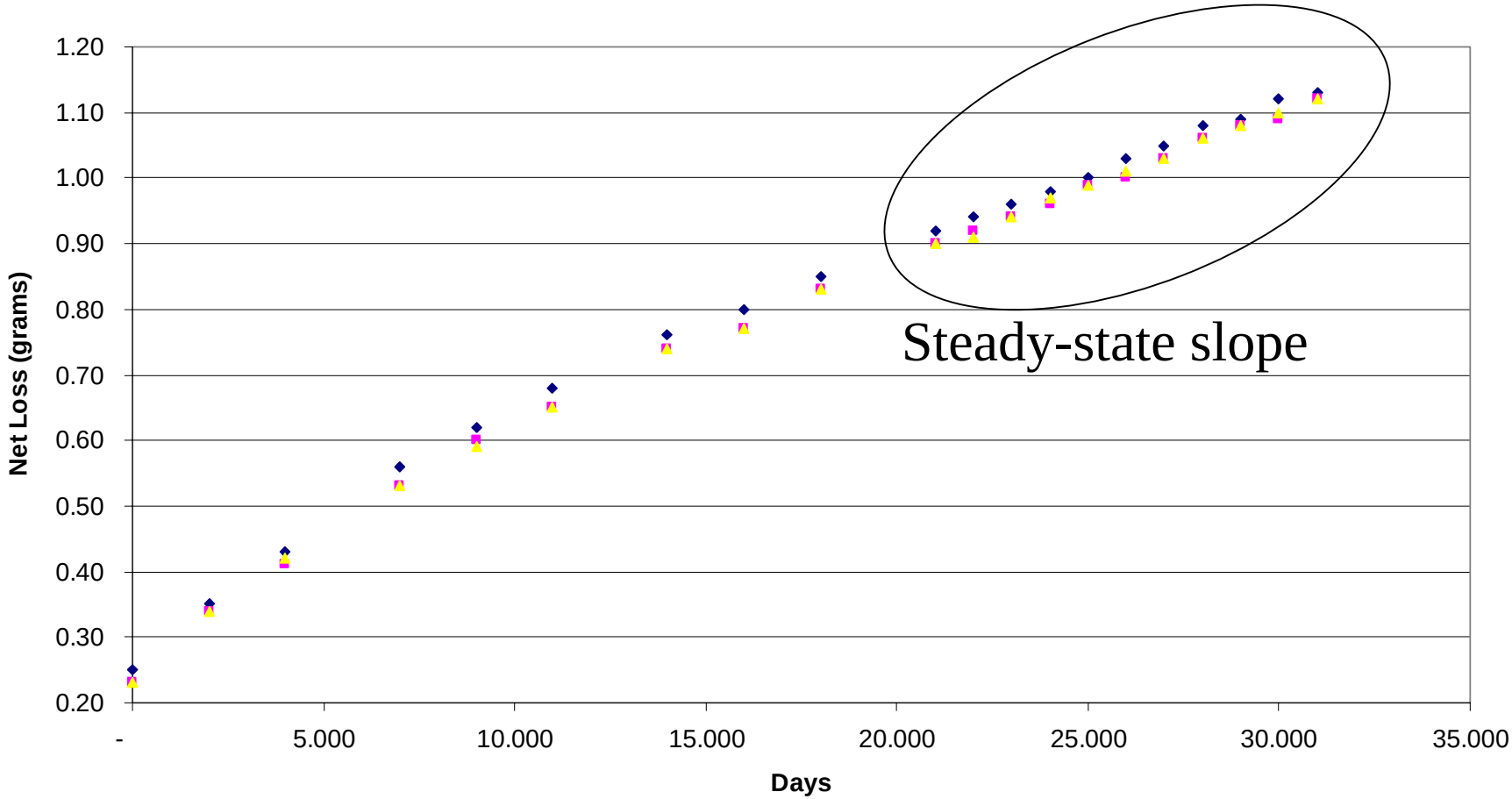
Test Method

- Steady state gravimetric test per SAE J2064 and ISO 8066.
  - 3 hoses and one volatility sample for each test
  - Assemblies were constructed to minimize extraneous losses

Test Method

- Test assemblies were weighed daily until steady state
  - Up to 70 days for some samples
  - This becomes an issue for gravimetric test methods at low temperatures and with extremely low permeation hoses, as experimental error can exceed refrigerant losses for short periods of time.
- The data gathered were plotted and analyzed to establish constant loss rates in industry standard units ($kg/m^2/year$)

Data Plot


1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
Net Loss (grams)
-
5.000
10.000
15.000
20.000
25.000
30.000
35.000
Days
Steady-state slope

Test Data

Hose type	Diameter (mm)	Emission rate ($kg/m^2/year$)			
		32.2°C	50°C	80°C	90°C
All Rubber	16	0.2694	0.9323	7.2017	13.5070
	19	0.2067	0.7619	5.7475	9.3154
Veneer	11	0.0631	0.0399	0.5850	1.3909
SLE Barrier	8	0.0010	0.0159	0.2971	0.7664
	10	0.0046	0.0209	0.3933	0.6951
	16	0.0101	0.0124	0.3429	0.8512
	19	0.0177	0.0501	0.3310	0.6623
ZE Barrier	10	0.0032	0.0064	0.0126	0.0423
	16	0.0037	0.0067	0.0264	0.0585

Normalized Data

Data normalized to 2.633 MPa using (Eq. 1.1).

Hose type	Diameter (mm)	Emission rate ($kg/m^2/year$)			
		32.2°C	50°C	80°C	90°C
All Rubber	16	0.8639	1.8611	7.2017	10.9681
	19	0.6627	1.5211	5.7475	7.5644
Veneer	11	0.2023	0.0797	0.5850	1.1295
SLE Barrier	8	0.0146	0.0416	0.3933	0.5644
	10	0.0323	0.0248	0.3429	0.6912
	16	0.0567	0.1000	0.3310	0.5378
	19	0.0031	0.0318	0.2971	0.6223
ZE Barrier	10	0.0102	0.0129	0.0126	0.0344
	16	0.0119	0.0135	0.0264	0.0475

Arrhenius-T factor

- From the normalized data, Arrhenius-T factors were established to best fit the curves
- As expected, the factors all have the same order of magnitude and are grouped according to hose type

Hose type	Diameter (mm)	Arrhenius-T factor (G) (Kelvin)
All Rubber	16	4850
	19	4850
Veneer	11	2400
SLE Barrier	8	9600
	10	8500
	16	5300
	19	4000
ZE Barrier	10	3300
	16	3300

Hose factors

- By combining the arrhenius-T equation, the pressure equation, the hose diameter factor and baseline emission rate at 80° C, we get

$$E_{(P,T,L)} = \frac{PL\pi\phi_{id}}{P_{(80C)}} \cdot E_{(80C)} \cdot e^{\left(\frac{G(T-353.16)}{T \cdot 353.16K}\right)}$$

- If we group all the constants for a given hose, we get

$$E_{(P,T,L)} = PLHe^{-G/T}$$

  - Where E = emission rate (g/yr)
  - P = absolute pressure (kPaa)
  - L = hose length (mm)
  - T = temperature (K)
  - and the hose constant, $H = \frac{E_{(80C)}\pi\phi_{id}}{P_{(80C)}} e^{\left(\frac{G}{353.16K}\right)}$

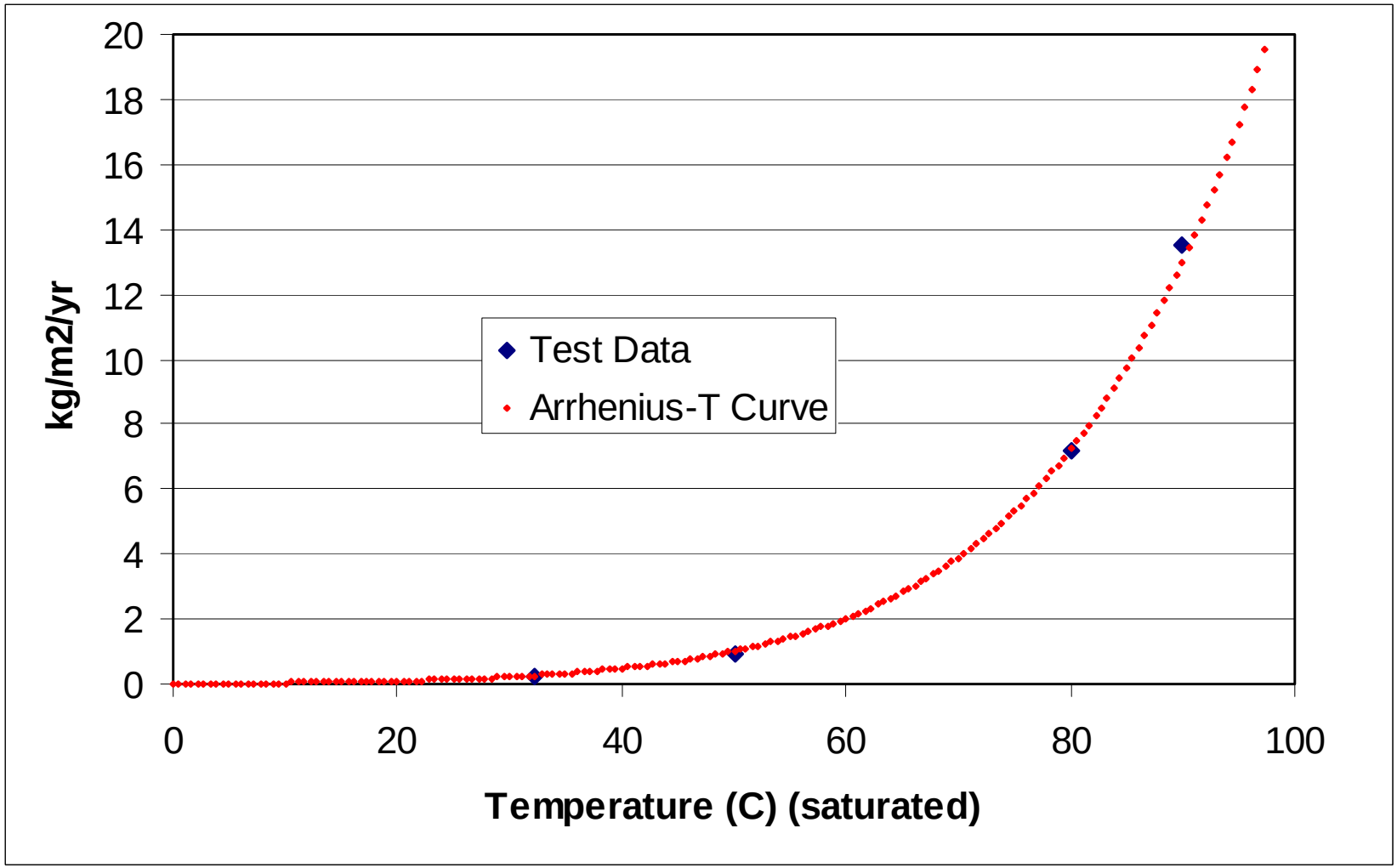
Arrhenius-T Equation

- Simplified Equation:

$$E = PLHe^{-G/T} \quad \text{Or:} \quad E = (h/8760)PLHe^{-G/T}$$

Hose type	Diameter (mm)	Arrhenius-T factor, G (Kelvin)	Hose Constant, H ($g \cdot mm^{-1} \cdot kPaa^{-1} \cdot yr^{-1}$)
All Rubber	16	4850	1.27E+02
	19	4850	1.20E+02
Veneer	11	2400	6.86E-03
SLE Barrier	8	9600	1.81E+06
	10	8500	1.33E+05
	16	5300	2.16E+01
	19	4000	6.23E-01
ZE Barrier	10	3300	1.72E-03
	16	3300	5.76E-03

Arrhenius-T Curve Fit



Annual Drive Cycle

		Temperature Cluster (Frankfurt)					Annual Emissions (grams / year)
		-20° to 0°C	0° to 10°C	10° to 20°C	20° to 30°C	30° to 40°C	
	Average Temperature (°C)	-3.1	5	14.8	23.8	33.6	
	Total hours per year	982	3806	3057	886	29	
	Hours in use per year (5%)	49	190	153	44	1	
	Hours not in use	933	3616	2904	842	28	
All lines conditions (not in use)	Internal Temperature (C)	0	5	15	25	35	
	Internal Pressure (bar)	3	3.5	4.9	6.6	8.9	
Discharge Line (10mm) - in use	Internal Temperature (°C)	0	15	40	60	80	
Hose Length (mm) 400	Internal Pressure (bar)	3	4.4	6.5	10.5	15.5	**Discharge**
Hose Type **SLE Barrier**	Emissions in g/yr (in use)	3.64E-06	9.64E-05	1.14E-03	2.55E-03	3.53E-04	0.0041
Arrhenius-T factor (G) 8500	Emissions (not in use)	6.94E-05	5.29E-04	1.61E-03	1.62E-03	1.77E-04	0.0040
Hose Factor (H) 1.33E+05						Total	**0.008**
Liquid Line (8mm) - in use	Internal Temperature (°C)	0	10	22	35	50	
Hose Length (mm) 400	Internal Pressure (bar)	3	4.3	6.3	10.3	15	**Liquid**
Hose Type **SLE Barrier**	Emissions in g/yr (in use)	8.84E-07	1.57E-05	6.92E-05	1.21E-04	1.66E-05	0.0002
Arrhenius-T factor (G) 9600	Emissions (not in use)	1.68E-05	1.38E-04	4.82E-04	5.50E-04	6.77E-05	0.0013
Hose Factor (H) 1.81E+06						Total	**0.001**
Suction Line (16mm) - in use	Internal Temperature (°C)	0	6	11	7	3	
Hose Length (mm) 600	Internal Pressure (bar)	3	3.6	4.5	3.8	3.2	**Suction**
Hose Type **All Rubber**	Emissions in g/yr (in use)	3.32E-03	2.17E-02	2.83E-02	5.57E-03	8.62E-05	0.0590
Arrhenius-T factor (G) 4850	Emissions (not in use)	6.32E-02	3.79E-01	7.31E-01	4.80E-01	3.52E-02	1.6879
Hose Factor (H) 1.27E+02						Total	**1.747**
						Total	**1.756**

Conclusion

- Emission rates can be predicted for different temperatures and pressures using the Arrhenius-T equation
- The method is expected to hold true for other elastomeric components (o-rings, seals)
- The method is expected to hold true for other refrigerants (R152a, CO_2, etc.)
- More focus is needed to establish emission rates at low temperatures (10° to 40° C)
  - New test methods?

Thank You

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